UNCLASSIFIED

AD NUMBER

AD234424

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; Jan 1960. Other requests shall be referred to the Wright Air Development Center, Wright-Patterson AFB, OH 45433.

AUTHORITY

AFML ltr, 21 Sep 1971

THIS PAGE IS UNCLASSIFIED

WADC TECHNICAL REPORT 59-427
AD0234424

OFFICIAL FILE COPY

CONFERENCE OF HIGH TEMPERATURE POLYMER AND FLUID RESEARCH

Materials Laboratory

JANUARY 1960

This report is not to be announced or distributed automatically in accordance with AFR 205-43A, paragraph 6d.

20040225218

WRIGHT AIR DEVELOPMENT DIVISION

BEST AVAILABLE COPY

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

- - - - -

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

- - - - -

Copies of WADC Technical Reports and Technical Notes should not be returned to the Wright Air Development Center unless return is required by security considerations, contractual obligations, or notice on a specific document.

WADC TECHNICAL REPORT 59-427

CONFERENCE ON HIGH TEMPERATURE POLYMER AND FLUID RESEARCH

Materials Laboratory

JANUARY 1960

Project No. 7340

WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

400 – March 1960 – 25-717

FOREWORD

This report was prepared by the Polymer Branch, Non-Metallic Materials Division and was initiated under Project 7340, Task No. 73404. It was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center with Dr. J. A. Seaton, 1/Lt USAF, as project engineer.

The technical papers contained in this report were presented at the Materials Laboratory, WADC conference on "High Temperature Polymer and Fluid Research" which was held at the Biltmore Hotel, Dayton, Ohio, on 26, 27, 28 May 1959.

The conference was opened with an official welcome by Colonel J. C. Dieffenderfer, Chief of the Materials Laboratory, and introductory remarks by Mr. P. S. Forsyth of the Office of the Director of Defense Research and Engineering, Department of Defense. General Chairman for the conference was Captain C. H. Schmid, Chief of the Polymer Section. The conference was divided into six sessions. These sessions were chairmaned by: Dr. H. Rosenberg; Dr. C. T. Tamborski; Dr. W. E. Gibbs, 1/Lt USAF; Dr. I. J. Goldfarb, 1/Lt USAF; Dr. J. A. Seaton, 1/Lt USAF; and Dr. A. M. Lovelace. Discussion leaders were: Prof. H. Mark, Brooklyn Polytechnic Institute; Dr. A. J. Barry, Dow Corning; Dr. M. Sprung, General Electric; Prof. J. Margrave, University of Wisconsin; Dr. Lee Wall, Bureau of Standards; Prof. Fred Basole, Northwestern University; Prof. W. C. Fernelius, Pennsylvania State University; and Dr. G. Barth-Wehrenalp, Pennsalt Chemical Company. The Conference Administrator for the University of Dayton Research Institute was Mr. E. A. Janning.

ABSTRACT

This report is the collection of papers presented at the Materials Laboratory, WADC conference on "High Temperature Polymer and Fluid Research" held in Dayton, Ohio, on 26-28 May 1959.

The purpose of this conference was to review the recent progress in both contractual and internal research programs sponsored by the Polymer Branch of the Non-Metallic Materials Division in the area of synthesis of new polymers and fluids.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

A. M. Lovelace

A. M. LOVELACE
Chief, Polymer Branch
Non-Metallic Materials Division
Materials Laboratory

TABLE OF CONTENTS

Page

ALUMINUM-OXYGEN-ALUMINUM POLYMERS
William G. Woods, Marlowe L. Iverson, U. S. Borax Research Corporation 1

ORGANOMETALLIC POLYMERS CONTAINING TIN OR ALUMINUM
R. D. Crain, P. E. Koenig, Ethyl Corporation 15

RESEARCH ON ORGANOSILYLOXY-METAL COMPOUNDS AND METALLO-ORGANIC COMPOUNDS CONTAINING METAL-NITROGEN BONDS
D. C. Bradley, Birkbeck College 29

THE APPLICATION OF LIGHT SCATTERING TO THE STUDY OF THE HYDROLYTIC AGGREGATION OF IONS
R. Stuart Tobias, S. Young Tyree, Jr., University of North Carolina 41

SILICON AND BORON POLYMERS
R. P. Anderson, M. M. Sprung, General Electric Research Laboratory. 55

ORGANO-METALLIC AND ORGANO-METALLOIDAL STUDIES ON HIGH-TEMPERATURE AND RADIATION-RESISTANT LUBRICANTS AND RELATED MATERIALS
Henry Gilman, Iowa State College 71

SYNTHESIS OF POLYXYLYLYLDIMETHYLSILANE AND POLYXYLYLYLTETRAMETHYLSILOXANE
Glenn R. Wilson, Ford Motor Company 81

POLYMERS CONTAINING TIN
E. C. Evers, University of Pennsylvania 95

SYNTHESIS AND EVALUATION OF SILOXANYLFERROCENES
R. L. Schaaf, P. T. Kan, Wyandotte Chemicals Corporation 101

ORGANOSILICON DERIVATIVES OF INORGANIC "BENZENOID" COMPOUNDS
Dietmar Seyferth, Massachusetts Institute of Technology 117

SILOXANES
L. W. Breed, Midwest Research Institute 121

THE PREPARATION OF CERTAIN HETEROCYCLIC POLYMERS BY CYCLIC POLYMERIZATION
George B. Butler, University of Florida 139

TABLE OF CONTENTS (Cont'd.)

Page

PERFLUOROALKYL AMIDINE POLYMERS
Henry C. Brown, University of Florida 155

NEW THERMALLY STABLE POLYMERS
C. S. Marvel, University of Illinois. 161

ANIONIC POLYMERIZATION
Charles G. Overberger, Polytechnic Institute of Brooklyn. 175

FLUORINE-CONTAINING CONDENSATION POLYMERS AND RESINS
Carl J. Verbanic, Hooker Chemical Corporation 191

SOME ASPECTS OF ORGANOTIN HYDRIDE CHEMISTRY WITH A VIEW TO THE POSSIBILITY OF PREPARING ORGANOTIN POLYMERS
Dr. J. G. Noltes, Institute for Organic Chemistry T.N.O. 217

NOVEL EPOXY RESINS
P. E. Ritt, Melpar, Incorporated 227

THERMAL DEGRADATION OF POLYMERS AT TEMPERATURES UP TO 850°C
S. L. Madorsky, National Bureau of Standards 247

DIFFERENTIAL THERMAL ANALYSIS AND THERMOGRAVIMETRIC ANALYSIS AS METHODS FOR ASSESSING THE INTRINSIC THERMAL STABILITIES OF EXPERIMENTAL POLYMERS
C. D. Doyle, General Electric Company 269

HIGH TEMPERATURE SYNTHESES OF NEW, THERMALLY STABLE CHEMICAL COMPOUNDS
Russell C. Phillips, Stanford Research Institute 279

SYNTHESIS OF 1000°F. STABLE FLUIDS
J. W. Dale, I. B. Johns, E. A. McElhill, J. O. Smith, Monsanto Chemical Company. 309

INVESTIGATIONS INTO THE RADIATION CHEMISTRY OF POLYPHENYL FLUIDS
Josef J. M. Schmidt, George E. Bohner, Denver Research Institute. 325

MATERIALS LABORATORY POLYMER RESEARCH
Dr. G. Ehlers, Materials Laboratory, WADC 339

MATERIALS LABORATORY FLUIDS RESEARCH
Stanley I. Goldberg, Materials Laboratory, WADC 347

TABLE OF CONTENTS (Cont'd.)

Page

COORDINATION POLYMERS
John C. Bailar, Jr., University of Illinois 353

THERMALLY STABLE COORDINATION POLYMERS
W. C. Drinkard, Jr., D. N. Chakravarty, University of California. 367

PI-BONDED INORGANIC SYSTEMS
A. F. Clifford, Purdue University 373

RESEARCH ON TRANSITION METAL-CARBON CHEMISTRY
Geoffrey Wilkinson , Imperial College of Science and Technology . 379

SYNTHESIS OF FERROCENE DERIVATIVES
Kenneth L. Rinehart, Jr., University of Illinois. 381

POLYMERS OF GROUP III AND V ELEMENTS
Anton B. Burg, University of Southern California 389

PHOSPHINOBORINE POLYMERS
Ross I. Wagner, American Potash & Chemical Corporation 405

BORON POLYMERS
Allen L. McCloskey, U. S. Borax Research Corporation 423

INORGANIC POLYMER FLUIDS
John A. Parkins, E. I. du Pont de Nemours and Co., Inc. 439

SOME REACTIONS OF THE PHOSPHONITRILIC HALIDES
L. F. Audrieth, University of Illinois 449

RESEARCH ON SULFUR-PHOSPHORUS-NITROGEN POLYMERS
Dr. Margot Becke-Goehring, Chemisches Institut Universitat
Heidelberg 455

SOME ASPECTS OF PHOSPHONITRILIC HALIDE CHEMISTRY
R. A. Shaw, Birkbeck College 479

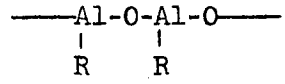
ALUMINUM-OXYGEN-ALUMINUM POLYMERS

William G. Woods and Marlowe L. Iverson

U. S. Borax Research Corporation
Anaheim, California

A. INTRODUCTION

Inorganic polymers based on an alternating aluminum-oxygen backbone with suitable substituent groups are attractive as materials for high temperature applications. A polyaluminoxane may be viewed as a modified form of alumina:



This structure should possess exceptional high temperature stability towards homolytic cleavage of the main chain because of the high value of the Al-O bond energy. The critical problem is to find substituents (R) capable of withstanding elevated temperatures in the presence of the catalytic effects of the electron-deficient aluminum atoms. In order to select such thermally stable groups, a number of prototype compounds with a variety of substituents have been prepared. These model compounds have been thermally degraded and, in many cases, their pyrolysis products have been identified. In an attempt to obtain detailed mechanistic information about the course of the degradation reaction, a study has been made of the thermal decomposition of aluminum isopropoxide. The results of the pyrolysis studies have shown the important role of ionic mechanisms in the pyrolysis reactions. Preliminary attempts have also been made to prepare polyphenoxyaluminoxane and poly(triphenylsiloxy)aluminoxane, using partial hydrolysis and heterofunctional condensation as methods of polymerization.

B. DISCUSSION

1. Bond Energy Considerations

Recent data (Reference 1a) have made it possible to calculate the Al-O bond energy in aluminum isopropoxide. From a consideration of the energies (Table I) of the bonds comprising the backbone of other well known polymers, the high Al-O bond energy indicates that a poly-

Manuscript released by Polymer Branch, Materials Laboratory, October 1959, for publication as a WADC Technical Report.

aluminoxane should be superior in high-temperature stability. Part of the expected stability might be due to the relatively high ionic character of the Al-O bond (Reference 2).

TABLE I

BOND ENERGIES AND IONIC CHARACTER

Bond	Compound	Bond Energy, Kcal./mole	% Ionic Char.*	Ref.
C-C	Ethane	86	0	3
C-O	Diethyl Ether	83	23	4
Si-O	Polysiloxanes	101.5	51	5
Al-O	$Al\left[OCH(CH_3)_2\right]_3$	136**	63	-
Al-O	Al_2O	128	--	6
Al-O	AlO	120	--	6, 7

* Calculated by Pauling's method (References 8 and 9). ** Calculated from the data of Gibbs, et. al. (Reference 1a).

2. Prototypes and Monomers

a. In the course of selecting substituents expected to exhibit comparable thermal stability, a number of prototypes and monomers were prepared. Those compounds which are new or which have been prepared in a pure form for the first time are listed in Table II, along with their methods of preparation.

b. As a suitable intermediate for the preparation of polyphenoxyaluminoxane and as a model for comparing the relative stabilities of the isopropoxy and phenoxy groups, diisopropoxyphenoxyaluminum (I) was prepared. It was an analytically pure syrup which decomposed to give a resin when distillation was attempted. Pyrolysis near 315°C gave propylene, isopropyl alcohol, a trace of isopropyl ether and a resin. This resin, which may have had a partial polyphenoxyaluminoxane structure, was insoluble in the common solvents and was stable in vacuo above 400°C.

c. As an example of an aluminum oxygen prototype containing highly fluorinated substituents, aluminum 1H,1H,7H-dodecafluoro-1-heptoxide (II) was prepared and found to rapidly decompose to a black tar above 210°C. It is concluded that the 1H,1H,7H-dodecafluoro-1-heptoxy group is undesirable as a substituent on polyaluminoxanes.

d. In an effort to incorporate a coordinating group on aluminum, diisopropoxypicolinoxyaluminum (III) was prepared by the reaction of aluminum isopropoxide and one molar equivalent of picolinic acid. This crystalline solid decomposed with gas evolution at 335-340°C.

TABLE II

PREPARATION OF ALUMINUM-OXYGEN COMPOUNDS

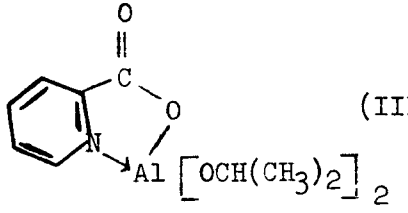
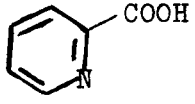
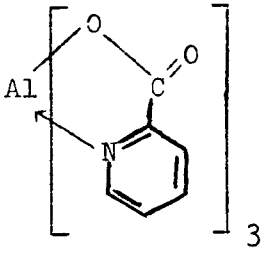
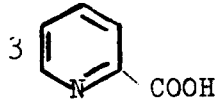
Compound		Preparative Reaction[a]	M.p., °C[b]
$\phi OAl\left[OCH(CH_3)_2\right]_2$	(I)	$\phi OH + Al\left[OCH(CH_3)_2\right]_3$	syrup[c]
$Al\left[OCH_2(CF_2)_6H\right]_3$	(II)	$3\ H(CF_2)_6CH_2OH + Al\left[OCH(CH_3)_2\right]_3$	syrup
	(III)	 $+ Al\left[OCH(CH_3)_2\right]_3$	240 - 244
	(IV)	 $+ Al\left[OCH(CH_3)_2\right]_3$	368 - 370 (dec.)

TABLE II (CONTD.)

PREPARATION OF ALUMINUM-OXYGEN COMPOUNDS

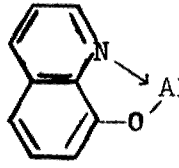
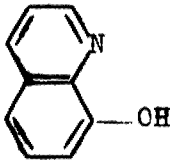
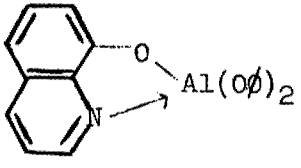
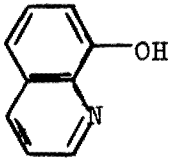
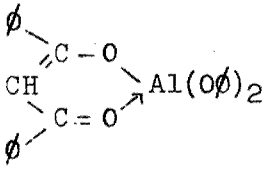
Compound		Preparative Reaction[a]	M.p., °C[b]
	(V)	 + $Al(OC_2H_5)_3$	342 - 345 (dec.)
	(VI)	 + 2 ϕOH - $Al\left[OCH(CH_3)_2\right]_3$	94 - 120
	(VII)	$(\phi CO)_2CH_2$ + 2 ϕOH + $Al\left[OCH(CH_3)_2\right]_3$	246[d]
$(CH_3)_3SiOAl\left[OCH(CH_3)_2\right]_2^e$	(VIII)	$(CH_3)_3SiOCOCH_3$ + $Al\left[OCH(CH_3)_2\right]_3$ (in C_6H_{12})	154.5-155.8
$Al\left[OSi(CH_3)_3\right]_3^e$	(IX)	3 $(CH_3)_3SiOCOCH_3$ + $Al\left[OCH(CH_3)_2\right]_3$	224.8-226.5

TABLE II (CONTD.)

PREPARATION OF ALUMINUM-OXYGEN COMPOUNDS

Compound	Preparative Reaction[a]	M.p., °C[b]
$\phi_3SiOAl\left[OCH(CH_3)_2\right]_2$[e] (X)	a) $\phi_3SiOH + Al\left[OCH(CH_3)_2\right]_3$	84 - 87
	b) $\phi_3SiOCOCH_3 + Al\left[OCH(CH_3)_2\right]_3$	68.5-75.5

[a] Reactions carried out in boiling toluene unless otherwise indicated.
[b] Determined in sealed, evacuated tubes.
[c] Slowly crystallizing on long standing.
[d] Contained 1 molecule of toluene as solvent of crystallization.
[e] These materials have been reported previously (Reference 1).

Similarly, aluminum picolinate (IV) decomposed with gas evolution at its melting point (368-370°C).

e. The high temperature stability of quinolin-8-oxy groups was indicated by the fact that aluminum oxinate /tris-(quinolin-8-oxy)aluminum/ m.p. 414-418°C, was unchanged below 400°C and was a red-orange liquid at 500°C in an evacuated tube. Consequently, diethoxyquinolin-8-oxyaluminum (V) was prepared as indicated in Table II. This material was probably a mixture of disproportionation products, as indicated by fractional extraction experiments. Pyrolysis at 350-410°C produced ethanol as the major product plus some diethyl ether. A similar compound, diisopropoxyquinolin-8-oxyaluminum, was prepared as reported by Gibbs (Reference 1a). When pyrolyzed at 250-270°C, it slowly evolved isopropyl alcohol, propylene and a trace of isopropyl ether. Further work with the quinolin-8-oxy substituent on aluminum is contemplated.

f. In an effort to combine in one molecule the expected stability of the phenoxy and quinolin-8-oxy groups, diphenoxyquinolin-8-oxyaluminum (VI) was prepared. It darkened slowly above 350°C in an evacuated tube and was dark brown at 460°C. Diphenoxy-1,3-diphenyl-1-ketoprop-2-ene-3-oxyaluminum (VII) was synthesized since it has been reported (Reference 1a) that chelated aluminum compounds from dibenzoyl methane were exceptionally thermally stable. Compound VII was a tan liquid in vacuo at 350°C and became dark brown on slow heating to 390°C. Additional pyrolytic information, including product analyses, will be obtained for compounds VI and VII.

g. It has been reported that polytriethylsiloxyaluminoxane polymers form hard films on the surface of metals (Reference 10) which are heat resistant (Reference 11). Since it is known that methyl and phenyl substituents on silicones are more resistant to high temperatures than are ethyl groups (Reference 12), prototypes and monomers containing trimethylsiloxy and triphenylsiloxy groups were synthesized. Diisopropoxy(trimethylsiloxy)aluminum (VIII) was prepared by the reaction of trimethylsilyl acetate and aluminum isopropoxide (Reference 1a). The same reaction recently has been reported for a number of other metal alkoxides (Reference 13). The product, obtained as a crystalline solid, decomposed at 260°C with the formation of propylene, isopropyl alcohol, isopropoxytrimethylsilane and a benzene-insoluble residue. Tris-(trimethylsiloxy)aluminum (IX), prepared in a pure form by the same reaction, produced one-half of a molar equivalent of hexamethyldisiloxane when heated at 260-280°C. The resulting red, resinous, benzene-soluble residue had a molecular weight of 1200. Diisopropoxytriphenylsiloxyaluminum (X) was produced as a glassy solid from the reaction of triphenylsilanol or triphenylsilyl acetate with one molar equivalent of aluminum isopropoxide.

3. Pyrolysis Studies

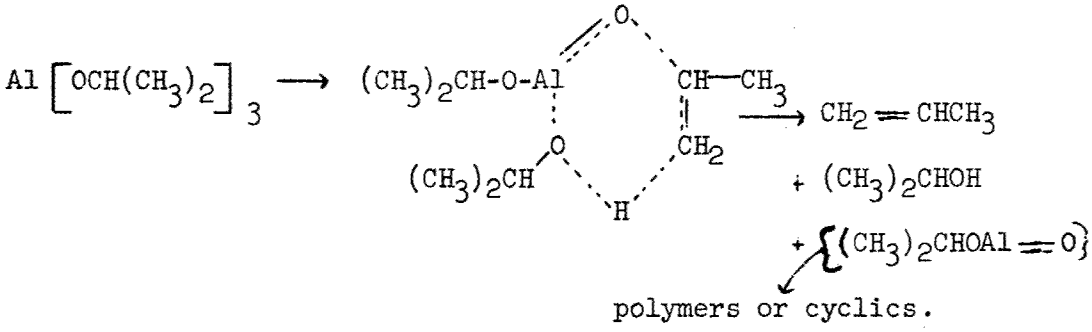
a. In all of the above examples, the pyrolysis of aluminum compounds substituted with isopropoxy groups gave very little isopropyl ether. This result was also obtained when aluminum isopropoxide was pyrolyzed under similar condition (liquid, 240-260°C); i.e., propylene and isopropyl alcohol were the major products while only a trace of isopropyl ether was formed. These results stand in contrast to those observed in the pyrolyses of aluminum methoxide, ethoxide and phenoxide under comparable conditions. Heating aluminum methoxide at 280°C gave dimethyl ether as the only product. The major volatile products from the liquid-phase pyrolysis of aluminum ethoxide in the range 335-405°C have been identified as diethyl ether, ethylene and ethanol, with relatively more of the latter two at the higher temperatures. A similar decomposition at 300-340°C was reported (Reference 14) to have produced mainly diethyl ether. Similarly, diphenyl ether and a tarry residue were obtained when aluminum phenoxide was heated over a low flame (Reference 15); higher temperatures gave phenol. It was observed during the present study that aluminum phenoxide decomposed at a moderate rate at 410°C to give diphenyl ether, varying amounts of phenol, and a tarry residue.

b. From the above observations, a generalization can be drawn concerning the mode of formation of ethers in the pyrolysis of aluminum-oxygen compounds. Those materials which have given ethers or ether-like products are: aluminum methoxide, ethoxide and phenoxide, diisopropoxy(trimethylsiloxy)aluminum (VIII) and tris(trimethylsiloxy)aluminum (IX). In all cases, the alcohol (or silanol) from which the aluminum compound was derived is more acidic than isopropyl alcohol (Reference 20). The stronger the acid from which a metal salt is derived, the more ionic is the salt: Consequently, the above materials probably form ethers by an ionic mechanism. It is significant that diisopropoxy(trimethylsiloxy)aluminum (VIII) evolved isopropoxytrimethylsilane considerably faster than hexamethyldisiloxane was released from tris(trimethylsiloxy)aluminum (IX). In the case of VIII, the trimethylsiloxy groups ionize as the trimethylsilanolate ion and attack the positive carbon of the isopropoxy groups. In IX, the trimethylsilanolate ion must attack the silicon of an unionized trimethylsiloxy group, which is less favorable, and hence occurs at a slower rate. It is pertinent that acetoxyisopropoxyphenoxyaluminum has been prepared from the reaction of acetic anhydride and diisopropoxyphenoxyaluminum and found to lose isopropyl acetate above about 100°C. This is in accord with the above considerations and suggests the following:

$$\phi OAl(OAc)\left[OCH(CH_3)_2\right] \longrightarrow \phi OAl^{\oplus}\left[OCH(CH_3)_2\right]\,OAc^{\ominus}$$

$$\phi OAl\left[OCH(CH_3)_2\right]^{\oplus}\ OAc^{\ominus} \xrightarrow[\text{or intermolecular}]{\text{intramolecular}} \text{products} + AcOCH(CH_3)_2$$

c. A series of experiments were carried out to study the vapor phase decomposition of aluminum isopropoxide. At 315°C, it was found that isopropyl ether again was a minor product, the major products being propylene, isopropyl alcohol, water and a solid residue which accumulated in the pyrolysis tube. It is well known that alumina can catalyze the dehydration of alcohols and ethers (References 16 and 17). This suggested that isopropyl ether may have been formed as a primary product, but had subsequently decomposed over the alumina-like residue to give secondary products. When isopropyl ether was passed over the residues deposited from a decomposition of aluminum isopropoxide, an almost complete conversion to propylene and water occurred. The high activity of the residues was shown by the fact that a sample of commercial alumina gave a lower conversion under the same conditions. Isopropyl alcohol was not produced in significant amounts in the decomposition of isopropyl ether. It was found, however, that the amount of isopropyl ether produced in the pyrolysis of aluminum isopropoxide did not increase when the flow rate was increased or when the pyrolysis temperature was lowered. The increased flow rate increased the yield of isopropyl alcohol. Furthermore, it was observed that comparably small quantities of isopropyl ether were formed when isopropyl alcohol was passed over the active residues. It is concluded that isopropyl ether was not a primary product in the thermal decomposition of aluminum isopropoxide and that the water and isopropyl ether were formed by the dehydration of isopropyl alcohol. The important primary reactions probably involve the simultaneous splitting off of isopropyl alcohol and propylene, either intramolecularly:



or intermolecularly:

$$2\ Al\left[OCH(CH_3)_2\right]_3 \longrightarrow \left[(CH_3)_2CHO\right]_2 AlOAl\left[OCH(CH_3)_2\right]_2 + CH_2{=}CHCH_3 + (CH_3)_2CHOH$$

d. The isolation of dihydroxycyclohexoxyaluminum and cyclohexene from the thermal decomposition of aluminum cyclohexoxide (Reference 18) suggests that consecutive reactions of the following type may be involved in the formation of Al-O-Al bonds:

$$Al(OR)_3 \longrightarrow Al(OR)_2OH + Olefin$$

$$Al(OR)_2OH + Al(OR)_3 \longrightarrow (RO)_2AlOAl(OR)_2 + ROH$$

or

$$2\ Al(OR)_2OH \longrightarrow (RO)_2AlOAl(OR)_2 + H_2O$$

$$Al(OR)_3 + H_2O \longrightarrow Al(OR)_2OH + ROH$$

$$Al(OR)_2OH \longrightarrow ROH + \{ROAl{=}{=}O\} \longrightarrow \text{Polymer or cyclics.}$$

As yet, insufficient information is available to decide which of the above reactions are of major importance in the Al-O-Al bond-forming mechanism. It is of interest that dialkoxytitanium oxides have been reported as stable, monomeric species (Reference 19). Molecular orbital calculations are currently being carried out by Dr. H. H. Jaffe in an effort to estimate the stability of alkoxy- and aryloxyaluminum oxides.

4. Polymerization Reactions

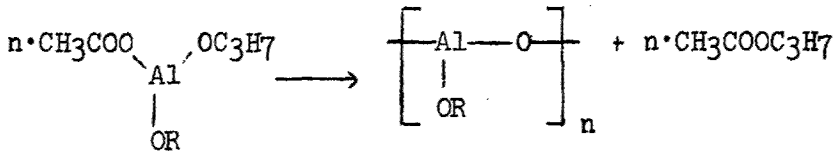
a. Intermolecular heterofunctional condensation reactions have been employed with limited success in the preparation of polymers containing boron-oxygen-silicon bonds (Reference 21), antimony-oxygen-silicon bonds (Reference 22), tin-oxygen-silicon bonds (References 23 and 24), boron-oxygen-phosphorous bonds (Reference 22) and aluminum-oxygen-silicon bonds (Reference 1b) by the condensation of dialkoxy metal derivatives with diacyloxy metal compounds.

$$R_mM(OR)_2 + R_nM'(OOCR')_2 \longrightarrow RO{-}\underset{\displaystyle R_m}{M}{-}O{-}\underset{\displaystyle R_n}{M'}{-}OOCR' + R'COCR$$

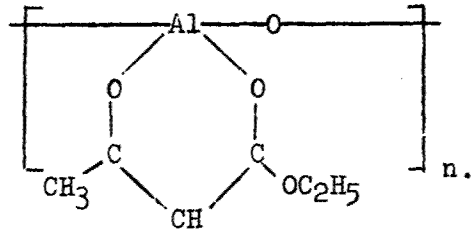
$$x{\cdot}RO{-}\underset{\displaystyle R_m}{M}{-}O{-}\underset{\displaystyle R_n}{M'}{-}OOCR' \longrightarrow RO\left[{-}\underset{\displaystyle R_m}{M}{-}O{-}\underset{\displaystyle R_n}{M'}{-}O{-}\right]_{\displaystyle x}OCR + x{\cdot}R'COOR.$$

b. A few reports of the preparation of polyaluminoxanes by this method are described in the literature. The formation of "chain-like polymers with alkoxy and carboxy groups attached to the aluminum atoms" from aluminum alkoxides and organic acids or amides is claimed

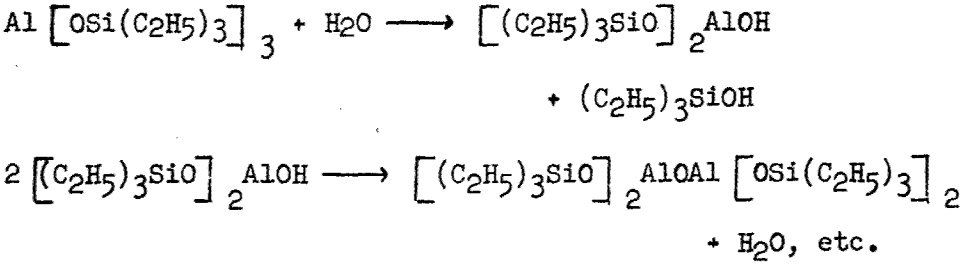
(Reference 25). Theobald (Reference 26) obtained a brittle, toluene-soluble polymer with a molecular weight of 5730 believed to have been a polyheptanoxyaluminoxane by heating isopropoxydiheptanoxyaluminum. It has been observed in this work that acetoxyisopropoxyphenoxyaluminum lost the elements of isopropyl acetate at 310°C with the formation of a brown, partially toluene-soluble resin. This resin decomposed in a vacuum above 380°C and was presumed to have a polyphenoxyaluminoxane structure. A similar pyrolysis of acetoxyisopropoxy(triphenylsiloxy)-aluminum at 175°C gave only 15 percent of the expected isopropyl acetate.



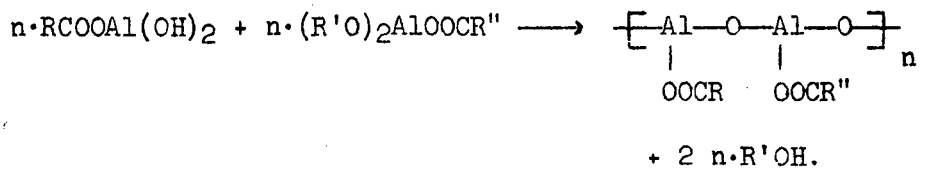
c. Another approach to the preparation of polyaluminoxanes is through the partial hydrolysis of aluminum monomers. In a recent paper, Kugler (Reference 27) reported the preparation of an "aluminum resin" by the hydrolysis of diethoxy(-1-carbethoxyprop-1-ene-2-oxy)-aluminum. This polymer was a solid, brittle, light yellow, clear resin which was very soluble in a number of organic solvents:



Andrianov, et al.(Reference 10), obtained poly(triethylsiloxy)aluminoxanes by passing moist air through tris-(triethylsiloxy)aluminum at 165-170°C.

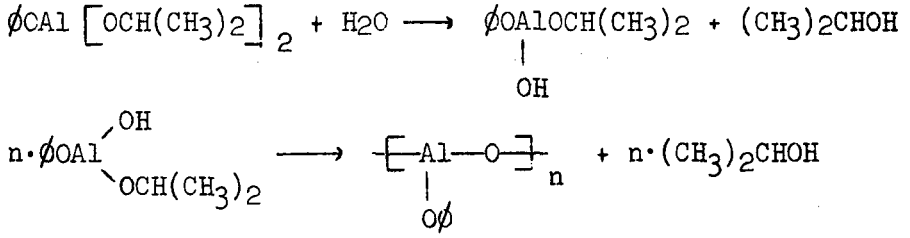


A method of forming polyacyloxyaluminoxanes utilizing dihydroxy and di-alkoxyaluminum acylates has been described in a British patent (Reference 28):



+ 2 n·R'OH.

d. A number of attempts were made to prepare polyphenoxyaluminoxane by the partial hydrolysis of diisopropoxyphenoxyaluminum:



Reaction with one molar equivalent of water followed by heating at 160-165°C gave a toluene-soluble solid, shown by its aluminum content to be a low polymer. Attempts to increase the molecular weight by going to higher temperatures or by using diphenyl ether as a solvent led to insoluble, crosslinked products. Isopropoxy and phenoxy groups bonded to aluminum may not be widely different in their hydrolytic reactivity.

e. The partial hydrolysis of diisopropoxy(triphenylsiloxy)-aluminum in boiling toluene solution gave the quantitative amount of isopropyl alcohol and a benzene-soluble resin which was visually unchanged after heating to 500°C in an evacuated tube. Although the aluminum content was close to that calculated for a poly(triphenylsiloxy)aluminoxane, the material had a cryoscopic molecular weight close to that of a dimer.

f. The reaction of triphenylaluminum and excess water at 0°C was violent and gave benzene; neither biphenyl nor phenol could be detected, contrary to a report by earlier workers (Reference 29). Partial hydrolysis of triphenylaluminum in tetrahydrofuran solution gave a toluene-insoluble infusible solid which decomposed slowly above 310°C and had an aluminum content below that calculated for polyphenylaluminoxane.

C. CONCLUSIONS

a. From the thermal stability data reported above, it is evident that phenoxy-, quinolin-8-oxy-, triphenylsiloxy- and trimethylsiloxy-groups bear further investigations as substituents in polyaluminoxane polymers. It is planned to obtain product analyses and semiquantitative kinetic data for the thermal degradation of prototype compounds containing these groups. In addition, pyrolysis experiments are con-

templated to test the ionic mechanism proposed above for the elimination of ethers and esters and to demonstrate whether the reaction is intramolecular or intermolecular.

b. The preliminary polymerization results suggest a number of experiments:

(1) Heterofunctional condensation reactions of acetoxyisopropoxyphenoxyaluminum and acetoxyisopropoxytriphenylsiloxyaluminum should be carried out at other temperatures and in high-boiling solvents.

(2) As an extension of the ionic mechanism proposed above, chloroacetoxy derivatives rather than acetoxy monomers will be examined as precursors of polyaluminoxanes, since chloroacetates should be eliminated more easily than acetates.

(3) Partial hydrolyses of difunctional aluminum monomers containing the quinolin-8-oxy and trimethylsiloxy groups will be studied.

This work was carried out in the period September, 1958 to April, 1959 under Air Force Contract AF 33(616)-5931.

REFERENCES

1. (a) C. F. Gibbs, H. Tucker, G. Schlapenko and J. C. Park, "Development of Inorganic Polymer Systems", WADC Technical Report 55-453, Part I (1956). (b) Part II (1956).
2. R. L. Rau, The Air Force Inorganic Polymer Program, WADC Technical Report 58-160, June 1958 (p.25).
3. G. E. Hansen and D. M. Dennison, J. Chem. Phys., 20, 313 (1952).
4. G. Glockler, J. Phys. Chem., 62, 1049 (1958).
5. T. Tanaka and T. Watase, Bull. Chem. Soc. Japan, 28, 258 (1955); cited by A. H. Sehon and M. Szwarc, Ann. Rev. Phys. Chem., 8, 444 (1957).
6. G. DeMaria, J. Drowait and M. G. Inghram, J. Chem. Phys., 30, 318 (1959).
7. R. F. Porter, P. Schissel and M. G. Inghram, ibid., 23, 339 (1955).
8. L. Pauling, "The Nature of the Chemical Bond", 2nd Ed., Cornell University Press, Ithaca, New York (1940).
9. H. Gilman and G. E. Dunn, Chem. Revs., 52, 83 (1953).
10. K. A. Andrianov, A. A. Zhadanov and V. G. Dulova, Doklady Akad. Nauk SSSR, No. 6, 1050 (1957).
11. K. A. Andrianov, Uspekhi Khimii, 26, 895 (1957).
12. K. A. Andrianov and N. N. Sokolov, Khim. Prom., 329 (1955); Chem. Abstr., 50, 7499d (1956).
13. D. C. Bradley and I. M. Thomas, Chem. and Ind., 1231 (1958).
14. F. Henle, Ber., 53, 719 (1920).
15. A. N. Cook, J. Am. Chem. Soc., 28, 608 (1906).
16. H. Adkins and P. P. Perkins, J. Am. Chem. Soc., 47, 1163 (1925).
17. F. Whitmore et al., J. Am. Chem. Soc., 64, 2970 (1942).
18. H. Meerwein and T. Bersin, Ann., 476, 113 (1929).
19. A. N. Nesmeyanov and O. V. Nogina, Doklady Akad. Nauk SSSR, 117, 249 (1957).
20. J. Hine and M. Hine, J. Am. Chem. Soc., 74, 5266 (1952).
21. F. A. Henglein, R. Lang and K. Scheinost, Makromol. Chem., 15, 177 (1955).
22. Idem., 18, 102 (1956); 19, 118 (1956).
23. P. E. Koenig, "Conference on High Temperature Polymer and Fluid Synthesis", WADC Technical Report 57-657, January 1958, p. 50.
24. F. A. Henglein, R. Land and L. Schmack, Makromol. Chem., 22, 103 (1957).
25. British Patent No. 772,480 (April 17, 1957).
26. C. W. Theobald, U. S. Patent No. 2,744,074 (May 1, 1956).
27. V. Kugler, J. Poly. Sci., 29, 637 (1958); Czech. Patent No. 85,300 (1955).
28. British Patent No. 783,679 (September 25, 1958).
29. S. Hilpert and G. Grüttner, Ber., 45, 2828 (1912); Chem. Abstr., 7, 482 (1913).

ORGANOMETALLIC POLYMERS CONTAINING TIN OR ALUMINUM

R. D. Crain and P. E. Koenig
(Ethyl Corporation)

There has been considerable effort in the past few years directed towards polymers which not only have good mechanical properties but are also thermally stable. The organometallic oxide polymers, of which the siloxanes are the prototype, have long been considered likely possibilities. The siloxanes have many of the desired properties except their limitations to heat stability. Improvements along this line can be made by adding small amounts of other metal compounds as cross-linking agents, such as aluminum (1, 2, 3).

Reports on the preparation of the metallosiloxanes have appeared in recent literature in the areas of borosiloxanes (4), antimonosiloxanes (5), titanosiloxanes (6), arsenosiloxanes (7), aluminosiloxanes (8), and stannosiloxanes (6, 9, 10). The stabilities of these polymers have been good, but not outstanding, and very few have been made in high molecular weight form.

Tin Polymers

The major portion of Ethyl's work on stannosiloxanes was presented at last years conference. However, for clarity it might be well to give the general methods of preparation before discussing the evaluation of the polymers.

$$R_2SnO + R'_2Si(OH)_2 \rightarrow \{R_2SnO\}_m(R'_2SiO\}_n$$

$$R_2SnCl_2 + R'_2Si(ONa)_2 \rightarrow \{R_2SnO\}_m(R'_2SiO\}_n$$

$$R_2SnCl_2 + R'_2SiCl_2 \xrightarrow{OH^-} \{R_2SnO\}_m(R'_2SiO\}_n$$

$$R_2SnO + R'_3SiOH \rightarrow R'_3SiO\{R_2SnO\}_nSiR'_3$$

The molecular weights of the polymers soluble in benzene ranged from 1000 to 5000. The properties of the polymers will be considered from the viewpoint of their Sn:Si ratios, taking into consideration the differences of phenyl and methyl groups substituted on the metal atoms.

Behavior on Reaching a Melting Point. A Fischer-Johns melting point apparatus was used. The polymers tested and the results obtained are given in the following table:

Sn:Si Ratio	R_2Sn	R'_2Si	Softing Point, °C	Melting Point, °C	Liquid °C	Temp. at which Odor is Detected, °C
1:10	ø	ø	120	155	165	None
1:3	ø	ø	45	55	70	Slight at 175
1:10	Me	ø	100	180	Milky Liquid	None
1:3	Me	ø	70	135	170	None
1:1	ø	Me	55	-	Brittle at 190	90
1:3	Me	Me	<25	Bubbles at 120	Brittle at 200	Sharp at 90
1:10	Me	Me	<25	190	-	205

Hydrolytic Stability. Based on the procedure of the American Society for Testing Materials, polymer samples up to 0.1 gram were conditioned in an oven at 55°C for 24 hours. After conditioning, the samples were weighed and placed in a small beaker and covered with distilled water. After 24 hours the samples were removed, dried, and weighed. The results were as follows:

Sn:Si	R_2Sn	R'_2Si	Increase in Weight
1:10	Me	ø	0%
1:3	ø	ø	0.25%
1:10	ø	ø	0.36%
1:3	Me	ø	0.65%
1:1	ø	Me	1.95%

No results were determined for (Sn)dimethyl-(Si) dimethylstannosiloxanes of ratios of 1:10 and 1:3.

Oxidation and Weight Loss. Samples were weighed in weighing bottles and put into an oven at a constant temperature of 245°C. The samples were weighed every 8 hours for 72 hours. The oxidation and weight loss of these polymers are shown in Figures 1 and 2.

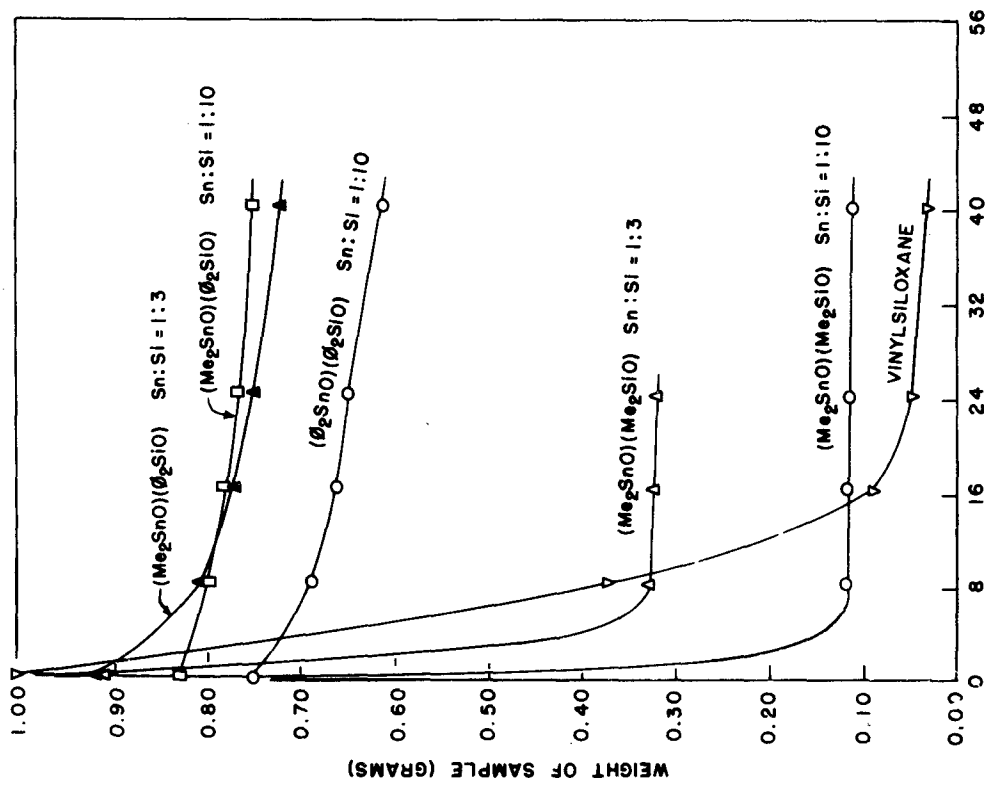


FIGURE 2

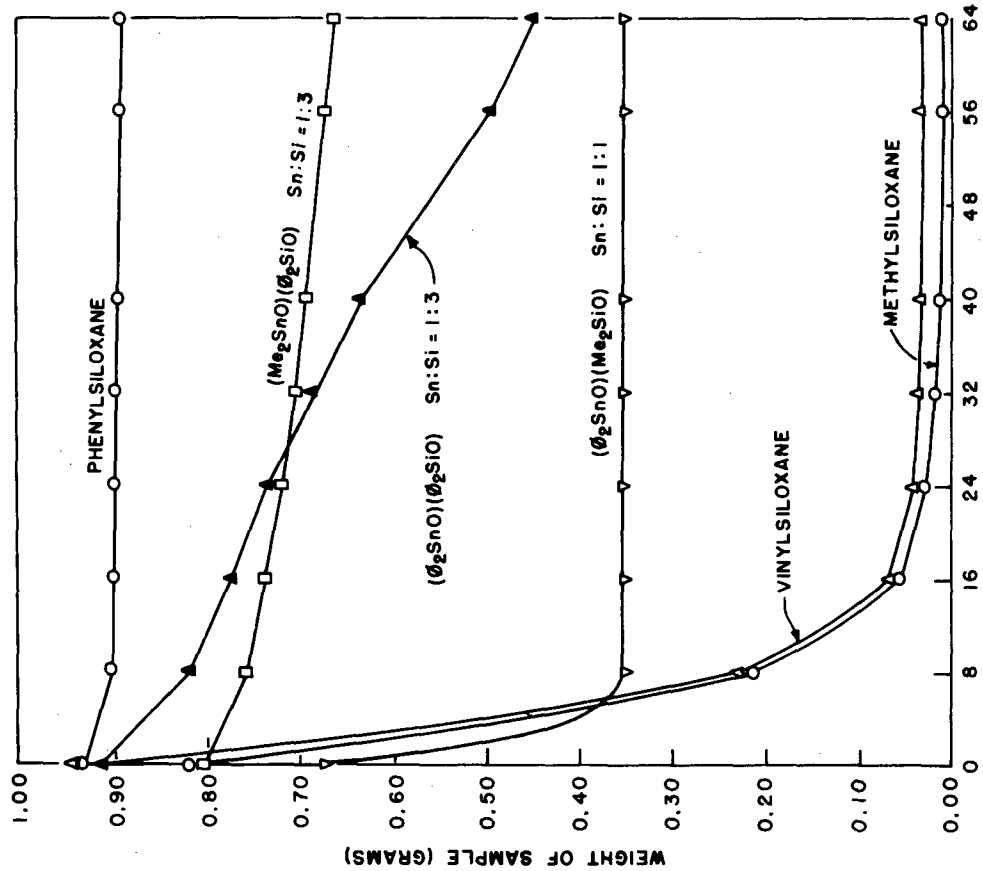
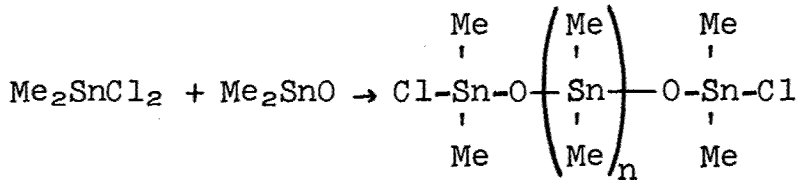


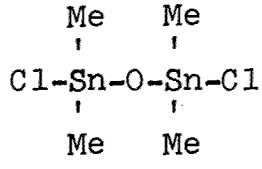
FIGURE 1

From these graphs it is apparent that none of the compounds tested are as stable as poly(diphenylsiloxane); however, all the stannosiloxane polymers were less affected by prolonged heating than were poly(methylsiloxane) and poly(vinylsiloxane). Considering the stannosiloxanes as a group, those containing phenylsilicon moieties were more stable than their methylsilicon counterparts. The same conclusions may be drawn from consideration of the behavior of the polymers on heating on a melting point block. It is also of interest that the polymers appear to become more stable as the relative amount of tin is decreased.

Because of their close relation to stannosiloxane polymers, we have also studied the "double salt" compounds initially described by Harada (11): These compounds result when disubstituted organotin halides are partially hydrolyzed, or are heated with the corresponding organotin oxide. They presumably have a stannoxane structure, the chains being terminated by halogen or other anionic groups:



From equimolar amounts of dimethyltin dichloride and dimethyltin oxide we prepared a compound with a composition in fair agreement with that calculated for the "double salt" shown:



It was thought that analogous reactions might be observed between dichlorosilanes and organotin oxides, producing stannosiloxanes which could be hydrolyzed to polymers. Compounds of the desired composition were obtained but they are apparently quite unstable. During attempted recrystallization these compounds evidently disproportionated to regenerate the starting materials. This surprisingly facile rearrangement provides no encouragement for the stability of the stannosiloxane polymers.

The rather unusual stabilities of the organotin sulfides have led to earlier speculation by us that organostanthiane polymers might be of interest. Some of these compounds have been prepared by interaction of mixed organotin halides with sodium hydrogensulfide. A more elegant synthesis has now

been devised by reacting mixtures of dialkyl and/or diaryl tin with elemental sulfur in liquid ammonia solution. The reaction proceeds smoothly and rapidly to produce the copolymers.

The products obtained by this method have been (probably) of low molecular weight, for they are mobile fluids at room temperature. They frequently possess a disagreeable sulfurous odor - possibly due to the presence of impurities such as trialkyltin sulfides. The resins are not thermally stable above 200°C, but seem to retain their fluidity down to -20°C and are not brittle even at solid CO_2 temperatures.

Another type of polymer which is of interest is the true organometallic polymer with a chain that contains metal-carbon bonds rather than inorganic metal-oxygen bonds. These polymers have not been extensively investigated because of the difficulties inherent in the preparation of suitable monomers.

A possible synthesis route to these types of polymers can be realized by using a dialkyltin disodium with a dihalide. Elastomeric polymers

$$\emptyset_2SnNa_2 + Br(CH_2)_4Br \rightarrow \left[\emptyset_2Sn(CH_2)_4\right]_n$$

were obtained by this reaction. A more interesting polymer from the standpoint of thermal stability would no doubt be the phenylene-linked polymer prepared as follows:

$$\emptyset_2SnNa_2 + Br\text{-}C_6H_4\text{-}Br \rightarrow \left[\emptyset_2Sn\text{-}C_6H_4\right]_n$$

We have observed that reaction does in fact take place between the two reactants (bromide ions present) but the results are not conclusive.

Difficulties encountered with these reactions led to a more fundamental examination of the tin disodium derivatives. Attempts to repeat the preparation of tetramethyltin (12) by the reaction of dimethyltin disodium and methyl iodide were unsuccessful. It may well be that the compound "dimethyltin disodium" does not exist at all, or at least does not react as expected with alkyl halides.

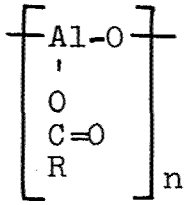
Aluminum Polymers

The area of aluminum polymers has been receiving a great deal of attention lately. One of the major pieces of

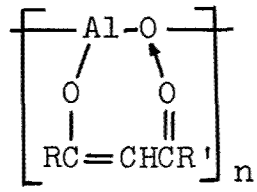
work has been conducted by Andrianov et al. (8, 13, 14, 15, 16) on the aluminosiloxanes. The method used involves the addition of water to an aluminosiloxane monomer and heating. These resins show the properties of cross-linked polymers in that most of them are infusible and insoluble solids. Work in this country was first applied to modifying existing polysiloxanes by the addition of small quantities of aluminum compounds as cross-linking agents (1, 2, 3).

The organoaluminum polymers have not been neglected. In fact, there seems to be much more varied activity in this area than credited to the aluminosiloxanes. Some work, as with the siloxanes, consists of modifying existing resins to render them more thermally stable (17, 18, 19, 20, 21). Reaction of aluminum alkoxides with acids gives resins which can be applied as water repellants or surface active materials or used in the preparation of lacquers. These resins range from gums to hard brittle solids (22, 23, 24, 25, 26, 27).

The aluminum oxide structure seems to offer more potential in a high temperature polymer since it is known to be very stable thermally and, hence, should impart similar properties to polymers in which it is incorporated. Resins of the following two types have been investigated (25, 28) (29, 30):



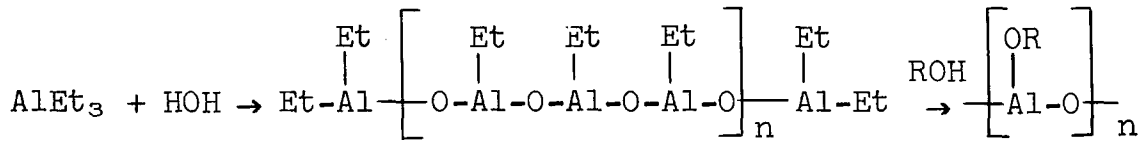
and



There is some doubt now, based on our work, that these structures are linear as shown. In fact, they are probably highly cross-linked.

The accessibility of the aluminum alkyls and hydrides to this laboratory provides convenient starting materials for the preparation of polymers containing an aluminum atom in the backbone of the molecule. The extreme reactivity of the carbon-aluminum bond should also give a facile reaction and aid in the formation of high molecular weight polymers. Such considerations have encouraged us to conduct explorations in this area.

It was reasoned that, if the reaction of difunctional molecules such as water and diols with triethylaluminum were controlled, a polymer with active ethyl groups would be formed. These ethyl groups could then be reacted with an alcohol to give a stable aluminum polymer:

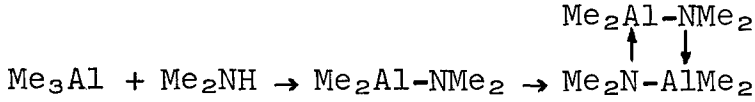


It was anticipated that the ethyl groups along the polymer chain would be relatively less reactive than the two ethyl groups at each end of the growing chain.

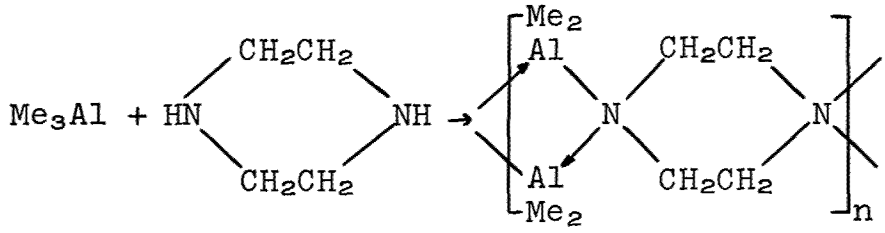
The first step proceeds smoothly, liberating the expected quantity of gas. However, reaction of the formed ethylaluminum oxide polymer with triphenylsilanol or t-butanol resulted in a precipitate and gave approximately 60% of the theoretical amount of gas evolution. Attempts to account for the other 40% of ethyl groups through the presence of oxygen (requiring over 100 cc) and/or water (0.2 g needed) do not seem logical since extra precautions were taken for the exclusion of air and moisture from the reaction apparatus and materials used. It may be that the ethyl groups are buried deeply enough in the cross-linked structure to prevent attack by these alcohols.

The formed polymers are insoluble in organic solvents and do not fuse, even at their decomposition points. All are stable up to 250°C and some are stable up to 400°C. These properties are characteristic of a high degree of cross-linking. Since there are two different types of ethyl groups in the linear polymer available for reaction (ethyl groups along the chain, and terminal ethyl groups), it is evident that the statistical probability of an active hydrogen reacting with an ethyl group along the chain quickly overcomes the difference in reactivity of the terminal ethyl groups, with the resultant formation of cross links.

Reactions of amines with trialkylaluminums have also been explored. The literature (31) reports that reaction of trimethylaluminum with dimethyl amine first gives a single Al-N bond with the evolution of methane. Upon heating, this material dimerizes to form a stable product:



Applying this idea for use in a polymer might give the desired property of high temperature stability. When trimethylaluminum was reacted with anhydrous piperazine, an infusible and insoluble solid was formed having the aluminum content of the expected polymer:

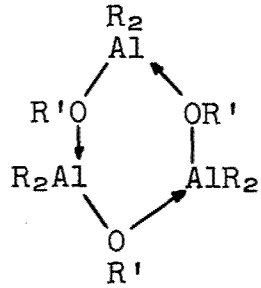


Although the physical properties are similar to those of the previous polymers, there is no proof for linerity or cross-linking. The polymer is not reactive toward water but it decomposes in air at temperatures above 200°C.

In an attempt to eliminate cross-linking, dialkylaluminum monomers were used. Such compounds can be readily prepared by reacting a trialkylaluminum with one equivalent of an alcohol. Trimethylsiloxydimethylaluminum was chosen as a convenient starting material. Reaction with molar quantities of diphenylsilanediol gave an infusible solid with a molecular weight of 798. When heated to 180°C, hexamethyldisiloxane and benzene were formed. Similar disproportionation products are obtained from the stannosiloxanes.

Reaction of trimethylsiloxydimethylaluminum with 2,2-dimethyl-1,3-propanediol gave an infusible and insoluble solid which was stable up to 300°C. This material was, in most respects, quite similar to the previous cross-linked polymers.

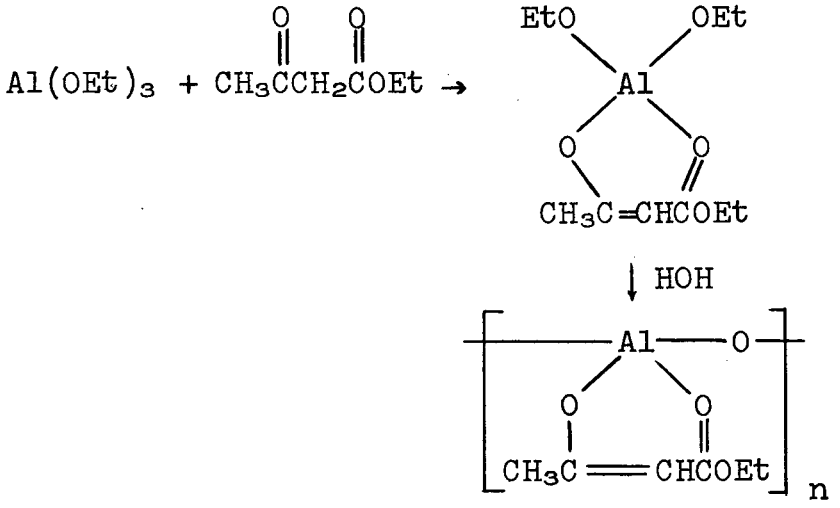
Molecular weight studies of the dialkylaluminum compounds have led to an explanation of this observed infusibility. Cryoscopic studies of the dimethylaluminum methoxide show that it is a trimer rather than a monomer (31). The trimer is stable thermally and exists as such in the gas phase. It is also stable towards trimethylamine. A trimeric structure for trimethylsiloxydimethylaluminum readily explains the formation of a three dimensional polymer due to the presence of six reactive sites in the molecule. A check was made by preparing a similar compound, dimethoxyaluminum-t-butoxide, which was also a trimer. The general formula for these trimers is believed to be:



With the object of eliminating cross-linking, it was assumed that the use of a large bulky group for R' might sterically hinder the oxygen and aluminum, thereby eliminating the tendency to form trimers. A highly hindered molecule like 2,6-di-t-butylphenol should accomplish this. However, studies showed that the obtained dimethylaluminum-2,6-di-t-butylphenoxide was also a trimer. The use of an ether solvent like dioxane in the cryoscopic molecular weight determination still gave a trimeric formula. Hydrolysis of the trimer of dimethylaluminum-2,6-di-t-butylphenoxide with 1,5-pentanediol gave an infusible and insoluble polymer consistent with a high degree of cross-linking. This reaction proceeded much slower due to the steric hinderance of the phenol. It is believed that replacement of the methyl groups with larger alkyl groups may give a monomer, but the reactivity of the aluminum-alkyl bond will be sacrificed.

There is very little known on the chemistry of preparing monochelates of aluminum. The B. F. Goodrich Company has reported their work in this area (30) and to date no high molecular weight polymers have been made with good thermal properties. In view of a recent report in the literature (29) on the preparation of diethoxyaluminum ethylacetoacetate, a closer study of these reactions was undertaken.

Aluminum ethoxide reacts with ethyl acetoacetate with the splitting out of one mole of ethanol. The product is reported to be a very viscous material giving the proper aluminum analysis for a 1:1 product. Hydrolysis with water forms a solid with retention of the chelate and liberation of two moles of ethanol.



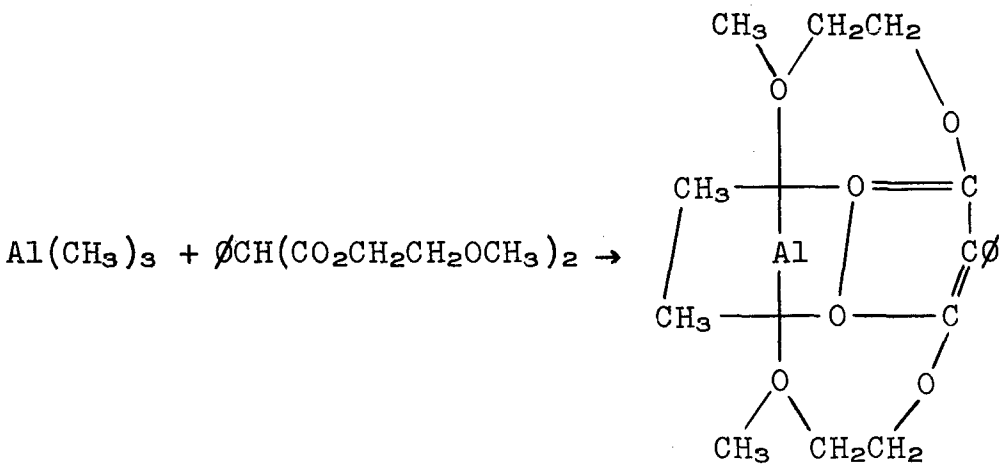
This reaction was repeated except the intermediate chelate was not isolated. Instead, the chelate was reacted with 1,5-pentanediol to give a yellow brittle solid. A similar reaction using 2,4-pentanedione formed a yellow brittle glass which also gave a brittle solid when reacted with 1,5-pentanediol. Neither resin was fusible or soluble in organic solvents. When both heat and pressure (greater than 10,000 psi) were applied, brittle films could be formed. Exposure to moisture in the atmosphere for a few days caused hydrolysis of the resins. If these resins are heated above 180°C, the odors of the diketone or ester can be detected.

These results indicate a fair amount of cross-linking. The isolation of the diethoxyaluminum ethylacetoacetate confirmed this. Instead of being a monomer, as reported, the compound is actually a resin with about three times the expected molecular weight of a monomer. Hydrolysis with 1,5-pentanediol gave an infusible and insoluble resin which, when heated, had the odor of ethyl acetoacetate. Hydrolysis with diphenylsilanediol formed a fusible brittle resin with a molecular weight of 1230. Again, when heated the odor of the ester could be detected. Attempts to increase the molecular weight were unsuccessful.

Since attempts to get monomer chelate materials from aluminum ethoxide failed and no high molecular weight polymers were obtained, the use of the trialkylaluminum as a starting material was investigated. The product from the reaction of triisobutylaluminum and 1,3-diphenyl-1,3-propanedione is insoluble in benzene and is presumably the monochelate (32). Reaction of trimethylaluminum with 2,4-pentanedione gave a deep red brittle glass. With ethyl acetoacetate a distillable liquid was obtained. The infrared spectrum showed the characteristic absorption bands for Al-Me and also a band for an Al-O chelate bond. Hydrolysis of this liquid with 1,5-pentanediol gave an insoluble and infusible solid similar to those obtained from the hydrolysis of triethylaluminum.

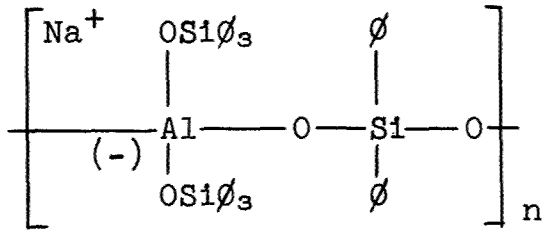
One possible explanation of the observed cross-linking of the chelate polymers is the fact that aluminum readily forms compounds such as aluminum acetylacetonate where three covalent bonds and three coordinate covalent bonds are formed. A tetradentate molecule could be used whereby the aluminum has only two reactive groups available for formation of linear polymers. Molecular models show that one of the six-membered rings formed from a tetradentate is not stable sterically and that seven-membered rings will most likely be more suitable. A readily available material of this nature can be found in di(methoxyethyl)phenylmalonate. This ester was easily prepared by transesterification of diethyl phenylmalonate with 2-methoxyethanol. Trimethylaluminum should then react with the enolizable hydrogen, liberating one mole of

methane, and the remaining oxygens in the diester could then form the octahedral structure.



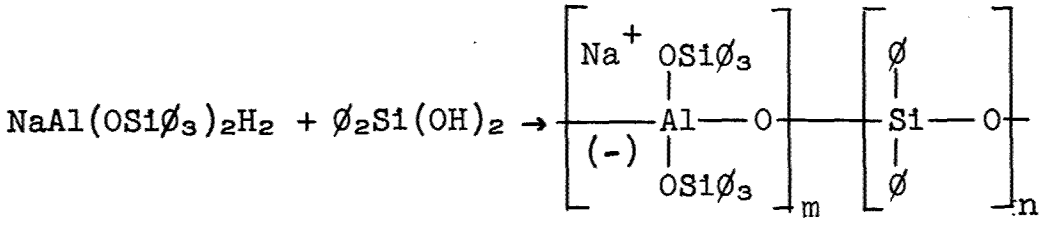
Attempts to carry out this chelation reaction in the laboratory did not give the expected chelate. When the reaction was run in 1:1 mole ratios a viscous liquid was isolated with a molecular weight greater than 500 (calculated molecular weight is 352). Further treatment of this liquid with 1,5-pentanediol gave an infusible and insoluble solid decomposing at a temperature above 230°C. Using two moles of trimethylaluminum and one of the diester gave a similar viscous liquid. However, none of the excess trimethylaluminum could be isolated, indicating that instead of forming a simple chelate intramolecularly, an intermolecular reaction was occurring.

Chain interaction should be preventable by the elimination of reactive sites along the chain. Thus, if the electron-accepting sites in a chain can be satisfied by groups or structures other than those in a neighboring chain, there will be little interaction. This is, of course, the concept which Ruigh (33) explored in his studies of quadricovalent boronic acids and other chelated structures. Another approach to this problem of neutralization of reactive sites involves use of anions as electron donors, as in the following structure:



While the particular structure indicated might be subject to facile hydrolysis, the analogous polymer using different cations in place of sodium might be quite inert both to hydrolytic and to thermal decomposition. We have attempted the synthesis of the compound represented above by reaction of sodium aluminum hydride with two moles of triphenylsilanol followed by one mole of diphenylsilanediol:

$$NaAlH_4 + 2\ \phi_3SiOH \rightarrow NaAl(OSi\phi_3)_2H_2$$



The compound obtained was fairly stable to heat but was easily hydrolyzed.

The data presented on aluminum polymers substantiate the thermal stability of the aluminum-oxygen bond. However, one factor complicates the formation of a linear polymer - the ability of the aluminum atom to have a coordination number of either four or six. Thus, attempts to make monomeric materials led to substances which were low molecular weight polymers and these, in turn, formed cross-linked polymers.

References

1. M. C. Agens (to General Electric Company), U. S. Pat. 2,714,585 (Aug. 2, 1955); Chem. Abs. 49, 1433j (1955).

2. A. J. Barry (to Dow Chemical), U. S. Pat. 2,460,799 (Feb. 8, 1949); Chem. Abs. 43, 3234a (1949).

3. Dow Corning Corp., Brit. 651,699 (Apr. 4, 1951); Chem. Abs. 45, 7818c (1951).

4. F. A. Henglein, R. Lang, and K. Scheinost, Makromol. Chem., 15, 177 (1955).

5. F. A. Henglein, R. Lang, and K. Scheinost, ibid., 18-19, 102-118 (1956).

6. K. A. Andrianov, T. N. Ganina, and E. N. Khrustaleva, Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk, 1956, 798.

7. R. M. Kary and K. C. Frisch, J. Am. Chem. Soc., 79, 2140 (1957).

8. K. A. Andrianov and A. A. Zhdanov, J. Polymer Sci., 30, 513 (1958).

9. P. E. Koenig, Conference on High Temperature Polymer and Fluid Synthesis, WADC TR 57-657, 50 (1958).

10. J. F. O'Brien, WADC TR 57-502.

11. T. Harada, Sci. Papers Inst. Phys. and Chem. Res. (Tokyo), 35, 318ff (1939).

12. C. A. Kraus and W. N. Greer, J. Am. Chem. Soc., 47, 2568 (1925).

13. K. A. Andrianov, A. A. Zhdanov, and E. Z. Annovich, Doklady Akad. Nauk S.S.S.R. 118, 1124-7 (1958); Chem. Abs. 52, 12803a (1958).

14. K. A. Andrianov and T. N. Ganina, Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk, 1956, 742; Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1956, 71-7.

15. K. A. Andrianov, A. A. Zhdanov, and S. A. Pavlov, Doklady Akad. Nauk S.S.S.R., 102, 85 (1955); Chem. Abs. 50, 4772a (1956).

16. K. A. Andrianov and A. A. Zhdanov, Doklady Akad. Nauk. S.S.S.R., 114/5, 1005 (1957).

17. G. L. Brown and B. B. Kline (to Rohm and Haas Co.), U. S. Pat. 2,754,280 (July 10, 1956); Chem. Abs. 50, 15100c (1956).

18. Badische Aniline- and Soda Fabrik Akr.-Ges (J. Thewalt and F. Mühlbauer), Ger. 828,007 (Jan. 14, 1952); Chem. Abs. 50, 3802e (1956).

19. C. Dangelmajer (to Resistoflex Corp.), U. S. Pat. 2,408,377 (Oct. 1, 1946); Chem. Abs. 41, 624c (1947).

20. Chemische Werke Albert., Brit. Pat. 721,938 (Jan. 12, 1955); Chem. Abs. 49, 92921 (1955).

21. Chemische Werke Albert., Brit. Pat. 740,576 (Nov. 16, 1955); Chem. Abs. 50, 10448f (1956).

22. C. W. Theobald (to E. I. duPont de Nemours and Co.), U. S. Pat. 2,744,074 (Apr. 18, 1951).

23. Peter Lunt and Co., Ltd. and E. J. Lush, Brit. Pat. 573,083 (Nov. 6, 1945); Chem. Abs. 43, 4894c (1949).

24. Chemische Werke Albert., Brit. Pat. 718,283 and 718,340.

25. Koninklijke Industrieele Maatschapp. Voorheen Noury and Van der Lande N. V., Brit. Pat. 783,679 (Sept. 25, 1956); ibid., Brit. Pat. 803,768.

26. K. C. Pande and R. C. Mehrotra, Z. anorg. u. allgem. Chem., 286, 291 (1956); Chem. Abs. 51, 3348g (1957).

27. Farbwerke Hoechst A.-G. Vorm. Meister Lucius and Brüning, Brit. Pat. 772,480 (Apr. 17, 1957); Chem. Abs. 51, 12549d (1957).

28. W. J. C. Viveen and P. L. Stedehouder, Ger. 1,019,468 (Nov. 14, 1957).

29. V. Kugler, J. Polymer Sci., 29, 645 (1958).

30. C. F. Gibbs, H. Tucker, G. Shkapenko, and J. C. Park, WADC TR 55-453 (May 1956).

31. N. Davidson and H. C. Brown, J. Am. Chem. Soc., 64, 316 (1942).

32. C. F. Gibbs, H. Tucker, G. Shkapenko, and J. C. Park, WADC TR 55-453 (1957).

33. W. L. Ruigh, et al., WADC TR 55-26.

Research on Organosilyloxy-Metal Compounds and Metallo-organic Compounds containing Metal-Nitrogen Bonds

By D.C. Bradley,

Department of Chemistry,

Birkbeck College,

Malet Street,

London, W.C.1;

U.K.

Paper presented at the Conference on High Temperature Polymer and Fluid Research, A.R.D.C., Dayton, Ohio, May, 1959.
Contract No. AF 61(052)-174.

1. The synthesis of trialkylsilyloxy-derivatives of titanium, zirconium, niobium and tantalum

The work described in this section was completed before Contract No. AF 61(052)-174 and it involved a study of the preparation and properties of compounds containing M-O-Si bonds, where M is a transition metal. Metal alkoxides $M(OR)_n$ are polymeric and also give rise to polymeric hydrolysis products $MO_x(OR)_{n-2x}$ and hence it was important to compare the thermal and hydrolytic stability of the M-O-Si system with that of the M-O-C system in order to assess the possibilities of forming stable M-O-Si polymers.

English and Sommer[1] first reported a trialkylsilyloxy-transition metal compound when they prepared tetrakis-trimethylsilyloxy-titanium in 18% yield from the reaction involving the silanol, titanium tetrachloride, and ammonia in benzene solution:

$$TiCl_4 + 4\ Me_3SiOH \longrightarrow Ti(OSiMe_3)_4 + 4\ NH_4Cl \quad . . . . . (1)$$

They realised that the low yield was caused by hydrolysis involving the water produced by the facile acid catalysed condensation of the silanol, e.g.:

$$-TiCl + HOSi- \longrightarrow Ti-O-Si + HCl \quad . . . . . (2)$$

$$TiCl_4 + HCl \longrightarrow TiCl_5^- + H^+ \quad . . . . . (3)$$

$$2\ Me_3SiOH \xrightarrow{H^+} Me_3Si-O-SiMe_3 + H_2O \quad . . . . . (4)$$

We decided to avoid this condensation by a silanolysis of the metal alkoxide in which no strong acid was involved. Trimethylsilanol was caused to react with titanium <u>iso</u>-propoxide in boiling benzene and the liberated <u>iso</u>propanol was removed by fractionation as the binary azeotrope with benzene.

$$Ti(OPr^i)_4 + 4\ Me_3SiOH \longrightarrow Ti(OSiMe_3)_4 + 4\ Pr^iOH \quad . . . (5)$$

However, we noted that the ternary azeotrope of benzene-<u>iso</u>propanol-water was first produced and moreover, although the 47% yield of tetrakis-trimethylsilyloxy-titanium represented an advance on English and Sommer's method, it was clear that condensation of the silanol must still have occurred. This was confirmed by Zeitler and Brown[2] who obtained a 56% yield of $Ti(OSiMe_3)_4$ from the reaction involving titanium <u>n</u>-butoxide and trimethyl-

silanol in boiling toluene. These authors also isolated some trimethyl butoxysilane as a product of reaction, evidently from the condensation involving the silanol and the butanol liberated in the silanolysis:

$$BuOH + Me_3SiOH \longrightarrow Me_3SiOBu + H_2O \quad \ldots\ldots\ldots \quad (6)$$

Clearly the best way to avoid the condensation reactions is to keep the concentrations of silanol and alcohol low. By slow addition of silanol to the boiling solution of titanium isopropoxide in benzene, with simultaneous removal of the liberated isopropanol, we obtained a quantitative yield of tetrakis-trimethylsilyloxy-titanium.[3] Quantitative yields of the whole series of methyl ethyl silyloxy-titaniums $Ti(OSiMe_xEt_{3-x})_4$ where $x = 3$, 2, 1 or 0 and of the isomeric propyldimethylsilyloxy-titaniums were also obtained. Other workers have independently prepared similar titanium compounds. For example, Dolgov and Orlov[4] prepared some of the methyl ethyl silyloxy-titaniums and methyl di-n-propylsilyloxy-titanium from reactions involving titanium ethoxide and the silanol in the presence of a trace of sodium. They obtained only a 50% yield of the trimethylsilyloxy-derivative. The same authors prepared $Ti(OSiMeEt_2)_4$ and $Ti(OSiEt_3)_4$ by reactions involving the addition of titanium tetrachloride to the silanol in benzene in the presence of a tertiary base:

$$TiCl_4 + 4\ R_3SiOH + 4\ base \longrightarrow Ti(OSiR_3)_4 + 4\ base,\ HCl. \quad (7)$$

Yields of ca. 90% were obtained with dimethylaniline but pyridine gave poorer results. Andrianov et al.[6] obtained tetrakis-trimethylsilyloxy-titanium by the reaction involving the tetrachloride and the sodium salt of trimethylsilanol:

$$TiCl_4 + 4\ Me_3SiONa \longrightarrow Ti(OSiMe_3)_4 + 4\ NaCl \quad \ldots\ldots \quad (8)$$

Our preliminary communication[3] also gave the first recorded preparation of organosilyloxy-derivatives of zirconium, niobium and tantalum. The preparation of trimethylsilyloxy-derivatives of these metals is more difficult than for the titanium compound and this is believed to be due to two factors. (1) These metal alkoxides are more easily hydrolysed than titanium alkoxides. (2) Zirconium alkoxides are stronger "Lewis-acids" than titanium alkoxides and will thus cause condensation reactions of the silanol more readily. Using the technique which gave a quantitative yield of tetrakis-trimethylsilyloxy-titanium the corresponding yields of the other metal compounds

were: $Zr(OSiMe_3)_4$, 73%; $Nb(OSiMe_3)_5$, 54%; and $Ta(OSiMe_3)_5$, 48%. With zirconium isopropoxide it was interesting to find that the yield of methyl ethyl silyloxy-compound increased steadily from 73 to 79 to 95 to 99% as methyl groups were replaced by ethyls. A similar trend occurred with the tantalum derivatives and it is clear that the yield of product becomes greater as the ease of condensation of the silanol is reduced. To demonstrate the reversibility of the silanolysis reaction (6) we added n-butanol slowly to tetrakis-trimethylsilyloxy-titanium in boiling toluene, removing the trimethylsilanol by fractional distillation. However, the presence of water in the distillate and the low yield of titanium tetra-n-butoxide (22%) proved that condensation of the silanol was very marked.

In contrast to the condensation observed in the trimethylsilanolysis of metal alkoxides the silanolysis of the metal trimethylsilyloxides did not cause significant condensation:

$$M(OSiMe_3)_n + n\ R_3SiOH \longrightarrow M(OSiR_3)_n + nMe_3SiOH \quad . \ . \ . \quad (9)$$

These reactions were conducted in boiling hexamethyldisiloxane with which trimethylsilanol forms a convenient minimum boiling azeotrope and practically quantitative yields of the higher organosilyloxy-metal compounds were thus obtained.

In another preliminary communication[7] we reported a new method of synthesis not involving the silanols. This method is a transesterification involving metal alkoxide and organosilyl acetate:

$$M(OR)_n + n\ CH_3CO_2SiR'_3 \longrightarrow M(OSiR'_3)_n + nCH_3CO_2R \quad . \ . \ . \quad (10)$$

The metal ethoxides or isopropoxides were used and cyclohexane was the solvent. The latter forms minimum boiling azeotropes with ethyl acetate or isopropyl acetate and thus facilitates the removal of these products. Complications were found with trimethylsilyl acetate, which tends to form metal acetate instead of metal trimethylsilyloxide. Detailed investigation has shown that the acetylation occurs towards the end of the transesterification and probably involves the metal trimethylsilyloxide and excess trimethylsilyl acetate. By slow addition of trimethylsilyl acetate to the metal alkoxides the following yields were obtained: $Ti(OSiMe_3)_4$, 95%; $Zr(OSiMe_3)_4$, 56%; and $Ta(OSiMe_3)_5$, 74%. With the higher alkylsilyl acetates the trans esterification became very slow although the tendency to acetylate was less and the final yield of metal alkyl-

silyloxide practically quantitative.

2. Chemical and physical properties of trialkylsilyloxy-metal compounds

The work reported in this section and in section 1. was presented as a paper at the International Conference on Co-ordination Chemistry, London, April, 1959.[8]

2(a). Physical properties

Some physical data on the derivatives of titanium, zirconium and tantalum are given in Table 1.

Table 1. Alkylsilyloxy-derivatives of Titanium, Zirconium and Tantalum

Compound	M.p.°C	B.p. °C/mm.Hg	Mol.wt.	Degree of Polymer-isation
$Ti(OSiMe_3)_4$	Liquid	60/0.1	488	1.21
$Ti(OSiMe_2Et)_4$	"	86/0.1	462	1.00
$Ti(OSiMeEt_2)_4$	"	120/0.1	508	0.99
$Ti(OSiEt_3)_4$	110	150/0.1	569	1.00
$Ti(OSiMe_2Pr^n)_4$	Liquid	112/0.2	511	0.99
$Ti(OSiMe_2Pr^i)_4$	"	115/0.2	516	1.00
$Zr(OSiMe_3)_4$	152	135*/0.1	916	2.05
$Zr(OSiMe_2Et)_4$	105	105/0.1	602	1.20
$Zr(OSiMeEt_2)_4$	30	120/0.1	586	1.05
$Zr(OSiEt_3)_4$	Liquid	147/0.1	602	0.98
$Zr(OSiMe_2Pr^n)_4$	60	103/0.5	621	1.11
$Zr(OSiMe_2Pr^i)_4$	Liquid	110/0.1	568	1.01
$Ta(OSiMe_3)_5$	80	84/0.05	678	1.08
$Ta(OSiMe_2Et)_5$	135	135*/0.1	681	0.98
$Ta(OSiMeEt_2)_5$	180	170*/0.1	763	1.00
$Ta(OSiEt_3)_5$	210	210*/0.1	824	0.98
$Ta(OSiMe_2Pr^n)_5$	Liquid	170/0.1	765	1.00
$Ta(OSiMe_2Pr^i)_5$	180	165*/0.1	783	1.02

*Sublimes

These molecular weights were determined ebullioscopically in benzene with a probable error of not more than ± 2%. These data emphasise the profound effect that small changes in constitution may exert on physical properties. For example, in the methyl ethyl silyloxy-series all of the titanium compounds except $Ti(OSiEt_3)_4$ are liquids whilst with zirconium the situation is exactly reversed. Although differences in degree of polymerisation may well be important in some cases, it is interesting to note that both of the triethylsilyloxy-derivatives are monomeric and have practically the same volatility yet the titanium compound melts at 110° while the zirconium compound appears to be liquid down to 20°c. Moreover, in the zirconium series the melting point decreases steadily as methyl groups are replaced by ethyls yet for tantalum the trend is exactly reversed. Again, in the isomeric propyldimethylsilyloxy-derivatives the less branched zirconium derivative (n-propyl) melts higher than the iso-compound whereas in the tantalum compounds the branched isomer has a high melting point and the straight chain derivative is a liquid.

The molecular weights also reveal some interesting features. Thus the compounds: $Zr(OSiMe_3)_4$; $Zr(OSiMe_2Et)_4$; $Zr(OSiMeEt_2)_4$; $Zr(OSiMe_2Pr^n)_4$; $Ti(OSiMe_3)_4$ and $Ta(OSiMe_3)_5$, are significantly polymeric whereas the analogous metal tertiary alkoxides are all monomeric. Polymerisation also affects volatility as exemplified by tetrakis-trimethylsilyloxy-zirconium which is dimeric and requires a temperature of 135° at 0.1 mm. pressure before it sublimes, in striking contrast to zirconium tert.-butoxide which is a mobile liquid distilling at ca. 50°/0.1 mm. However, in the methyl ethyl silyloxy-zirconium series the degree of polymerisation steadily decreases as methyl groups are replaced by ethyls, which suggests that steric effects are operative. This is further supported by the effect of chain branching in the isomeric propyldimethylsilyloxy-derivatives. Moreover, for the same organosilyloxy-groups the degree of polymerisation is much greater for zirconium than for titanium or tantalum, as would be expected if steric effects were involved. Before discussing these steric effects we must first consider any electronic effects which may result from the replacement of the carbinol carbon atoms in $M(OR_3)_n$ by the silicon in $M(OSiR_3)_n$. There are clearly two opposing factors at play. On the one hand, due to the greater electronegativity of carbon, the electron release of R_3Si- will exceed that of R_3C-, and tend to increase the electron density on the oxygen in the R_3Si-O- group relative to that in the R_3C-O- group. In the case of the trialkylsilyloxy-groups there is the opposite electron drift due to partial double bonding $R_3Si{=}\overset{+}{O}$- involving a vacant d_π orbital on the silicon and a filled

p_π orbital on the oxygen. The net electronic effect appears to be that R_3SiO-groups are more electron attracting than R_3CO-groups because the silanols are definitely more acidic than the corresponding tert.-alcohols. Hence, we deduce that the oxygen in the $R_3\bar{S}i-\bar{O}-M$ system is a poorer donor than in the R_3C-O-M system and this should cause the intermolecular O-M bonds to be weaker in the organosilyloxy-compounds than in the alkoxides and hence polymerisation in the silyloxy-compounds should be less than in the tert.-alkoxides from the electronic point of view. The fact that the trialkylsilyloxy-compounds are actually more polymeric indicates that steric effects are the more important. The steric consequences of replacing carbon atoms by the larger silicon atoms are also rather complex. Thus the silicons will have greater shielding power than the carbons but this will be offset by the fact that the Si-O bond will be longer than the C-O bond. The latter effect causes the alkyl groups to be further from the central metal atom in the R_3SiO-derivative than in the R_3CO-derivative, and this reduces the shielding effect of the organosilyloxy-group and causes the organosilyloxy-compounds to be more polymeric than the tert.-alkoxides. It is possible that the $\bar{S}i=\dot{O}$ double bonding may cause the bond angle of the $Si\hat{O}M$ system to be greater than the $C\hat{O}M$ angle and this would also reduce the shielding efficiency of the trialkylsilyloxy-group.

2(b). Chemical properties

The organosilyloxy-metal compounds are perceptibly resistant towards hydrolysis by water compared with the metal alkoxides. This has not been studied quantitatively but it is a very important point. It is clear that the water-repellency of the trialkylsilyloxy-group or the silanol is important because hydrolysis by dilute acid is more facile than by water and it is well-known that the trialkylsilyloxy-groups are susceptible to acid attack. Apart from this it might have been expected that the trialkylsilyloxy-derivatives would be more prone to hydrolysis involving nucleophilic attack by water molecules on the metal atom. Nevertheless, in homogeneous solution (e.g. acetone) hydrolysis by water is fairly rapid and the greater resistance to hydrolysis by liquid water may be due to the heterogeneity of the system coupled with the water-repellent effect already stated. Another interesting fact is the greater thermal stability of trialkylsilyloxy-metal compounds compared with metal tert.-alkoxides. A detailed study of the latter[9] has shown that in a closed glass system in the temperature range 200-250°C the decomposition of the metal tert.-alkoxide is a hydrolytic chain reaction.

This is due to the rapid heterogeneous dehydration of the tertiary alcohol which produces water for the hydrolysis.

$$Me_3COH \longrightarrow H_2O + Me_2C{=}CH_2 \quad \ldots\ldots\ldots\ldots (11)$$

$$H_2O + Zr(OCMe_3)_4 \longrightarrow ZrO(OCMe_3)_2 + 2\ Me_3COH \quad \ldots (12)$$

For every molecule of water used in the hydrolysis two more are produced by dehydration of the resulting tert.-alcohol (see equations 11 and 12) and this leads to a branching chain mechanism. However, this mechanism cannot operate in the case of organosilyloxy-compounds because in the condensation of the silanol (13), only one molecule of water is produced from every two molecules of silanol.

$$2\ Me_3SiOH \longrightarrow Me_3Si\text{-}O\text{-}SiMe_3 + H_2O \quad \ldots\ldots\ldots (13)$$

Thus a branching chain cannot develop and, in addition, the metal-trialkylsilyloxide is less readily hydrolysed so that propagation of the hydrolytic decomposition is also retarded.

3. The synthesis of metallo-organic compounds containing metal-nitrogen bonds

Gilman et al.[10] obtained tetrakis-diethylamido-uranium^{IV} by the reaction involving uranium tetrachloride and the lithium derivative of diethylamine:

$$UCl_4 + 4\ LiNEt_2 \longrightarrow U(NEt_2)_4 + 4\ LiCl \quad \ldots\ldots (14)$$

We have now shown that the lithium dialkyl-amide reaction is applicable to the preparation of other metal alkylamides. These new metallo-organic compounds which contain metal-nitrogen bonds are relatively volatile substances which are very readily hydrolysed. Some data are presented in Table 2. Molecular weight determinations in benzene (ebullioscopically) showed that tetrakis-diethylamido-titanium and tetrakis-piperidino-titanium were both monomeric and it is reasonably certain that the higher dialkylamido-derivatives of titanium must also be monomeric. It is possible that the tetrakis-dimethylamido-titanium has a small degree of polymerisation and that the zirconium derivatives are more polymeric than the corresponding titanium compounds. For example, in the dimethylamido-derivatives the zirconium compound is a solid (m.p. 60°) and is less volatile than the titanium compound which is liquid at room temperature. In comparing the amido-metal compounds with the metal alkoxides we should expect some interesting differences to emerge as a result of the change in steric and electronic factors. From the electronic point of view there is the

Table 2. Alkylamido-metal Compounds

Compound	M.p.(°C)	B.p.(°C/mm.)
$Ti(NMe_2)_4$	Liquid	54/0.1
$Ti(NEt_2)_4$	"	112/0.1
$Ti(NPr^n_2)_4$	"	150/0.1
$Ti(NBu^i_2)_4$	"	160/0.1
$Ti(NC_5H_{10})_4$*	ca. 60	180/0.1
$Ti(NMe_2)(NC_5H_9Me)_3$≠	Liquid	160/0.1
$Ti(NMe_2)_3(NC_5H_8Me_2)$≠≠	"	125/0.1
$Zr(NMe_2)_4$	ca. 60	75/0.1
$Zr(NEt_2)_4$	Liquid	120/0.1
$Zr(NC_5H_{10})_4$*	ca. 60	190/0.1

*Piperidino-group; ≠2-Methyl piperidino-group; ≠≠2:6-Dimethyl piperidino-group.

probable difference in bond energy between M-O and M-N bonds. In addition there is the possibility that the energy of the intermolecular bond may be greater for M-N than for M-O because of the greater donor power of the nitrogen. Also, the tendency for π-bonding, using a vacant d-orbital of the metal ($\bar{M}{=}\dot{N}$ or $\bar{M}{=}\dot{O}$), may differ significantly when oxygen is replaced by nitrogen. From the steric viewpoint the situation is especially interesting because in the amido-metal compounds the branching in the organo-group is one atom closer to the metal than in the alkoxides. This should cause steric effects to be more marked in the amido-compounds. This can be illustrated by reference to the data in Table 2. For example, tetrakis-dimethylamido-zirconium, $Zr(NMe_2)_4$ b.p. 75°/0.1 mm., is much more volatile and hence probably less polymeric than zirconium iso-propoxide, $Zr(OCHMe_2)_4$ b.p. 160°/0.1mm. This is a crude comparison but it is certain that the four oxygen atoms in the isopropoxide could not cause such a decrease in volatility through normal intermolecular forces and it seems reasonable to suggest that the two methyls on the nitrogen cause better shielding of the metal atom than the more remote methyls of the isopropyl group.

Preliminary experiments indicate that steric effects in the metal-nitrogen compounds may be concerned in aminolysis reactions of the type shown in equation 15.

$$M(NR_2)_4 + 4\ RR'NH \longrightarrow M(NRR')_2 + 4\ R_2NH \quad \ldots\ldots (15)$$

Thus piperidine $C_5H_{10}NH$ displaces all of the dimethylamido groups from the titanium or zirconium compounds. However, with 2-methyl piperidine it appears that only three groups are readily placed round titanium and the volatile mixed amido-compound $Ti(NMe_2)(NC_5H_9Me)_3$ (b.p. 160°/0.1 mm.) results. As would be predicted on steric grounds the resistance to replacement of dimethylamido-groups by 2:6-dimethyl piperidine is even greater and only mono-substitution occurs giving $Ti(NMe)_3(NC_5H_8Me_2)_3$ (b.p. 125°/0.1 mm.).

Preliminary experiments using primary amines have revealed some interesting results. It appears that polymeric compounds of the formula $[Ti(NR)_2]_x$ are produced by aminolysis of titanium tetrakis-dimethylamide. For example, with either aniline or isopropylamine insoluble non-volatile solids were obtained which were extremely susceptible to hydrolysis. With ethylene diamine an insoluble product approximating in composition to $Ti(NHC_2H_4)_2$ was obtained and this underwent vigorous exothermic hydrolysis.

Finally, we should mention that some remarkable compounds have been obtained from the quinquevalent metals niobium and tantalum. From the reactions involving the pentachlorides and lithium diethylamide it appears that pentakis-diethylamido-derivatives are unstable and that de-alkylation of one amido-group occurs with the formation of the compounds $(Et_2N)_3Ta{=}NEt$ or $(Et_2N)_3Nb{=}NEt$. In these there are both secondary and primary amido-groups but the most striking feature is the presence of the metal-nitrogen double bond between the metal and primary amido-group. Moreover, in alcoholysis reactions it is clear that the doubly bonded primary amido-groups are more difficult to replace than the secondary amido-groups. These and other related research are currently being conducted under Contract No. AF 61(052)-174.

References

1. English, W.D. and Sommer, L.H., J. Amer. Chem. Soc., 1955, 77, 170.
2. Zeitler, V.A. and Brown, C.A., ibid., 1957, 79, 4616.
3. Bradley, D.C. and Thomas, I.M., Chem. and Ind., 1958, 17.
4. Dolgov, B.N. and Orlov, N.F., Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk, 1957, 1395.

5. Idem, Dokl. Akad. Nauk S.S.S.R., 1957, 117, 617.

6. Andrianov, D.A., Zhadanov, A.A., Kurasheva, N.A. and Dvlova. V.G., ibid., 1957, 112, 1050.

7. Bradley, D.C. and Thomas, I.M., Chem. and Ind., 1958, 1231.

8. Idem, J. Chem. Soc., in the press.

9. Bradley, D.C. and Faktor, M.M., J. Appl. Chem, and Trans. Farad. Soc., in the press.

10. Jones, R.G., Karmas, G., Martin, G.A., and Gilman, H., J. Amer. Chem. Soc., 1956, 78, 4285.

Contribution from the Department of Chemistry
of the
University of North Carolina

THE APPLICATION OF LIGHT SCATTERING TO THE STUDY OF THE HYDROLYTIC AGGREGATION OF IONS

R. Stuart Tobias and S. Young Tyree, Jr.

Abstract

The use of light scattering measurements on systems of polyelectrolytes in the presence of supporting electrolytes is discussed with particular emphasis on low molecular weight inorganic polymers of relatively high charge.

Equations are developed for the determination of the degree of aggregation of charged species in the presence of supporting electrolyte. Estimates are made of the error caused by the assumption that the turbidities of the various components are additive under these conditions.

Although the theory of light scattering in multicomponent systems has been rather thoroughly discussed [2,10,14], the application of light scattering measurements to the determination of molecular weights and degrees of aggregation of polymers with high charge to weight ratios has not been considered in detail.

Equations have been developed for the determination of molecular weights of charged protein molecules in the presence of supporting electrolyte [5]; however, the experimental conditions for the study of proteins are considerably different from those used in the study of ionic aggregation. The light scattering of these inorganic polyelectrolytes must be studied at relatively high concentrations to permit accurate turbidity measurements. This, in turn, necessitates the use of rather high concentrations of the supporting electrolyte. Since the differential refractive index of the supporting electrolyte is not negligible in comparison to that of the polymer, as is usually true with proteins, the contributions of all of the components in the system to the turbidity must be carefully

considered. In many respects, this paper is a parallel of the discussion by Johnson, Kraus, and Scatchard [8] of the application of sedimentation equilibrium in the ultracentrifuge to the study of similar systems.

Several workers have used light scattering measurements to determine approximate molecular weights of the isopoly and heteropoly acids and their salts [1,3,4,9,15] and aggregates formed by the hydrolysis of multivalent metal ions [11,12].

It has been observed that the equation which describes the scattering in relatively dilute solutions of non-electrolytes, i.e.,

$$Hc/\tau = 1/M_w + 2Bc \qquad (1)$$

appeared to be obeyed when the measurements on the inorganic polyelectrolytes were made on solutions with a relatively large and constant concentration of supporting electrolyte [15]. Similar behavior was also observed with a large but variable concentration of supporting electrolyte [1,11,12]. In a study of the scattering by solutions of phosphotungstic acids [9], it was observed that equation (1) failed, presumably because of charge effects. It was also observed that the scattering by these solutions followed equation (1) at very low values of the pH. This was probably a result of two factors, the reduction in charge of the species by protonation and also the presence of relatively high concentrations of the 1:1 supporting electrolyte $HClO_4$.

It has been suggested [9] that a separate determination of $(\partial \ln a_2/\partial c_2)$ by e.m.f. or isopiestic methods would allow the calculation of M_2 in a two component system when equation (1) is not obeyed, since the general relation describing the scattering in 2 component systems is given by the equation

$$\tau = \frac{H M_2}{(\partial \ln a_2/\partial c_2)} \cdot \qquad (2)$$

This method involves some difficulty in the separate determination of $(\partial \ln a_2/\partial c_2)$ which would limit it to very favorable systems.

In general light scattering measurements are most useful for studying systems at relatively high degrees of polymerization. The more usual methods of e.m.f. titrations, spectrophotometry, cryoscopy, etc., are particularly useful at the beginning of the aggregation where the degree of polymerization is low.

1. Turbidity of Multi-Component Systems

The equation for the turbidity, τ, in excess of that due to density changes, i.e., in excess of that due to the scattering by the pure solvent, has been given by Stockmayer [14]:

$$\tau = \frac{32\pi^3 n^2 kT}{3\lambda^4 N} V \sum_{2}^{c}{}_i \sum_{2}^{c}{}_j \frac{(\partial n/\partial m_i)(\partial n/\partial m_j) B_{ij}}{(\partial \mu_i/\partial m_j)} \qquad (3)$$

n = refractive index of solution

V = volume of the solvent, component 1

B_{ij} = cofactor of the determinant $|(\partial \mu_i/\partial m_j)|$

m_i = quantity of component i in the system

$|(\partial \mu_i/\partial m_j)|$ represents the determinant of all $(\partial \mu_i/\partial m_j)$, omitting the first component, the solvent.

It is convenient to rewrite equation (3) in terms of the molarities of the components, assuming the volume fraction of component 1 to be unity. As suggested by Edsall et al. [5], the equation will be written in terms of the derivatives of the activities rather than the chemical potentials with respect to the molarities. This gives the following equation for the turbidity.

$$\tau = \frac{3200\pi^3 n^2}{3N \lambda^4} \sum_{2}^{c}{}_i \sum_{2}^{c}{}_j \frac{\psi_i \psi_j A_{ij}}{|a_{ij}|} \qquad (4)$$

$\psi_i = (\partial n/\partial m_i)$, A_{ij} = cofactor of $|a_{ij}|$

$a_{ij} = (\partial \ln a_i/\partial m_j) = a_{ji}$,

a_i is the activity of the i-th species.

Grouping constant terms together, letting $H'' = 32000\pi^3 n^2/3N \lambda^4$

$$\tau = H'' \sum_{2}^{c}{}_i \sum_{2}^{c}{}_j \frac{\psi_i \psi_j A_{ij}}{|a_{ij}|} \quad . \qquad (5)$$

2a. Equations for a Three Component System

A three component system consisting of a solvent, a monodisperse polymeric electrolyte and a supporting electrolyte will be considered. The general equation for scattering in a three component system has been given by Edsall et al. [5]

$$\tau/H'' = \frac{\psi_2^2 a_{33} - 2\psi_2\psi_3 a_{23} + \psi_3^2 a_{22}}{a_{22} a_{33} - a_{23}^2} \quad . \qquad (6)$$

If we designate the solvent, water, as component 1, the polymeric electrolyte PX_z as component 2, and the supporting 1:1

electrolyte BX as component 3, we may write down the following expressions for the activities:

$$\ln a_2 = \ln m_2 + \nu_{2a} \ln m_a + \beta_2$$

$$\ln a_3 = \nu_{3c} \ln m_c + \nu_{3a} \ln m_a + \beta_3$$

where

ν_{2a} = number of anions X^- in component 2
ν_{3c} = number of cations B^+ in component 3 = 1
ν_{3a} = number of anions X^- in component 3 = 1
m_c = total molarity of B^+
m_a = total molarity of X^-
β_i = $\ln \gamma_i$, the logarithm of the activity coefficient of the i-th species.

It should be noted that although the following derivations are given in terms of a polymeric cation P^{z+} with univalent anions X^-, the treatment is symmetrical with respect to charge and applies equally well to the case of a polymeric anion P^{z-} with univalent cations B^+ .

It has been found extremely advantageous to study these systems in a constant ionic medium, i.e., with a high concentration of supporting electrolyte. This procedure has been used with e.m.f. and spectrophotometric measurements, sedimentation equilibrium in the ultracentrifuge, etc. This allows one to assume to a close approximation that activity coefficients remain constant during the measurements and reduces the number of variables by one-half [16]. Under these conditions, $(\partial \beta_i / \partial m_j) \simeq 0$. Taking derivatives of the activities, we obtain the following:

$$a_{22} = 1/m_2 + \frac{\nu_{2a}}{m_a} \frac{\partial m_a}{\partial m_2}$$

$$a_{33} = \frac{1}{m_c} \frac{\partial m_c}{\partial m_3} + \frac{1}{m_a} \frac{\partial m_a}{\partial m_3}$$

$$a_{23} = \frac{\nu_{2a}}{m_a} \frac{\partial m_a}{\partial m_3}$$

$$m_c = m_3, \quad m_a = m_3 + Z_2 m_2 \quad \text{since} \quad \nu_{2a} = Z_2 \ .$$

Since a_{23} is of the same order of magnitude as a_{22} and a_{33}, and ψ_3 is not negligible in comparison to ψ_2 as is the case with proteins in the presence of 1:1 electrolytes such as NaCl, the cross terms in equation (6) are not negligible. This makes it

impossible to obtain a convenient expression for the turbidity in terms of the molecular weight of PX_z .

2b. Alternate Definition of Components

In order to reduce the effect of variations in concentration of the supporting electrolyte on the activity of the polymeric component, a different set of components has been suggested by Scatchard [13] for use in the study of polyelectrolytes. These definitions have also been found useful in the study of sedimentation equilibrium in these systems [8] and the study of light scattering by proteins [5]. Instead of defining the polymeric component as PX_z, one defines a new component 2, $PX_{z/2}B_{-z/2}$, i.e., $PX_z - \frac{z}{2} BX$. The addition of one mole of component 2 to the solution gives one mole of particles, and the molecular weight of component 2 is $M_{PX_z} - \frac{z}{2} M_{BX}$. The molarity of component 2 is the same as with the previous definition; the activity is different. This also necessitates a redefinition of component 3 which now differs in molarity but not in activity from the previous definition. We may now write down the following expressions for the activities:

$$\ln a_2 = \ln m_2 + \nu_{2c} \ln m_c + \nu_{2a} \ln m_a + \beta_2$$

$$\ln a_3 = \nu_{3c} \ln m_c + \nu_{3a} \ln m_a + \beta_3 \quad .$$

The constant ionic medium makes the assumption $(\partial\beta_i/\partial m_j) = 0$ valid to a close approximation, so the following expressions are obtained:

$$a_{22} = 1/m_2 + \frac{\nu_{2c}}{m_c} \frac{\partial m_c}{\partial m_2} + \frac{\nu_{2a}}{m_a} \frac{\partial m_a}{\partial m_2}$$

$$a_{23} = \frac{\nu_{2c}}{m_c} \frac{\partial m_c}{\partial m_3} + \frac{\nu_{2a}}{m_a} \frac{\partial m_a}{\partial m_3}$$

$$a_{33} = \frac{\nu_{3c}}{m_c} \frac{\partial m_c}{\partial m_3} + \frac{\nu_{3a}}{m_a} \frac{\partial m_a}{\partial m_3} \quad .$$

Also

$$m_c = m_3 - Z_2 m_2/2 \qquad \nu_{2c} = -Z_2/2 \ , \qquad \nu_{3c} = 1$$

$$m_a = m_3 + Z_2 m_2/2 \qquad \nu_{2a} = Z_2/2 \ , \qquad \nu_{3a} = 1 \quad .$$

Setting $\eta = Z_2 m_2/2m_3$

$$a_{22} = 1/m_2 + Z_2^2/2m_3(1 - \eta^2) \tag{7}$$

$$a_{23} = \frac{-Z_2}{m_3} \left(\frac{\eta}{1 - \eta^2}\right) \tag{8}$$

$$a_{33} = 2/m_3(1 - \eta^2) \quad . \tag{9}$$

So long as Z_2 is relatively small and the measurements are made with dilute polymer solutions at large values of m_3, $\eta \simeq 0$ and the cross term a_{23} in equation (6) vanishes. Then the turbidities become additive.

$$\tau/H'' = \frac{\psi_2^2}{1/m_2 + Z_2^2/2m_3(1 - \eta^2)} + \frac{\psi_3^2}{2/m_3(1 - \eta^2)} \quad . \qquad (10)$$

Again so long as $(1 - \eta^2) \simeq 1$, the term $\frac{H'' \psi_3^2}{2/m_3}$ represents the turbidity of a solution of BX of concentration m_3. To a good approximation, a background experiment may be run on pure BX solutions to determine the contribution of the supporting electrolyte to the total turbidity of the solution containing the polymeric electrolyte. Subtraction of this background turbidity from the gross turbidity τ gives τ^*, a turbidity due to component 2. Converting from concentrations in moles/liter to g/cm^3 and assuming $(1 - \eta^2) = 1$, we obtain

$$\frac{\tau^*}{H'} = \frac{\varphi_2^2}{1/M_2c_2 + 1000Z_2^2/2m_3M_2^2} \qquad H' = 10^{-3}H''$$

φ_2 = weight refractive index increment of component 2

c_2 = concentration of component 2 in g/cm^3

M_2 = molecular weight of component 2 .

Letting $\varphi_2^2 H' = H$, and rearranging:

$$Hc_2/\tau^* = 1/M_2 + 1000Z_2^2\, c_2/2m_3M_2^2 \quad . \qquad (11)$$

Thus so long as careful consideration is given to the turbidity of the constant ionic medium used as a solvent, e.g., 1 M $MaClO_4$, a plot of Hc_2/τ^* versus c_2 should give a straight line when $(1 - \eta^2) \simeq 1$.

3. Scattering in Idealized Three Component Systems

In order to determine the accuracy with which the molecular weights can be obtained using equation (11), turbidities were calculated for several idealized systems subject to the restrictions that the polymer is monodisperse, the volume fraction of the solvent is unity, and that the activity coefficients of all species are constant. The parameters were selected to simulate distribution of low molecular weight inorganic polymers, and systems were chosen which were similar to those used by Johnson, Kraus, and Scatchard [8] to test the equations for distribution in a centrifugal field. For example, the value of $(\partial n/\partial m_3) = 0.01$ is similar to that for $NaClO_4$ which has been reported as 7.79×10^{-3} 1/M [7]. The value of $(\partial n/\partial c_2)$ has been reported as 0.103 cc/g for 12-phosphotungstic acid [9], 0.174 cc/g for the

isopolymolybdates [7], and 0.0957 cc/g for the cationic aggregates formed by the hydrolysis of Al^{3+} [11].

The calculations were made by substituting the values of a_{22}, a_{33}, and a_{23} calculated as a function of Z_2, m_2, and m_3, using equations (7), (8), and (9), into equation (6) and solving for τ. The constant value of the turbidity of the ionic medium τ_{BX} was obtained assuming it to be given by

$$\tau_{BX} = \frac{H'' \psi_3^2}{2/m_3} \quad .$$

Calculations were also made assuming that the turbidity of the solutions in excess of that attributable to the supporting electrolyte of the ionic medium was given by the simple relation for a two component system, equation (2). This quantity is tabulated as τ_{PX_z}. The magnitude of the difference between $\tau_{PX_z} + \tau_{BX}$ and τ is a measure of the effect of the cross terms in equation (6) on the total turbidity. These data are presented in Table I.

The turbidity $\tau^* = \tau - \tau_{BX}$ is plotted versus c_2 in Fig. 1. It can be seen from Fig. 1 that the curvature of the Hc_2/τ^* versus c_2 plots caused by the non-additivity of the turbidities at the higher concentrations does not preclude a reasonably accurate extrapolation to infinitely dilute solutions. The molecular weight M_2 can be obtained with good accuracy. The curvature does render the measurement of the limiting slope less accurate and tends to lead to low values of Z_2.

4. Consideration of Complexes with Ions from the Constant Ionic Medium

Some complexing of the polymeric electrolyte by ions of opposite charge from the constant ionic medium is to be expected, since these ions are present in a large excess. In general this effect is advantageous, since it reduces the charge on the polymeric species making the system more amenable to study. The light scattering measurements thus provide a means of measuring the interaction of the species with the constant ionic medium, data which cannot be obtained by equilibrium studies using e.m.f. measurements, etc.

When $\bar{\nu}$ ions of opposite charge to P^{z+} react to form a complex, the effective charge of the polymeric species is

$$Z_2^* = (Z_2 - \bar{\nu}) \quad .$$

Component 2 is now redefined as $(PX_{\bar{\nu}})^{(Z-\bar{\nu})}X_{(Z-\bar{\nu})} - (Z-\bar{\nu})BX/2$ or $PX_z - (Z-\bar{\nu})BX/2$. This necessitates a redefinition of

Table I

Summary of the Results of the Computations of the Turbidity in Idealized 3-Component Systems

$(\partial n/\partial m_2) = 0.1$ $M_2 = 1000$ $n_{solvent} = 1.34$

$(\partial n/\partial m_3) = 0.01$ $M_3 = 100$ $\lambda = 4360$ Å

mPX_z	η	$(1 - \eta^2)$	$\tau_{PX_z} \times 10^5$	$\tau \times 10^5$
	$Z_2 = 4$, $m_3 = 3.00$, $\tau_{BX} = 4.28 \times 10^{-5}$			
0.300	0.200	0.960	46.6	55.3
0.200	0.133	0.982	37.0	43.3
0.100	0.067	0.996	22.5	27.4
0.050	0.033	0.999	12.6	17.0
0.025	0.017	1.000	6.68	11.0
0.0125	0.0083	1.000	3.45	7.75
0.0061	0.0042	1.000	1.75	6.04
	$Z_2 = 8$, $m_3 = 3.00$, $\tau_{BX} = 4.28 \times 10^{-5}$			
0.300	0.400	0.840	17.8	31.0
0.200	0.267	0.929	17.3	26.2
0.100	0.133	0.982	13.7	19.5
0.050	0.067	0.996	9.28	14.1
0.025	0.033	0.999	5.62	10.0
0.0125	0.0167	1.000	3.14	7.46
0.0061	0.0083	1.000	1.67	5.96
	$Z_2 = 4$, $m_3 = 1.00$, $\tau_{BX} = 1.38 \times 10^{-5}$			
0.300	0.600	0.640	17.4	31.4
0.200	0.400	0.840	19.0	24.5
0.100	0.200	0.960	15.0	17.9
0.050	0.100	0.990	9.83	11.6
0.025	0.050	0.998	5.75	7.24
0.0125	0.025	0.999	3.14	4.55
0.0061	0.012	1.000	1.64	3.03

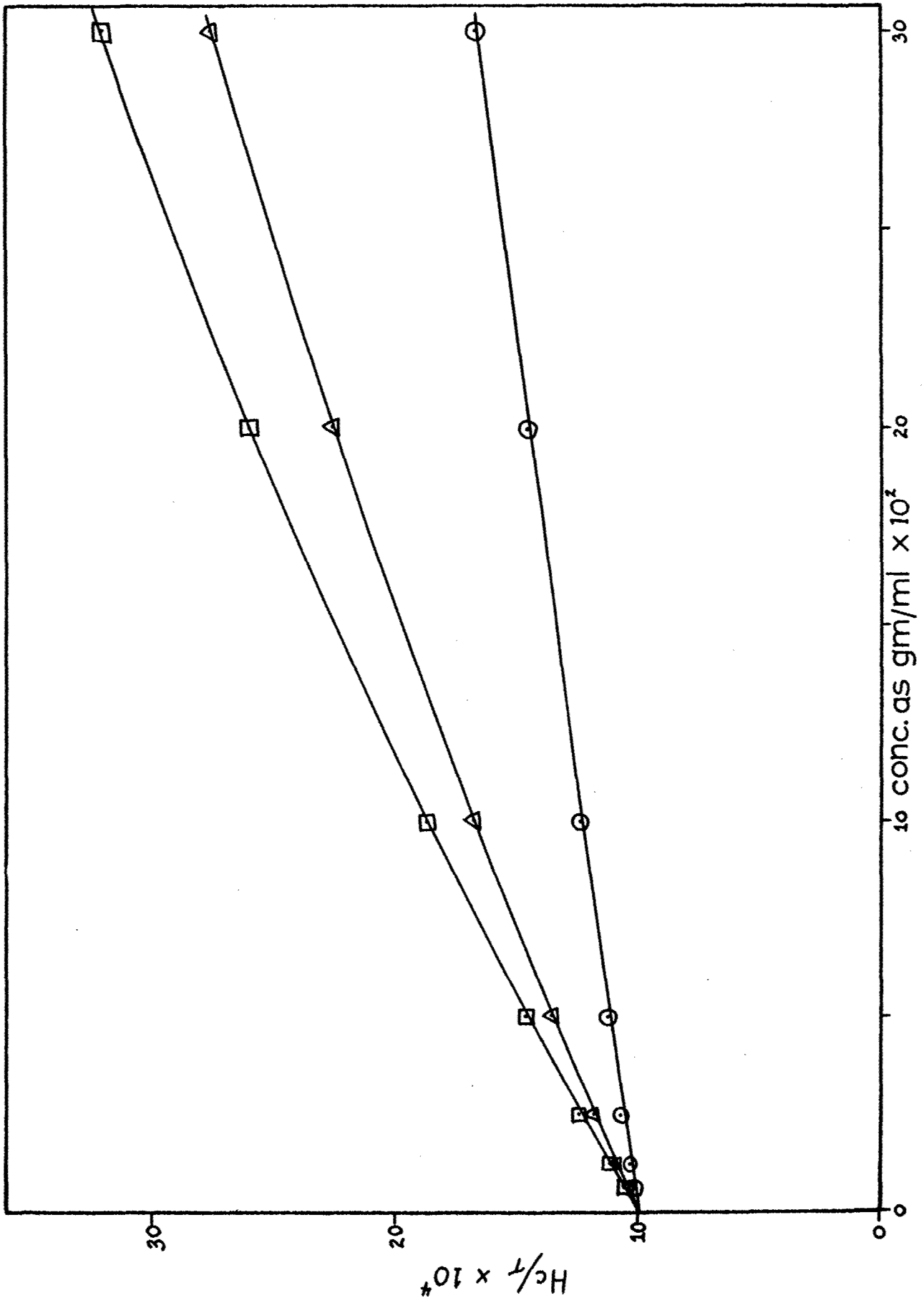
Title to Figure

Fig. 1.- Concentration expressed in g./ml.

○ , $Z_2 = 4$, $m_3 = 3.00$;

△ , $Z_2 = 8$, $m_3 = 3.00$;

□ , $Z_2 = 4$, $m_3 = 1.00$.


$H_c/\tau \times 10^4$
0
10
20
30
conc. as gm/ml $\times 10^2$
0
10
20
30

component 3 as $m_3^* = m_3 - \bar{\nu}m_2/2$. The difference in m_3^* and m_3 is quite small, and both may be assumed to be equal to the concentration of the supporting electrolyte at low values of η. Substitution of the activities based on these definitions into the scattering equation gives a new set of equations differing only in the replacement of Z_2 by Z_2^* and m_3 by m_3^*. Thus

$$Hc/\tau^* = 1/M_2 + 1000Z_2^{*2}/2m_3^*M_2^2 \quad . \qquad (12)$$

In the study of ionic aggregation, it is convenient to define a monomeric unit as $\left[M(H)_{\bar{n}}\, X_{\bar{\nu}}^{(Z+\bar{n}-\bar{\nu})}\right] X_{(Z-\bar{n}-\bar{\nu})}$ where Z is the charge on the ion M and $\bar{n}$, the average number of hydrogen ions consumed per mole of M, may be obtained by electrometric titrations. The average number of X^- bound, $\bar{\nu}$, may then be calculated from the values of $Z_2^{*'}$, the average charge per monomer unit using the relation $Z_2^{*'} = Z_2^*/\underset{\sim}{N}$, where there are $\underset{\sim}{N}$ monomer units in the polymer. Although it would appear that one could calculate values of M_2 from values of the slope of the Hc/τ^* versus c curve at different values of m_3^*, this is not generally possible since $\bar{\nu}$ is a function of m_3^* .

5. Equations for a Four Component System

A four component system consisting of a solvent, a polymeric component, and two supporting electrolytes HX and BX will be considered. In many systems, the ionic aggregation occurs at such low pH values that the free acid concentration cannot be neglected. The polymeric component 2 is assigned the formula

$$PX_{Z/2}\, H_{-Zm_3/2(m_3+m_5)}\, B_{-Zm_5/2(m_3+m_5)} \quad .$$

The supporting electrolytes HX and BX are components 3 and 5 respectively. The concentrations of the various ions are as follows.

$$m_P = m_2$$

$$m_H = m_3 - Z_2m_2m_3/2(m_3 + m_5) = m_3(1 - \eta^*)$$

$$m_B = m_5 - Z_2m_2m_5/2(m_3 + m_5) = m_5(1 - \eta^*)$$

$$m_X = m_3 + m_5 + Z_2m_2/2$$

$$\eta^* = Z_2m_2/2(m_3 + m_5) \quad .$$

With the same restrictions involving monodispersity, constancy of activity coefficients, as before, we obtain

$$a_{22} = 1/m_2 + Z_2^2/2(1 - \eta^{*2})(m_3 + m_5)$$

$$a_{33} = [2m_3 + m_5(1 - \eta^{*2})]/m_3(m_3 + m_5)(1 - \eta^{*2})$$

$$a_{55} = 2m_5 + m_3(1 - \eta^{*2})/m_5(m_3 + m_5)(1 - \eta^{*2})$$

$$a_{35} = (1 + \eta^{*2})/(1 - \eta^{*2})(m_3 + m_5) \quad .$$

As was the case in the three component system, the terms involving the change in activity of component 2 with the concentration of component 3 or 5 are negligible with this definition of components if η^* is small. So long as these cross terms involving the polymer are negligible, the scattering equation for a four component system may be written as

$$\tau = \frac{H''\psi_2^2}{a_{22}} + \frac{H''(\psi_3^2 a_{55} - 2\psi_3\psi_5 a_{35} + \psi_5^2 a_{33})}{(a_{33}a_{55} - a_{35}^2)} \quad . \qquad (13)$$

The second term in equation (13) is simply the turbidity of a mixture of m_3 moles/l of HX and m_5 moles/l of BX. This may be obtained by a background experiment and subtracted from the total turbidity of the solution to give the turbidity τ^* due to the polymeric component alone. Substituting the values of a_{22} into equation (10) we obtain

$$Hc_2/\tau^* = 1/M_2 + 1000Z_2^2c_2/2M_2^2(m_3 + m_5) \quad .$$

This equation is the same as for the three component system, except for the replacement of m_3 by $(m_3 + m_5)$.

6. Equations for a System with Polydisperse Aggregates and One Supporting Electrolyte

Applying the general equation for scattering in multicomponent systems with the same restrictions of the constancy of activity coefficients, small values of $\sum_i Z_i m_i/2m_3 = \eta'$, etc., we obtain

$$\tau^*/H'' = \sum_i \sum_j \psi_i\psi_j A_{ij} / |a_{ij}| \quad . \qquad (14)$$

τ^* is the turbidity corrected for that due to the supporting electrolyte, and the summation is extended over all even (polymeric) components. As before, we obtain the following equations

$$a_{ii} = 1/m_i + Z_i^2/2m_3(1 - \eta'^2)$$

$$a_{ij} = Z_iZ_j/2m_3(1 - \eta'^2) \quad , \text{ where } i \neq j.$$

If the polymeric ions are of the type $M[M(H)_t]_n$ where t is a constant which may be + or - and n is a variable, as has been observed by Sillén and co-workers [6] to be generally true in these systems, it seems likely that the weight refractive index increments φ_i will be approximately equal over a narrow range of n values.[1] In this case converting to weight refractive index increments,

$$10^3\tau^*/H'\varphi^2 = 10^3\tau^*/H = \sum_i \sum_j M_i M_j A_{ij} / |a_{ij}| \quad . \qquad (15)$$

Cross terms involving the polymeric components vanish only when the charge effects become negligibly small. The weight average molecular weight of the polymeric components may be obtained by extrapolation to $c = 0$ in the usual manner, since

$$\lim_{c \to 0} Hc/\tau^* = \sum_i c_i \Big/ \sum_i M_i c_i = 1/M_w \quad .$$

In order to relate the data obtained from light scattering measurements to those from experiments with the ultracentrifuge, the following quantities are defined:

$\underset{\sim}{N}$ = average degree of polymerization, i.e., the weight average number of metal atoms in the polymeric electrolyte PX_z (16)

$Z_2/\underset{\sim}{N} = \underset{\sim}{Z}'$, the average charge per monomer unit (17)

$M_2/\underset{\sim}{N} = \underset{\sim}{M}'$, the formula weight of the monomer . (18)

The quantities $\underset{\sim}{N}$ and $\underset{\sim}{Z}'$ are those generally given in the results obtained by the ultracentrifugation of these solutions. In practice, one attributes the formula $[M(H)_{\bar{n}}X_{(z+\bar{n})}]_N$ to the polymeric species. This average monomeric species is then used to calculate the weight concentrations.

In summary, it has been shown that the weight average degree of polymerization $\underset{\sim}{N}$ can be obtained independent of the charge by extrapolation of the plot Hc/τ^* versus c to infinite dilution. The charge per monomer unit $\underset{\sim}{Z}'$ may be obtained from the slope of the plot in systems with a monodisperse polymer. The average number of ions bound from the ionic medium may be calculated providing information unobtainable from electrometric titrations. The same information, i.e., $\underset{\sim}{N}$ and $\underset{\sim}{Z}'$, may be obtained by centrifugation, and hence a system can be studied by two independent experimental methods. Light scattering measurements afford, in addition, a particularly convenient method for measuring the aggregation as a function of time in systems where the equilibria are not rapidly attained.

References

1. Bettinger, D. J., and S. Y. Tyree, J. Am. Chem. Soc. 79, 3355 (1957).
2. Brinkman, H. C., and J. J. Hermans, J. Chem. Phys. 17, 574 (1949).
3. Debye, P., and R. V. Nauman, J. Chem. Phys. 17, 664 (1949).
4. --------J. Phys. Chem. 55, 1 (1951).
5. Edsall, J. T., H. Edelhoch, R. Lontie, and P. R. Morrison, J. Am. Chem. Soc. 72, 4641 (1950).

6. Hietanen, S., and L. G. Sillén, Acta Chem. Scand. 8, 1607 (1954).

7. Jenkins, L. H., Ph.D. dissertation, University of North Carolina, 1955.

8. Johnson, J. S., K. A. Kraus, and G. Scatchard, J. Phys. Chem. 58, 1034 (1954).

9. Kerker, M., D. Lee, and A. Chou, J. Am. Chem. Soc. 80, 1539 (1958).

10. Kirkwood, J. G., and R. J. Goldberg, J. Chem. Phys. 18, 54 (1950).

11. Ruff, J. K., and S. Y. Tyree, J. Am. Chem. Soc. 80, 1523 (1958).

12. --------Ibid., 5654.

13. Scatchard, G., ibid., 68, 2315 (1946).

14. Stockmayer, W. H., J. Chem. Phys. 18, 58 (1950).

15. Strauss, U. P., E. H. Smith, and P. L. Wineman, J. Am. Chem. Soc. 75, 3935 (1953).

16. Tobias, R. S., J. Chem. Ed. 35, 592 (1958).

SILICON AND BORON POLYMERS

R. P. Anderson
M. M. Sprung

General Electric Research Laboratory

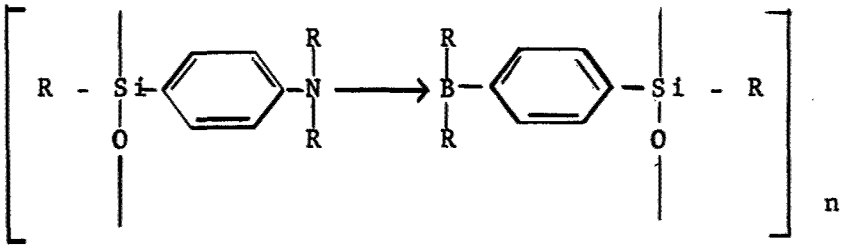
INTRODUCTION

The flexibility and toughness of useful elastomers and resins results from the fact that these materials contain long polymer chains that are capable of a limited degree of movement relative to one another. The extent of this movement is controlled by the binding forces between the main polymer chains. When there is very weak interchain attraction, liquids or soft materials of low flow point result. When the interchain forces are very strong, as in the case of polymers cross-linked with bonds as strong as those in the backbone itself, brittle or refractory solids are produced. For useful high temperature polymers an appropriate point between these extremes must be found. Forces of such strength as to permit partial interchain motion, but not complete chain separation, at useful temperatures, are needed.

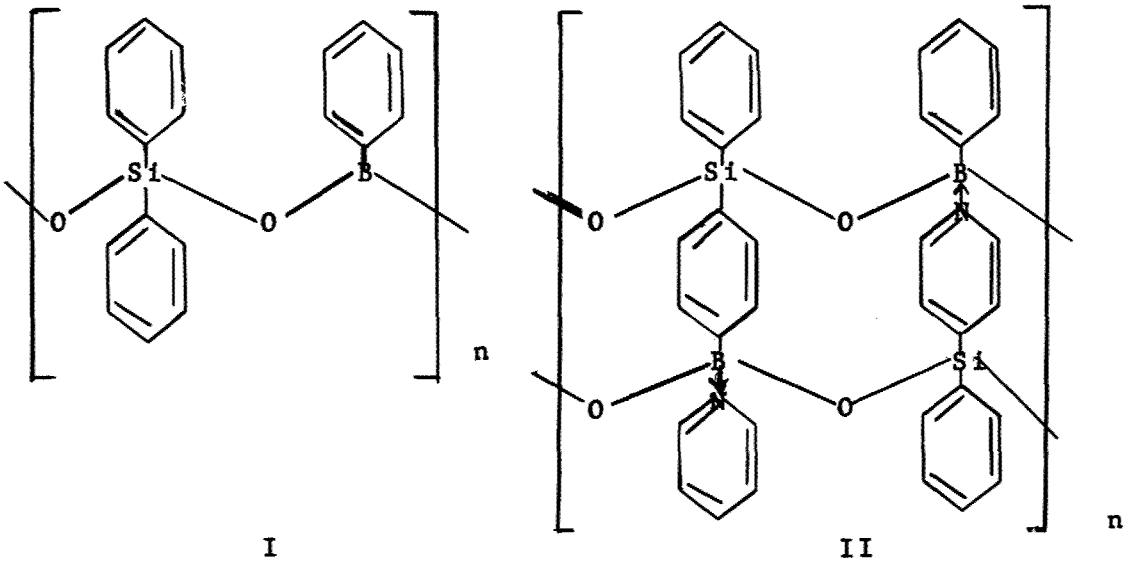
Random Van der Waal's forces, ordered Van der Waal's forces, random hydrogen bonding, and ordered hydrogen bonding - in that order - can lead to stronger, but reversible, interchain bonding. Individual bonds of this character have strengths in the range of about 2-10 kilocalories per mole. The dative (or coordinate) bond generally has a considerably higher intrinsic strength - probably in the range of 10-20 kilocalories per mole. The synthesis of polymers having stable backbond structures, suitable modifying organic groups to provide flexibility and workability, and appropriately placed dative bonds for interchain attractions should provide an interesting type of system for investigation of the general premise stated above.

A system that embodies all these prerequisites and yet affords a reasonable chance of a practical synthetic approach is a boroxane-siloxane copolymer having appropriately placed nitrogen atoms to serve as electron donors. This system has served as the starting point for the present attempt to prepare stable semi-organic polymers.

Rochow, Rosenberg and Aftandilian (1)(2) prepared nitrogen substituted silanes, with the purpose of combining them chemically with boron substituted silanes in polymers. Some of the intermediates were synthesized but the copolymers have not as yet been described. The structure of Rochow's polymer could be visualized as follows:



The copolymer system chosen for initial study in the present work is in many ways similar to that proposed by Rochow, et al., (1)(2) except that the boron is included in the main backbone chain and the nitrogen is part of an aromatic system.



I

Simple Copolymer

II

Copolymer with interchain coordinate bonding

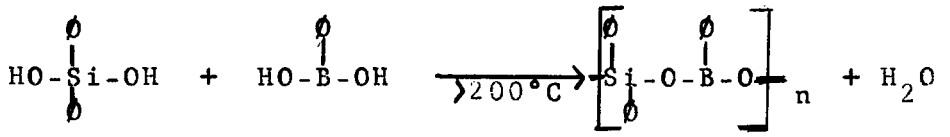
In this type of a copolymer one can presumably vary the B/Si ratio and therefore the amount of interchain interaction. The amount of interaction can also be varied by incorporating a certain proportion of groups having nitrogen in the 2-position rather than the 4-position. Thus some of the interchain bonding should be replaced by intrachain bonding. It would be of interest to compare the physical, mechanical and electrical properties of copolymers containing varying amounts and various types of coordinate bonding.

It is interesting to note that in this type of copolymer involving the interaction of Lewis acid (acceptor) and Lewis base (donor) atoms, the polymer chains might, if the proper regular structure is obtained, coil in a manner similar to proteins and nucleic acids. This should, of course, confer a degree of crystallinity upon the polymer and favorably affect the physical properties, even if the coiling were limited in extent.

In selecting the boron-oxygen-silicon copolymer system for study, one must ignore, at least initially, questions of oxidative and hydrolytic stability, and of physical properties at lower temperatures. It was anticipated that such a polymer might show decidedly suboptimal properties at room temperature.

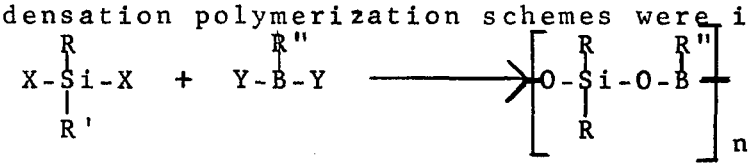
Boron polymers are in general susceptible to hydrolysis. However, the type of interaction proposed completes the tetracovalency of boron and therefore the hydrolytic stability of the resulting polymers should be improved.

Polymeric borosiloxanes have been prepared by a number of investigators (3)(4)(5)(6)(7). These borosiloxanes were prepared using borate esters or "boron acetate" and are potentially highly crosslinked. Upson (8), however, has described a linear borosiloxane polymer from benzeneboronic acid and diphenylsilanediol. This served as a starting point for the present



investigation. From a synthetic point of view, the nitrogen moiety could more easily be substituted on the silane than on the borane derivative.

The Upson polymer, which analyzes for the above composition when prepared at temperatures low enough to prevent dephenylation, is probably not a regular 1:1 copolymer but a random copolymer. Since a regular 1:1 copolymer was desired, other condensation polymerization schemes were investigated, i.e.



$X + Y = -OH, -OR, -OOCCH_3, -Cl$

This study has consisted of two parts: the preparation of the reactive monomers and the polymerization of these monomers to borosiloxanes. These are discussed separately in the following sections.

MONOMER PREPARATION

Reactive Borane Intermediates

Most derivatives of boric acid may be considered as potential intermediates for polyboroxane synthesis. However, available reactive boron compounds are limited, for practical purposes, to boric acid and its anhydrides, "boron acetates",

boron halides, and a few alkyl or arylboronic acids, their esters or halides.

Benzeneboronic acid is easily prepared via a low temperature reaction of phenylmagnesium chloride with methyl borate. Using a method similar to that reported by Ruigh (9), benzeneboronic acid has been prepared in 74% yield on a ten mole scale. Dichlorophenylborane (phenyl boron dichloride) and the dialkylbenzeneboronates can be prepared from the acid. The butyl esters are rather easily prepared by azeotropic distillation of water from mixtures of the boronic acid and n-butanol in the presence of an acid catalyst. The lower alkyl esters are much more difficult to prepare.

Dibutyl methaneboronate was prepared for this study in about 50% yield by a modification of Burg's method (10).

Acetoxy Silanes

The highly reactive chlorosilanes are not particularly will suited for coreaction with boron compounds. It is inherently more desirable to use the less available silanols, alkoxysilanes, aminosilanes, or acyloxysilanes. The acetoxysilanes have thus far proved to be the most useful.

The most convenient method for the preparation of acetoxy silanes was found to be that of Andrianov, Zhdanov and Bogdanova (11) who treated the chlorosilane with acetic anhydride and slowly distilled acetyl chloride from the reaction mixture. It has been observed in this laboratory that tertiary amines are effective catalysts for this reaction.

Pyridylsilanes

Grignard reactions with halopyridines are sluggish and proceed with difficulty in ether under normal conditions. However, these reactions were found to proceed smoothly in THF if the proper precautions are observed. The only reported uses of THF as a solvent for Grignard reactions with halopyridines are in patents issued to the Metal and Thermit Corporation (12)(13), who claim to have prepared 2-pyridylmagnesium chloride in 55% yield.

It was expected that the preparation of pyridylsilanes could be simplified by preparing the pyridylmagnesium halide and subsequently adding it in the cold to the chlorosilane. However, it was found that the 2-pyridylmagnesium halides are unstable and react with themselves. Pyridine has a very reactive

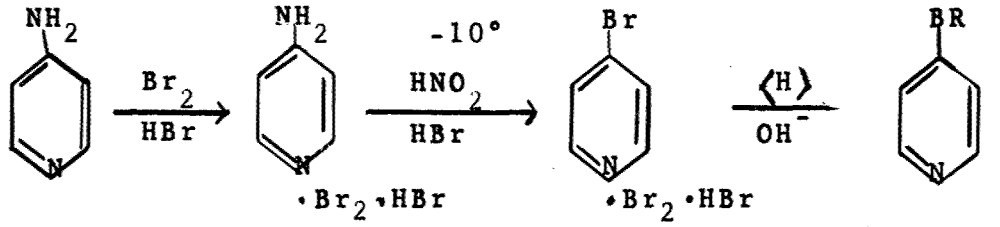
azomethine linkage and many organo-metallic reagents are known to react with it. As a result it has been necessary to prepare the pyridyl Grignard reagent in the presence of chlorosilanes. In this manner it is possible to get over a 90% yield of 2-trimethylsilylpyridine. The corresponding chloro- or alkoxypyridylsilanes can be prepared in 40-60% yield by a similar procedure. However, under the same conditions, 4-halopyridines give only a 20-30% yield of 4-trimethylsilylpyridine. The low yields in the case of the 4-halopyridines can probably be attributed to the facile polymerization of such compounds to polypyridinium polymers. Other side reactions also can occur. The azomethine link is probably much more reactive in 4-substituted pyridines than in 2-substituted pyridines because of the lack of a hindering group at the 2-position in the former case. Coupling is possible, but no 4,4' bipyridyl could be isolated. The by-product was a high boiling liquid which could not be purified.

The preparation of 2- and 3-lithiopyridine by exchange of the corresponding bromides with butyl lithium is a well known reaction (14)(15). Murray and Langham (16) prepared 4-lithiopyridine in this manner and subsequently isonicotinic-C^{14} acid in 83-96% yield. This method gave 4-lithiopyridine readily at low temperatures (-60°) and subsequent reaction with chloro- or alkoxysilanes gave reasonable yields (30-60%) of the pyridyl silanes. The lithium-halogen interconversion is therefore preferred for the synthesis of 4-pyridylsilanes while the Grignard reaction is best for the 2-pyridylsilanes.

The pyridylchlorosilanes are fuming liquids and are very difficult to handle except in a dry box. Contact with moisture liberates hydrogen chloride which immediately reacts with the pyridyl moiety, precipitating the pyridine hydrochloride. For this reason pyridylalkoxysilanes were also prepared. The synthesis is more difficult however because alkoxysilanes are less reactive toward organometallic reagents than the chlorosilanes.

2- and 3-Halopyridines are available, but it was necessary to develop a convenient synthesis for 4-halopyridines. The preparation of 4-chloropyridine by the diazotion of 4-aminopyridine had not been investigated very thoroughly, although 4-aminopyridine is available commercially. It has been generally assumed, mainly by analogy to 2-aminopyridine, that diazotization of 4-aminopyridine gives predominately 4-hydroxypyridine.

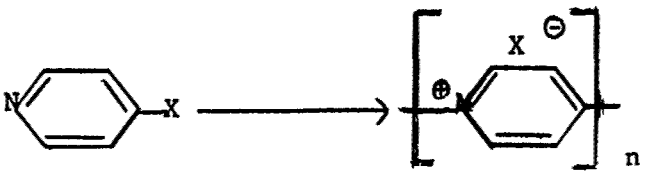
Recently Murray and Langham (16), using a modified procedure developed by Craig (17) for the preparation of 2-bromopyridine, prepared the corresponding 4-bromopyridine in yields of 85-95%.



The Craig procedure has never been adopted for the preparation of 2- or 4-chloropyridines, presumably less reactive than 4-bromopyridine. However, before applying the Craig method, the simple diazotization of 4-aminopyridine in concentrated hydrochloric acid was studied. There was indication from the work of Koenig (95)(96) that 4-aminopyridine differs from 2-aminopyridine and that the 4-chloro derivative might be prepared in this manner. Indeed it was found that 4-aminopyridine could be converted in essentially quantitative yields to 4-chloropyridine by diazotization at 0° in concentrated hydrochloric acid in the presence of excess sodium chloride. This provided a simple synthesis of 4-chloropyridine.

Using a similar procedure, 4-bromopyridine was prepared in yields greater than 70% from 4-aminopyridine. While the yields of 4-bromopyridine reported by Murray and Langham (16) (using the modified Craig procedure shown above) were greater than 85%, that procedure is not convenient on a large scale because of the large quantities of bromine required.

4-Halopyridines easily undergo an ionic polymerization, forming red to orange pyridinium polymers.

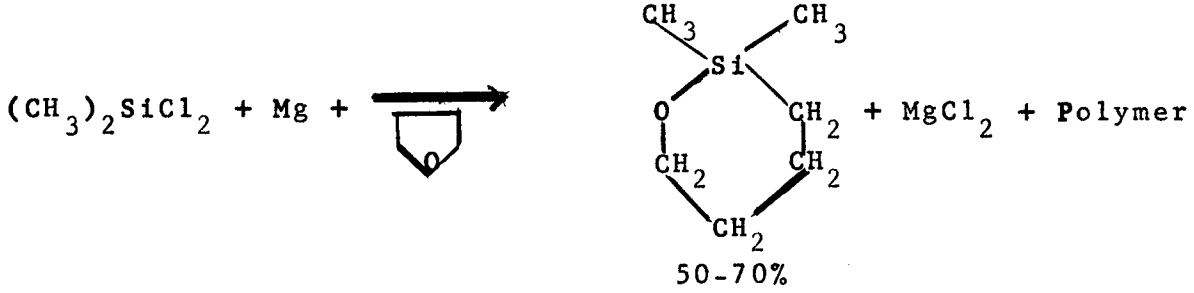


This polymerization is catalyzed by acids and by surfaces such as ground glass. However, the pure halopyridines are sufficiently stable for use and can be stored without decomposition at 0°C or below.

4-Bromo- and 4-chloropyridine were initially used without purification, since distillation at reduced pressure invariably caused polymerization. It was then found that the 4-halopyridines could be distilled without decomposition from a base such as sodium carbonate in a simple distillation apparatus containing no packing or ground glass joints. The apparatus was washed and then rinsed with 10% sodium carbonate before use. Rubber stoppers, where needed, were coated with paraffin wax.

Cleavage of Tetrahydrofuran

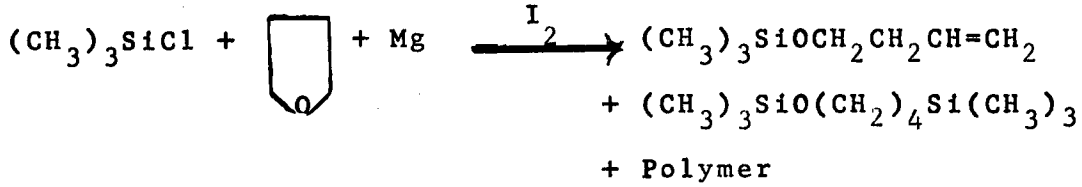
During the synthesis of pyridyl silanes, it was observed that (a) excess magnesium could never be recovered and that (b) the Grignard reaction mixtures continued to liberate heat long after the halide addition was completed. Further study showed, rather unexpectedly, that chlorosilanes react at an appreciable rate with magnesium in tetrahydrofuran solution. It was first assumed that the magnesium coupled the chlorosilane to form di- or polysilanes. The formation of disilanes from dichlorodimethylsilane and magnesium would be analogous to the rapid formation of polysilanes by the reaction of sodium with dimethyldichlorosilane in THF. However, purification of the products of the reaction of magnesium with dichlorodimethylsilane in THF showed that, while some polysilanes were formed, the major product resulted from a cleavage reaction.



The product, 2,2-dimethyl-1-oxa-2-silacyclohexane, has recently been prepared by Knoth and Lindsey (19) by a more involved method. The properties of the compounds prepared by the two methods are identical.

The THF cleavage reaction requires iodine as a catalyst. Iodine can be added in almost any form, i.e., as elemental iodine, as an alkyl iodide, as magnesium iodide, etc. The iodine does more than just activate the magnesium, since other conventional activators such as bromine, alkyl halides, etc. have a negligible effect.

Other chlorosilanes react with THF, though the products from these reactions have not been completely identified. Trimethylchlorosilane reacts as indicated below:



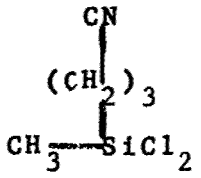
The reaction of chlorosilanes with magnesium, except in the case of trimethylchlorosilane, is quite exothermic. In

one experiment with phenyltrichlorosilane using a large excess of activated magnesium, the reaction became uncontrolably violent. However, under normal conditions in the presence of excess phenyltrichlorosilane, the reaction proceeds at a reasonable rate. The extent and mechanism of this THF cleavage reaction is under study.

Many of the experimental difficulties encountered in the synthesis of pyridylchlorosilanes by the Grignard reaction can be attributed to this reaction. However, it appears that tetrahydrofuran can be used for the "in situ" preparation and reaction of Grignard reagents if the magnesium is not activated with iodine or iodine compounds and if long reaction times are not used. The cleavage reaction, of course, can involve both the reacting chlorosilane and the product, if it is also a chlorosilane. The addition of a Grignard reagent to a chlorosilane in tetrahydrofuran should cause no trouble if excess magnesium is removed and long reaction times at reflux temperature are avoided.

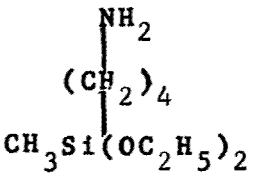
Synthesis of Nitrogen Containing Silanes

Because of the difficulty of pyridylsilane synthesis, other nitrogen containing silanes were investigated. Of these, I and II were available and III had been prepared previously.



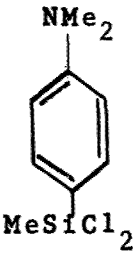
I

(Cyanopropyl) methyldichlorosilane



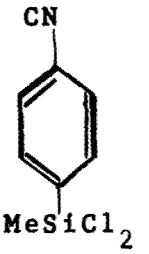
II

(ω-aminobutyl) methyldiethoxy silane



III

(4-dimethylaminophenyl)-methyldichlorosilane



IV

(4-cyanophenyl) methyldichlorosilane

Though 4-dimethylaminophenylmethyldichlorosilane can be prepared from p-dimethylaminophenyllithium (20) by the procedure of Rosenberg and Rochow (1), much higher yields (over 60%) could be obtained by a Grignard reaction with p-bromo-N,N-dimethylaniline and subsequent reaction with methyltrichlorosilane. The corresponding (4-dimethylaminophenyl) phenyldichlorosilane was also prepared in over 60% yield.

No cyanophenylchlorosilanes have been reported. A number of attempts to prepare p-cyanophenylmethyldichlorosilane by an

"in situ" Grignard reaction from p-chlorobenzonitrile were unsuccessful. A halogen-lithium interconversion reaction from p-bromobenzonitrile and n-butyl lithium was attempted, but no product was isolated, although Gilman and Melstrom (21) were able to accomplish this interconversion at -70° in low yield.

BOROSILOXANE FORMATION

The study of borosiloxane formation has been limited thus far to reactions between pairs of the following organoboron and organosilicon compounds:

Organoboron Component		Organosilicon Component	
$RB(OH)_2$	boronic acid (boranol)	R_xSiCl	chlorosilane
$RB(OR')_2$	boronic ester (alkoxyborane)	$R_xSi(OR')_y$	alkoxysilane
$B(OR)_3$	borate ester	$R_xSi(OH)_y$	silanol
$B_x(OAc)_y$	"boron acetate"	$R_xSi(OAc)_y$	acetoxysilane

The Boranol--Chlorosilane Reaction

This reaction has not yet been attempted, since it is believed to be one of the less promising approaches to the problem.

The Boranol--Alkoxysilane Reaction

This reaction, essentially a type of interesterification, has also not yet been studies, although it would appear, "a priori," to be more promising than the borano-chlorosilane reaction.

The Alkoxyborane--Chlorosilane Reaction

The reaction of dibutyl methaneboronate with dichlorodiphenylsilane was very sluggish, whether catalyzed or not. Butyl chloride was produced, but the reaction was incomplete even under rather drastic conditions, and complicated by side reactions.

The Boranol--Silanol Reaction

It was observed that diphenylsilanediol and benzeneboronic acid react readily in an aromatic hydrocarbon solvent that allows easy removal of water by azeotropic distillation. Low melting copolymers were obtained similar to those reported earlier by Upson (8). Analytical data on one copolymer indicate that under these conditions very little disproportionation occurs, nor is dephenylation a serious complication in this case. No further attention has yet been given to this reaction; first

because of the rarity of useful boranols, second because there is no obvious simple method to produce other than random copolymer this way, whereas it is desirable to have a more ordered type of copolymer for this study, and preferably an alternating (1:1) copolymer.

The Silanol--Alkoxyborane Reaction

As an example of this potential route to polyborosiloxanes, the reaction of diphenylsilanediol and dibutoxymethylborane was investigated in the absence of solvents. The net effect seems to be that diphenylsilanediol is dehydrated to poly(diphenylsiloxane), and the water formed partially hydrolyzes the boronic ester. Because of the peculiar equilibria that exist in a system consisting of dibutoxymethylborane, water, and butanol, a major portion of the boronic ester is recovered. There is no positive evidence of cocondensation.

The Boranol--Acetoxysilane Reaction

This method has been looked at only in a preliminary manner, using benzeneboronic acid with diacetoxydiphenylsilane and with phenyltriacetoxysilane. Reaction occurs quite readily at moderate temperatures and in absence of catalysts. The self-condensation of benzeneboronic acid is apparently kept to a minimum under these conditions. However, a serious side reaction is dephenylation of the boron component, which occurs either in presence or absence of an inert solvent. For example, a reaction between diacetoxydiphenylsilane and benzeneboronic acid is expressed empirically by

$$12\emptyset_2Si(OAc)_2 + 12\emptyset B(OH)_2 \longrightarrow 15HOAc + 9C_6H_6 + 12\emptyset_2SiO \cdot 3\emptyset BO \cdot 4.5Ac_2B_2O_4$$

In the reaction between phenyltriacetoxysilane and benzeneboronic acid extensive dephenylation also occurred.

Cohydrolysis of Alkoxysilanes and Alkoxyboranes

Diethoxydimethylsilane was hydrolyzed in the presence of ethyl borate and in the presence of dibutoxymethylborane. In the first case, evidence points to quite independent reaction of the two components; the major products are boric acid and its anhydrides, and poly(dimethylsiloxane). In the latter case, the ethoxysilane was again hydrolyzed to poly(dimethylsiloxane). The boronic ester was only partially hydrolyzed, once again because of the nature of the equilibria that are established.

From a mixture of diethoxydiphenylsilane, dibutoxymethylborane and water, about two-thirds of the silane component was recovered unchanged. At best, only a minor portion of cohydrolysate could have been produced. This method does not new seem to hold a great deal of promise.

The Acetoxysilane-Alkoxyborane Reaction

This reaction has been studied in greatest detail. For convenience in following the succeeding discussion, the reaction pairs so far studied are listed below.

Acetoxysilane	Alkoxyborane
$Me_2Si(OAc)_2$	$B(OBu)_3$ $MeB(OBu)_2$ $C_6H_5B(OEt)_2$
$MeSi(OAc)_3$	$MeB(OBu)_2$ $C_6H_5B(OEt)_2$ $C_6H_5B(OPr)_2$
$(C_6H_5)_2Si(OAc)_2$	$B(OBu)_3$ $MeB(OBu)_2$ $C_6H_5B(OEt)_2$ $C_6H_5B(OBu)_2$
$C_6H_5Si(OAc)_3$	$MeB(OBu)_2$
$CN(CH_2)_3SiCH_3(OAc)_2$	$C_6H_5B(OBu)_2$

The reaction occurs readily at moderate temperatures, requires no catalyst, and seems to be relatively uncomplicated by functional group exchange or elimination reactions. Oxidation and dearylation of the boronic ester do, however, appear to occur under some circumstances.

The resinous product obtained from methyltriacetoxysilane and dibutyl methaneboronate appeared to have considerable hydrolytic stability. The reaction between phenyltriacetoxysilane and dibutyl methaneboronate was next tried. When 77% of the calculated quantity of butyl acetate was driven off, a viscous oil remained that contained some solid. (This may have been diacetoxymethylborane, but a positive identification has not yet been made.) On standing in air the oil changed to a soft, slightly opalescent, translucent, flexible solid. Reaction with diacetoxydiphenylsilane was somewhat more sluggish, requiring a temperature above 250° to bring it near to completion. The thermoplastic, resinous product was badly discolored and presumably partially oxidized. The experiment should be repeated in absence of air or in vacuum.

Dipropyl benzeneboronate also reacted readily with methyltriacetoxysilane. Gelation occurred when about 70% of the calculated propyl acetate had been removed if the reactants were used in balanced amounts (3:2 molar quantities). A run made with excess of the acetoxysilane [2$C_6H_5B(OPr)_2$ to 3$MeSi(OAc)_3$] readily produced the calculated amount of propyl acetate, and

left a granular solid that could be a linear pentaacetoxydiborotrisiloxane. Analytical data are not yet available. This type of partial polymer should prove interesting in further copolymer syntheses.

In the reaction of diacetoxydiphenylsilane with tributyl borate, 95% of the theoretical quantity of butyl acetate was easily eliminated, leaving a fluid product that showed little tendency to gel on further heating. A bicyclic "monomer" ring structure would be suggested as a possibility.

Diacetoxydimethylsilane and butylborate reacted readily without catalyst. Gelation did not occur when 90% of the theoretical amount of butyl acetate was produced. The condensate, which should correspond empirically to the formula, $15Me_2SiO \cdot 5B_2O_3 \cdot 3BuOAc$ actually analyzed somewhat closer to the composition, $15Me_2SiO \cdot 4B_2O_3 \cdot 3BuOAc$.

Whendibutoxymethylborane was used instead of butyl borate, the reaction was surprisingly sluggish. Although a linear, thermoplastic polymer should be formed, only about 80% of the theoretical amount of volatile ester was obtained, and some oxidation was observed. Analyses have not yet been obtained.

Diethoxyphenylborane reacted somewhat more readily, but considerable dephenylation occurred and a discolored, somewhat tarry product was obtained.

The resinous product from methyltriacetoxysilane and dibutoxymethylborane appeared somewhat more promising. To test the reactivity of the residual functional groups in such a material, a partial polymer was prepared having excess butoxy groups. On treatment with ethylene glycol, a much less viscous product (an oil, in fact) was produced. The combined reactions can be expressed approximately as follows:

$$2MeSi(OAc)_3 + 4MeB(OBu)_2 + HOCH_2CH_2OH \longrightarrow 5BuOAc + 2BuOH + \left[MeBO(CH_2)_2O\right] + 3MeSiO_{1.5} \cdot BuOAc$$

The glycol did not have the desired effect; that is, it did not appear to propagate the polymer chain. There are, of course, many other reagents that might be investigated in this connection.

The reaction of methyltriacetoxysilane with diethoxyphenylborane gave about 80% of the calculated amount of volatile product, of which about 10% was benzene. The brittle solid that resulted corresponded roughly to $11C_6H_5BO \cdot 0.5B_2O_3 \cdot 8MeSiO_{1.5} \cdot 2EtOH$. With dipropoxyphenylborane, the balanced (2:3) reaction was about 70% complete at gelation, with very little dephenylation noted. The product from a 3:2 reaction was found by end

group analysis to approximate the expected pentaacetoxydiborotrisiloxane. Further studies of this interesting partial polymer have not yet been made.

Turning now to diacetoxydiphenylsilane, the reaction with butyl borate went over 90% to completion. Fractional extraction of the crude product gave a solid, a resinous fraction, and an oily fraction. It is assumed tentatively that the solid is the bicyclic "monomer", while the resin and oil are mixtures of end-group-stopped polymers. When dibutoxymethylborane was used instead of butyl borate, the low reactivity observed previously was again noted. A blanket of nitrogen did not materially minimize oxidation.

Still lower reactivity of diacetoxydiphenylsilane towards diethoxy- and dibutoxyphenylborane was noted. Both reactions resulted in very extensive dephenylation and left tarry products. In comparison, phenyltriacetoxysilane was considerably more reactive, required a lower temperature, and gave relatively little benzene as a side product.

Finally, γ-cyanopropyldiacetoxymethylsilane was tried, with dibutoxyphenylborane as the coreactant. Considerable benzene was again eliminated and a tarry product was formed. This is presently attributed more to the influence of the phenylborane component than to that of the cyanoalkylsilane. The latter will be studied further on its own merits.

The Alkoxysilane-Acetoxyborane Reaction

"Boron acetate" reacted very readily with the calculated amount of diethoxydiphenylsilane (this assumes the diboroxane structure is correct for the acetate). When the reaction was nearly 90% complete, a stiff balsam-like, moisture sensitive resin was obtained. This again suggests that an unsubstituted boron atom favors the formation of low-molecular ring species. Ethyltriethoxysilane was found to react even more readily. This polyfunctional condensation went nearly 85% to completion without gelation. The product was again apparently very moisture sensitive. The third alkoxysilane used was δ-aminobutyldiethoxymethylsilane, in which an amino group is available for potential dative bonding with boron. The elimination of ethyl acetate proceded fairly readily, but was complicated by side reactions presumably involving the primary amino group. The reaction was interrupted just short of gelation, to yield a brittle, glassy, heat-curable solid. This polymer seemed to be remarkably resistant to moisture, despite the high percentage of polar groups (OC_2H_5, $OCOCH_3$ and NH_2) still present, and the trifunctionality of the boron component. This stability can, of course, be attributed to the built-in dative bonding, and provides at least a tentative verification of the general thesis upon which the present work has been undertaken.

SUMMARY AND CONCLUSIONS

Reasonable efficient methods have now been developed for the synthesis of pyridylsilanes. The 2-pyridylsilanes can best be prepared by a Grignard reaction in tetrahydrofuran provided the THF cleavage reaction is avoided. 4-Pyridylsilanes can best be prepared by lithium-halogen interconversion from the 4-bromopyridine obtained by diazotization of 4-aminopyridine.

Nevertheless the chloropyridylsilanes are not easy materials to synthesize or handle. Attention has therefore been focused on more easily obtainable nitrogen containing silanes, e.g. [p-(dimethylamino)phenyl] -methyldichlorosilane. When the conditions for forming dative bonded polymers are more fully determined, the pyridylsilanes should find a place in the broader picture.

A satisfactory general method of preparation of 1:1 borosiloxane copolymers has not yet been found. The most easily controlled reaction is still the coreaction of silanols and boranols under azotropic conditions. Unfortunately, desirable hydroxy-substituted silanes and boranes are neither available nor easy to prepare. A further disadvantage, of course, is that there is no assurance that 1:1 copolymers will result; in fact, random copolymerization is much more likely. A third problem results from the likelihood that steric crowding will occur in those systems of special interest to this investigation, where a donor atom such as nitrogen is present either as part of or in addition to an aryl substituent. Although difficulties in the preparation of pyridyl-substituted silanols have already been encountered, and more are anticipated, this approach may be successful with other nitrogen-substituted alkyl- or aralkylsilanols.

Various reactions between silanes and boranes, having different rather than the same functional groups, have been studied. The most promising is the elimination of a volatile ester from an acyloxyborane and alkoxysilane. The chief limitations of the first method are, as pointed out above, the ease of dephenylation of phenylboranes, the relatively low reactivity and susceptibility to oxidation of alkylboranes, and the difficulties attending synthesis of necessary starting materials. Less is known at this time about the second alternative. Only one acyloxyborane has this far been obtainable. The initial results appear promising, and the method will be extended further.

REFERENCES

1. E. G. Rochow and S. D. Rosenberg, WADC Technical Report 54-102, Part 1, July 1954.

2. E. G. Rochow and V. D. Aftandilian, WADC Technical Report 54-102, Part II, February 1956.

3. E. Wiberg and U. Kruerke, Z. Naturforschung, 8b, 608 (1953).

4. F. A. Henglein, R. Lang and K. Scheinost, Die Makromolekular Chemie, 15, 177 (1955).

5. C. F. Gibbs, H. Tucker, G. Shkapenko and J. C. Park, WADC Technical Report 55-453 (II) (Sept., 1957).

6. K. A. Andrianov, 9th Congress on the Chemistry and Physics of High Polymers, Moscow, U.S.S.R., January, 1957.

7. K. A. Andrianov and L. M. Volkova, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1957, 303. C.A. 51, 14544 (1957).

8. R. W. Upson, U.S. Patent 2,517,945 (Aug. 8, 1950).

9. W. L. Ruigh, C. E. Erickson, F. Gunderloy and M. Sedlak, WADC Technical Report 55-26 (II) (May, 1955).

10. A. B. Burg, J. Am. Chem. Soc., 62, 2228 (1940).

11. K. A. Andrianov, A. A. Zhdanov and A. A. Bogdanova, Doklady. Akad. Nauk, S.S.S.R., 94, 697 (1954); C.A. 49, 6087 (1955).

12. Metal and Thermit Corp., French Patent 552,993, November 28, 1956.

13. Metal and Thermit Corp., French Patent 552,995, November 28, 1956.

14. D. Wittenberg and H. Gilman, Chem. and Ind., 1958, 390.

15. H. Gilman and S. M. Spatz, J. Am. Chem. Soc., 62, 446 (1940).

16. A. Murray and W. H. Langham, J. Am. Chem. Soc., 74, 6289 (1952).

17. F. C. Craig, J. Am. Chem. Soc., 56 232 (1934).

18. E. Koenigs, G. Kinne and W. Weiss, Ber., 57 1172 (1924).

19. E. Koenigs (with H. Gruschke), Angewandte Chemie, 50, 911 (1937).

20. R. A. Hubbard II and U. P. Strauss, WADC Technical Report 54-599, August, 1955.

21. H. Gilman, E. A. Zoellner and W. M. Selley, J. Am. Chem. Soc., 55, 1252 (1933).

22. H. Gilman and D. S. Melstrom, J. Am. Chem. Soc., 70, 4177 (1948).

Organo-metallic and Organo-metalloidal Studies on High-Temperature and Radiation-Resistant Lubricants and Related Materials.

Henry Gilman
(Iowa State College)

The chief phases of the studies reported at this time are concerned with the development of the chemistry of organosilicon compounds by reactions involving the Si-H and the Si-M groupings.

I. Preparation and Reactions of Compounds Containing the Silicon-hydrogen Group.

A. Preparation

A series of compounds containing the Si-H, $Si-H_2$, and $Si-H_3$ units has been prepared. These syntheses which involve numerous new compounds have been effected, in part, by conventional procedures like reduction by means of lithium aluminum hydride.

B. Reactions with Organometallic Compounds Leading to Unsymmetrical Molecules.

As mentioned in a preliminary prior report, it is now possible to synthesize conveniently a wide variety of R_3SiH and R_4Si compounds in which all of the R groups in each of these types may be unlike. An illustration of one of the first compounds prepared in this manner is the synthesis of phenyl-o-tolyl-p-phenoxyphenyl-p-tolyl-silane. It will be observed that in a synthesis of this kind the two variations are: first, the type of organometallic compound (for example, the Grignard reagent and organolithium compounds); and, second, the type of solvent (such as tetrahydrofuran and diethyl ether). From reaction of phenylsilane and o-tolylmagnesium bromide in tetrahydrofuran there is obtained an 87% yield of phenyl-o-tolyl-silane. This R_2SiH_2 compound when treated with p-phenoxyphenylmagnesium bromide in tetrahydrofuran gives a 56% yield of phenyl-o-tolyl-p-phenoxyphenylsilane. Finally, this R_3SiH (having three unlike groups) is brought into reaction with p-tolyllithium in ether to give a 68% yield of phenyl-o-tolyl-p-phenoxyphenyl-p-tolyl-silane. This particular R_4Si product (containing four unlike aryl groups) is a semi-glass which volatilizes with no significant change at 480°C, and which distils at 249-251° at 0.004 mm. We have purposely selected

this non-polymeric tetraarylsilane as one of a number of possible examples because it was prepared about three years ago and still has the consistency of a semi-glass. We have here an illustration of a signal advantage of organosilicon chemistry over carbon chemistry because it is uncommonly difficult to synthesize an R_4C compound in which the four aryl groups are unlike.

The essential means are now at hand for the preparation of a series of polysilanes in which all of R groups may be unlike. As one step in such syntheses one can prepare R_3SiH types (in which the R groups are unlike); then convert the R_3SiH to R_3SiX; and then by direct or indirect procedures prepare polysilanes having two or more silicon atoms joined directly or separated in a non-polymeric molecule.

C. Reactions with organometallic compounds leading to replacement of R groups.

Incidental to extensive studies involving the formation of organosilicon compounds having two or more unlike elements or groups, we have observed an occasional displacement of one R group by another, where the organometallic type is the Grignard reagent and where the solvent is tetrahydrofuran. For example, in a reaction between tribenzylsilane with allylmagnesium chloride one of the benzyl groups was displaced by the allyl group to give allyldibenzylsilane. The benzyl group was found in benzylmagnesium chloride inasmuch as carbonation followed by hydrolysis yielded phenylacetic acid. Fortunately, this particular displacement reaction is highly restricted. So far the displacement of a benzyl group from dibenzylsilane and tribenzylsilane by allylmagnesium chloride in tetrahydrofuran are the chief cases which have been demonstrated. The solvent effect of the tetrahydrofuran is an important factor in these displacement reactions. Attempts to extend the displacement (under our conditions) of an R group from triphenylsilane, tri-gamma-phenylpropylsilane, tetrabenzylsilane and tetraphenylsilane have been unsuccessful.

D. Disproportionation reactions in the absence of any added catalyst.

It was reported earlier that diphenylsilane undergoes disproportionation in the absence of any added catalyst to give all the possible disproportionation products; namely, tetraphenylsilane, triphenylsilane, diphenylsilane, phenylsilane, and silane (SiH_4). This and related disproportionation reactions undoubtedly occur in other transformations involving compounds containing the Si-H grouping, and provide a plausible explanation for some secondary reactions and by-products in some of our other syntheses. This reaction suggests that other substances may undergo disproportionation or

redistribution in the absence of added catalyst provided that their decomposition temperatures are not too low. More particularly, it did suggest an examination of the thermal behavior of some other compounds containing the Si-H group. Out of these studies came the finding that tribenzylsilane has pronounced thermal stability.

E. Thermal stabilities of some compounds containing the Si-H group.

After heating tribenzylsilane in a partially evacuated sealed tube for 24 hours between 300-310° there was no measurable evidence of decomposition. Under corresponding conditions, triphenylsilane underwent disproportionation to give 16% of tetraphenylsilane, 69% of triphenylsilane, 4.5% of diphenylsilane, 0.5% of phenylsilane, and trace amounts of silane.

Tri-(beta-phenylethyl)silane underwent disproportionation to give the R_4Si, R_3SiH, R_2SiH_2, and $RSiH_3$ products. It was observed that a related disproportionation occurred with tri-(gamma-phenylpropyl)silane, but to a slightly lesser extent than tri-(beta-phenylethyl)silane.

In general, it appears that dibenzylsilane undergoes disproportionation under conditions where tribenzylsilane is quite stable thermally. Also dibenzylsilane appears to undergo disproportionation to a lesser extent than diphenylsilane, di-(beta-phenylethyl)silane and di-(gamma-phenylpropyl)silane.

F. Reactions of some Si-H compounds with the carbonyl group.

It has been shown that triphenylsilylpotassium and also triphenylsilyllithium react with benzophenone to give the rearrangement product, benzhydryloxy-triphenylsilane. A similar reaction takes place (in a 62% yield) on heating triphenylsilane with benzophenone for three hours at 250-270°, in the absence of any added catalyst. Furthermore, diphenylsilane also reacts with benzophenone (on heating for two hours at 220-230°) in a corresponding manner, again in the absence of any added catalyst to give a 69% yield of benzohydryloxy-diphenylsilane. When phenylsilane was heated with benzophenone in a 1:1 ratio at 250° in a sealed tube, two products were isolated: benzohydryloxy-phenylsilane, $C_6H_5SiH_2OCH(C_6H_5)_2$ in a 20% yield; and bis(benzohydryloxy)phenylsilane in a 64% yield. Related reactions may take place with Si-H compounds and other functional groups. It should be mentioned here that other studies have shown that an Si-H compound like diphenylsilane has marked reducing properties at elevated temperatures. For example, benzophenone can be reduced to diphenylmethane.

G. Replacement of a bridged-sulfur by the diphenylsilylene group using diphenylsilane.

We have observed that some cyclic compounds containing one or more silicon atoms in the heterocyclic position of the molecule have attractive thermal characteristics. This suggested the replacement of a bridged-sulfur in some heterocyclic systems by the diphenylsilylene group, $(C_6H_5)_2Si$. The following heterocycles containing sulfur in the ring were examined: phenothiazine, 10-ethylphenothiazine, phenoxathiin, and thianthrene. From the reaction of each of these with diphenylsilane at elevated temperatures a sulfur atom was displaced by the diphenylsilylene group. For example, from a reaction in which equimolar parts of 10-ethylphenothiazine and diphenylsilane were heated for seven days at 240-255° there was obtained a 7.2% yield of 5-ethyl-10,10-diphenylphenazasiline. This compound has some interesting anti-oxidant properties.

A few observations should be made of some secondary reactions. Apropos the reducing action mentioned earlier of diphenylsilane with a compound like benzophenone, it was observed that diphenylsilane reduces 10-ethylphenothiazine-5-oxide to the corresponding parent sulfide. Dibenzylsilane deethylated 10-ethylphenothiazine rather than replaced the sulfur atom. Triphenylsilane underwent disproportionation in the presence of hydrogen sulfide; whereas with p-thiocresol and triphenylsilane there were formed triphenyl-(p-tolylthio)-silane and hydrogen.

In view of the promising properties of 5-ethyl-10,10-diphenylphenazasiline, other routes are being investigated for its synthesis as well as for the preparation of related types. One of these starts with 2,2'-dibromo-N-ethyldiphenylamine which is first converted to the corresponding dilithio compounds. This compound, in turn, reacts smoothly with diphenyldichlorosilane to give a satisfactory yield of the 5-ethyl-10,10-diphenylphenazasiline. Although this procedure involves more steps than the one using diphenylsilane with 5-ethylphenothiazine it has the merit of being more flexible. That is, it permits the introduction of unlike substituents on the 10,10-positions; it makes possible the preparation of "5,10,10" types having nuclear substituents such as chlorine and phenyl in the dibenzo portions of the molecule; spiro compounds can be prepared from the intermediate di-lithio compound; and from the di-lithio derivative there can be prepared heterocyclic types in which the silicon is replaced by metals and metalloids.

II Preparation and Reactions of Organosilyl-metallic Compounds.

A. Preparation.

There are several procedures for the preparation of R_3SiM compounds. One of broad applicability is concerned with the cleavage of disilanes. Two general factors should be considered. One of these is the nature of the R group, and the other is the solvent or medium in which the cleavage is carried out. R_3SiM compounds are readily prepared when one, two and all three groups are aryl. When the three R groups are alkyl, it is possible to prepare such compounds but the reaction is not so effective from a preparative viewpoint, at this time, as when one or more of the R groups are aryl.

Several solvents have been examined for the formation of R_3SiM types. One of the early ones was diethyl ether. For example, the cleavage of a compound like hexaphenyldisilane by sodium-potassium alloy proceeds satisfactorily in ether. However, this mode of preparation has two drawbacks. First, there is an excess of sodium-potassium alloy; and, second, the triphenylsilylpotassium is insoluble in ether. The excess of sodium-potassium alloy was readily taken care of by the use of mercury to form an amalgam. A subsequent development came in the replacement of diethyl ether by ethylene glycol dimethyl ether which provided a medium in which the triphenylsilylpotassium was soluble. However, the R_3SiK compound was not too stable in this solvent, which it cleaved appreciably over a period of time and particularly on heating. For example, when a solution of triphenylsilylpotassium in ethylene glycol dimethyl ether is refluxed for one hour all of the triphenylsilylpotassium is used up as evidenced by a negative Color Test I. The chief product formed by this cleavage reaction is methyltriphenylsilane, $(C_6H_5)_3SiCH_3$.

Later came the procedure for the preparation of triphenylsilyllithium by cleavage of hexaphenyldisilane in tetrahydrofuran. The yields by this synthesis are excellent; the R_3SiLi compound is soluble; and the solutions are satisfactorily stable. On protracted refluxing, or on heating at a more elevated temperature, the tetrahydrofuran is cleaved to give (subsequent to hydrolysis) 4-hydroxybutyl-triphenylsilane. Actually, if triphenylsilyllithium is heated for three hours at 125° there results a 71% yield of the 4-hydroxybutyl-triphenylsilane. For most purposes, reactions with triphenylsilyllithium in tetrahydrofuran proceed sufficiently satisfactorily so that there is no problem of contamination by any appreciable quantity of the 4-hydroxybutyl-triphenylsilane.

The triphenylsilyllithium can also be prepared by cleavage of hexaphenyldisilane in tetrahydropyran. The rate of formation of triphenylsilyllithium in this solvent is slower than in tetrahydrofuran, but the resulting R_3SiLi is more stable

in tetrahydropyran than in tetrahydrofuran.

A more recent development in the preparation of R_3SiM compounds is that involving the direct reaction of an R_3SiX with lithium in tetrahydrofuran. In short, these compounds can now be prepared by the simple, convenient procedure now used for the preparation of Grignard reagents and for the preparation of organolithium compounds. This so-called direct preparation appears to involve the intermediate formation of a disilane, which is then cleaved by the metal present. The disilane can actually be isolated when the preparation is halted at an appropriate stage. It also appears that a reaction takes place prior to the formation of the disilane. This reaction may be the direct formation of some of the R_3SiLi compound which is known to react very promptly with an R_3SiX compound to give a disilane. The syntheses may then involve the following transformations:

$$R_3SiX + 2M \longrightarrow R_3SiM + MX$$

$$R_3SiM + R_3SiX \longrightarrow R_3Si\text{-}SiR_3 + MX$$

$$R_3Si\text{-}SiR_3 + 2M \longrightarrow 2R_3SiM$$

Additional procedures will be discussed which involve other media and other reactants. Furthermore, it is possible to prepare organosilylmetallic compounds having more than one silicon atom, and organosilylmetallic compounds having more than one Si-M grouping.

B. Reactions of organosilylmetallic compounds with alkyl halides and with aryl halides.

The type of reaction which takes place between R_3SiM compounds and alkyl halides is markedly influenced by both the halogen and the R group of the RX compound. For example, in a reaction between triphenylsilyllithium and n-butyl chloride in tetrahydrofuran the chief products are a 75% yield of n-butyltriphenylsilane and a few percent of hexaphenyldisilane. In contrast, when a reaction is carried out under corresponding conditions with triphenylsilyllithium and n-butyl bromide; the main products are only a 10% yield of n-butyltriphenylsilane but a 60% yield of hexaphenyldisilane.

In a related manner, the reaction between triphenylsilyllithium and 1,3-dichloropropane gives a 73% yield of 1,3-(bis-triphenylsilyl)propane; but from the reaction between triphenylsilyllithium and 1,3-dibromopropane the chief product is a 71.5% yield of hexaphenyldisilane.

$$(C_6H_5)_3SiLi + Cl(CH_2)_3Cl \longrightarrow (C_6H_5)_3Si(CH_2)_3Si(C_6H_5)_3$$

$$(C_6H_5)_3SiLi + Br(CH_2)_3Br \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3$$

From reaction between triphenylsilyllithium and isopropyl chloride there results a 65% yield of isopropyl-triphenylsilane and a few percent of hexaphenyldisilane; whereas triphenylsilyllithium and isopropyl bromide give only a few percent of isopropyl-triphenylsilane but a 61% yield of hexaphenyldisilane.

A somewhat different reaction occurs with the two tertiary-butyl halides (the chloride and the bromide). Triphenylsilyllithium with tertiary-butyl chloride gives a 46% yield of triphenylsilane and a 6% yield of hexaphenyldisilane (no tert-butyl-triphenylsilane has as yet been isolated); but triphenylsilyllithium with tertiary-butyl bromide gives but a few percent of triphenylsilane and a 64% yield of hexaphenyldisilane.

Some other combinations of alkyl groups and of various halogens will be discussed. In some of these reactions, a halogen-metal interconversion may be involved.

Somewhat related differences are observed in reactions between triphenylsilyllithium and aryl halides like the four phenyl halides. Among the chief products formed from such combinations are tetraphenylsilane and hexaphenyldisilane. It appears that at least part of the tetraphenylsilane may owe its formation to the intermediate benzyne. In this connection some tetraphenylsilane is formed from reactions between triphenylsilyllithium and a variety of poly-halogenated benzenes. It is significant that triphenylsilyllithium reacts with benzonitrile to give an appreciable yield of tetraphenylsilane. We may be dealing here with the nitrilo group acting as a pseudo-halogen, and one might also consider a possible benzyne intermediate here too. On hydrolysis of such mixtures some hydrogen cyanide is evolved.

It should be stated that there appears to be a difference depending on whether one uses R_3SiK in ether or R_3SiLi in tetrahydrofuran.

C. Reactions of organosilylmetallic compounds with ethers.

We have already mentioned that ethylene glycol dimethyl ether and tetrahydrofuran have been used as solvents for the preparation of R_3SiM compounds and their reactions. These ethers, like many others, undergo cleavage by R_3SiM compounds, and such cleavages can be highly useful synthetically for making available organosilicon types which are either novel or which have been relatively inaccessible hitherto. Among some simple cyclic ethers or oxides which belong in this category are ethylene oxide, trimethylene oxide, cyclohexene

oxide, etc.

An illustration of another type of ether cleavage which provides a route to the introduction of nitrogen in an organosilicon compound is that between triphenylsilyllithium with n-butoxymethylpiperidine. Here the product obtained in satisfactory yield, by way of cleaving off the n-butoxy group, is N-(triphenylsilylmethyl)piperidine.

D. Reactions of organosilylmetallic reagents with carbonyl-containing compounds.

Very early in the history of organosilylmetallic compounds it was observed that triphenylsilylpotassium reacted with formaldehyde to give, subsequent to hydrolysis, the expected triphenylsilylmethanol.

$$(C_6H_5)_3SiK + HCHO \longrightarrow (C_6H_5)_3SiCH_2OH$$

A related reaction takes place with triphenylsilyllithium and with the analogous triphenylgermylmetallic compounds. Also triphenylgermyllithium reacts in a related normal manner with benzophenone to give triphenylgermyldiphenylcarbinol:

$$(C_6H_5)_3GeLi + (C_6H_5)_2CO \longrightarrow (C_6H_5)_3GeC(OH)(C_6H_5)_2$$

However, triphenylsilyllithium reacts with benzophenone to give the rearrangement product, benzhydryloxy-triphenylsilane:

$$(C_6H_5)_3SiLi + (C_6H_5)_2CO \longrightarrow (C_6H_5)_3SiOCH(C_6H_5)_2$$

The course of this reaction has not as yet been completely elucidated; however, one preliminary stage may involve the formation of triphenylsilyldiphenylcarbinol, $(C_6H_5)_3SiC(OH)(C_6H_5)_2$ which is known to rearrange with ease to benzhydryloxy-triphenylsilane.

A related reaction occurs between triphenylsilyllithium and benzaldehyde. Here, among the chief products, are benzyloxy-triphenylsilane and 1,2-diphenyl-1,2-dihydroxyethane.

The picture is somewhat different with aliphatic aldehydes and with aliphatic ketones. Here the reaction proceeds normally to give alpha-silylcarbinols. These carbinols can be rearranged generally by means of strong alkalis or by alkali metals or their combinations (such as sodium-potassium alloy).

The structure of a typical alpha-silylcarbinol was established by an orthodox synthesis. For example, from the reaction of triphenylsilyllithium and acetone there was obtained a 52% yield of triphenylsilyl-dimethylcarbinol. This was

shown to be identical with the carbinol prepared by the reaction of methylmagnesium iodide with methyl triphenylsilanecarboxylate. Incidentally neither phenylmagnesium bromide nor phenyllithium reacted smoothly with the methyl triphenylsilanecarboxylate.

In addition to the alpha-silylcarbinols obtained from a variety of aliphatic ketones and triphenylsilyllithium there was also formed some triphenylsilane which may owe its origin to reaction with the enol. A striking illustration of this was the reaction between triphenylsilyllithium with dibenzyl ketone which gave a 78% yield of triphenylsilane, and from which reaction no alpha-silylcarbinol has as yet been isolated.

E. Reactions of organosilylmetallic reagents with nitrogen-containing compounds.

Triphenylsilyllithium in tetrahydrofuran reacts readily with aliphatic amines to give the $R_3Si\text{-}NHR$ and $R_3Si\text{-}NR_2$ types. With di-n-butylamine there is obtained a 62% yield of di-n-butylamino-triphenylsilane:

$$(C_6H_5)_3SiLi + HN(C_4H_9\text{-}n)_2 \longrightarrow (C_6H_5)_3Si\text{-}N(C_4H_9\text{-}n)_2$$

The yield with n-butylamine is 56%; 83% with morpholine; 86% with piperidine; and 93% of the bis-product with piperazine. It is probable that these reactions proceed in the following two stages:

$$(C_6H_5)_3SiLi + HNR_2 \longrightarrow (C_6H_5)_3SiH + LiNR_2$$

$$(C_6H_5)_3SiH + LiNR_2 \longrightarrow (C_6H_5)_3SiNR_2 + LiH$$

In support of these reactions is, first, the expected metalation; and, second, the established reaction between triphenylsilane and lithium dialkylamides.

It might be mentioned at this point that most of the reactions described for an R_3SiM type have been carried out not only with triphenylsilyllithium, but also with methyldiphenylsilyllithium and dimethylphenylsilyllithium.

It has been shown that triphenylsilyllithium behaves as a selective nucleophile towards pyridine. The intermediate dihydro compound, after customary dehydrogenation by oxidation with a reagent like nitrobenzene, gave triphenyl-4-pyridylsilane in satisfactory yield. The thermal stabilities of related systems appear promising because the triphenyl-4-pyridylsilane volatilizes at 430-435° with only slight decomposition. Incidentally, the triphenyl-4-pyridylsilane shows no depression of melting point with tetraphenylsilane.

In extension of studies on the addition of triphenylwilyllithium to aza-aromatic systems, a study was made of the reaction with acridine. Here 9,10-addition takes place which, in this case, is analogous to that observed with alkyllithium and aryllithium compounds. Some of these types are being examined for anti-oxidant effectiveness.

F. Reaction of triphenylsilyllithium with tri-n-butyl phosphate.

In extension of syntheses leading to custom-made molecules the investigation is in progress of the reactions between organosilylmetallic compounds and a wide series of esters and related types. One particular reaction which should be mentioned at this time is that between triphenylsilyllithium in tetrahydrofuran with tri-n-butyl phosphate. The yield of n-butyltriphenylsilane from a prompt reaction was 90%. This is a particularly significant reaction when contrasted with some Grignard reagents and organolithium compounds. In addition there was obtained 1.2% of hexaphenyldisilane, as well as triphenylsilanol and hexaphenyldisiloxane.

A satisfactory yield of toluene was also obtained from triphenylsilyllithium and methyl phosphate.

III Preparation of Tetrakis(p-tribenzylsilylphenyl)silane.

There were two objectives in this particular synthesis. One was to incorporate within a molecule several tribenzylsilyl groups with the idea in mind that the special thermal characteristics described earlier for tribenzylsilane may impart added thermal stability to other molecules. The second was to synthesize a large non-polymeric organosilicon compound containing only carbon, hydrogen, and silicon.

The reactions used in the synthesis involved the conversion of p-tribenzylsilylphenyl bromide, by means of a halogen-metal interconversion reaction with n-butyllithium to p-tribenzylsilylphenyllithium. This, in turn was reacted with silicon tetrachloride to give in a 51% yield, the $[(p\text{-}C_6H_5CH_2)_3SiC_6H_4]_4Si$. This tetrakis(p-tribenzylsilylphenyl)silane melts at 159-161°, and was crystallized from petroleum ether, despite a molecular weight of 1538. It appears to be the highest molecular weight non-polymeric organosilicon compound. It is significant that this R_4Si compound volatilizes at 510°C, assuming a light yellow color at that temperature. Although this compound is probably the non-polymer of highest molecular weight which contains only silicon, carbon, and hydrogen, there is a higher molecular weight non-polymer which contains silicon, carbon, hydrogen, oxygen and titanium.

Synthesis of Polyxylylyldimethylsilane and Polyxylylyltetramethylsiloxane

Glenn R. Wilson

Ford Motor Company

Scientific Laboratory

Abstract

The synthesis of two series of organosilicon polymers, poly-p-xylylyldimethyl silane (A) and poly-p-xylylyltetramethylsiloxane, (B), expected to possess good thermal stability for use as lubricants or hydraulic fluid, was the purpose of this project.

The major efforts on this project were concerned with finding a suitable route to the synthesis of the monomeric building block of these polymers--bis(trimethylsilyl)-p-xylylene. After many disappointments, a successful method for preparing this compound was found and the o- and m-isomers were also prepared. The technique used was one that involved feeding a mixture of the respective xylylene dihalide and trimethylchlorosilane to magnesium in tetrahydrofuran.

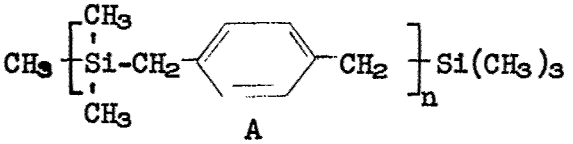
A polymerizable intermediate, bis(dimethylchlorosilyl)-p-xylylene was also prepared successfully by the same technique, i.e., reacting a mixture of p-xylylene dichloride and dimethyldichlorosilane with magnesium in tetrahydrofuran.

Polymerization of bis(dimethylchlorosilyl)-p-xylylene to the polysiloxane rather than to the polysilane was chosen on the basis that only one type of linkage would result in the former, whereas, hetero linkages were anticipated in the latter, i.e. the xylylene units could be linked through dimethylsilyl groups or bibenzyl groups.

The polymers resulting from treating bis(dimethylchlorosilyl)-p-xylylene with water in the presence of trimethylchlorosilane varied in molecular weights from ca 700-1100 and their elemental analyses indicate mixtures of cyclic and linear polymers.

INTRODUCTION

Among the many organosilicon compounds screened for thermal stability, Gilman and coworkers,[1] found that tribenzylhexadecylsilane possessed good thermal stability. By incorporating the benzyl silicon linkage in a polymeric silane or siloxane, it was reasoned that thermally stable polymers should result. One way of attaining such a linkage is through a xylylene linkage as in poly-p-xylylyldimethylsilane (A) and poly-p-xylylyltetramethyl siloxane (B).



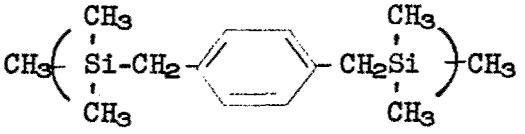
A

B

Synthesis of structures A and B then was the purpose of this project.

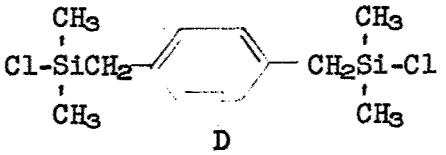
DISCUSSION

Examination of structures A and B reveals that each polymer contains a common building unit as indicated in the bracketed portion of C.



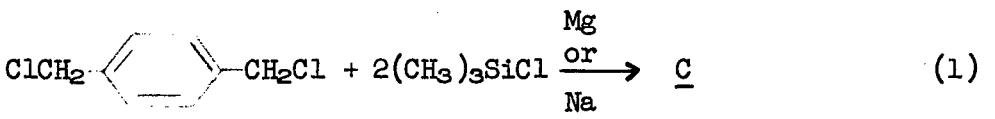
C

Consequently, structure C was selected as the model compound for working out the details of synthesis for a suitable monomeric intermediate, such as D, for subsequent polymerization.



D

The most direct method for preparing C would be a coupling reaction of the Grignard or Wurtz-type, Equation (1).

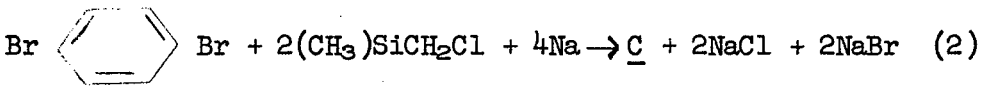


$$ClCH_2\text{-}C_6H_4\text{-}CH_2Cl + 2(CH_3)_3SiCl \xrightarrow[\text{or}]{\text{Mg}\atop\text{Na}} \underline{C} \qquad (1)$$

From the results of a literature survey, little hope of obtaining C by such coupling reactions was offered. Mann and Stewart[2] tried similar coupling reactions of xylylene dihalides with phosphorous chlorides and obtained only polyxylylene. An exception was noted, i.e., Hersh[3] inferred the formation of a di-Grignard intermediate of o-xylylene dichloride in a series of reactions[2] although this was never verified by subsequent investigators.

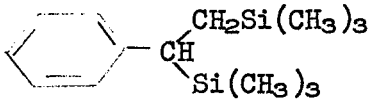
Despite evidence to the contrary, we also attempted to couple p-xylylene dihalide with trimethylchlorosilane by treating mixtures of the two reactants with magnesium in diethyl ether, di-n-butyl ether and p-dioxane or with metallic sodium in hydrocarbon solvents. The resulting product was poly-p-xylylene.

The next reaction considered involved the coupling of dibromobenzene and chloromethyltrimethylsilane with metallic sodium, Equation (2).



$$Br\text{-}C_6H_4\text{-}Br + 2(CH_3)SiCH_2Cl + 4Na \rightarrow \underline{C} + 2NaCl + 2NaBr \qquad (2)$$

In one instance a very small quantity of material (2 - 3%) was obtained. whose elemental analysis was exactly that calculated for bis(trimethyl silyl)-p-xylylene, C, and it was at first believed that the coupling was successful. However, the infrared absorption spectrum did not confirm this structure. The exact structure of this material is still unresolved but is postulated to be an isomer, such as structure E. Subsequent



E

efforts to prepare the same compound were unsuccessful and complex mixtures of unidentified compounds were obtained.

The attempted coupling of p-chlorobenzyltrimethylsilane and chloromethyl-trimethylsilane with sodium likewise did not yield C.

Other types of coupling reactions tried and found unsuccessful include the following:

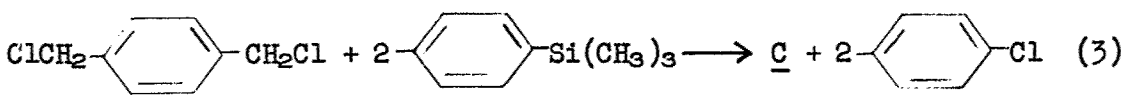
A. Treating trimethylsilylmethylmagnesium chloride and p-dibromobenzene with catalytic quantities of anhydrous cobaltous chloride.

B. Treating p-phenylenedilithium with chloromethyltrimethylsilane or bis(chloromethyl) tetramethyldisiloxane yielded compounds of indefinite composition.

Another Grignard reaction investigated was the reaction of p-benzoquinone with trimethylsilylmethylmagnesium chloride. The anticipated reaction here would yield a dihydroxycyclohexene that could be dehydrated and aromatized to give C or an isomer thereof, however, the product isolated was a high melting, dark-colored material whose elemental analysis did not correspond to a simple structure.

Alkylation reactions were also investigated in which benzene or benzyltrimethylsilane were treated with chloromethyltrimethylsilane or chloromethyldimethylchlorosilane in the presence of aluminum trichloride. Rearranged products and disiloxanes resulted upon hydrolysis.

Since a phenyl group attached to silicon is readily cleaved by acid, the following reaction, Equation (3), was investigated by refluxing the two reactants. The



(3)

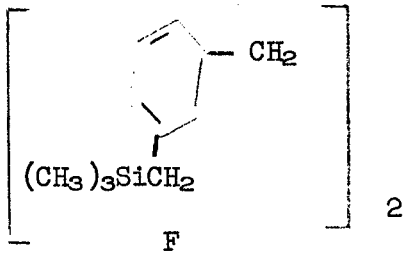
reaction, however, proceeded via a different course and yielded instead trimethylchlorosilane, benzene, and an insoluble polymer of xylene.

At this point, we were contemplating abandoning this particular problem in favor of another but decided on one last effort. This decision was based upon the statement of Mann and Stewart[2] that of the three isomeric alkoxymethylbenzyl halides, only the meta isomer yielded a Grignard reagent--the o and p isomer (like the corresponding xylylene dihalides) with magnesium yielded polyxylylenes.

Fortuitously, tetrahydrofuran was selected as the solvent for this last attempt. In the first experiment, m-xylylene dibromide was reacted with magnesium in tetrahydrofuran, in an effort to prepare a di-Grignard intermediate, followed by addition of trimethylchlorosilane. The only product isolated in this instance was poly-m-xylylene, containing traces of halogen and silicon. In contrast to poly-p-xylylene, the meta isomer was a low-melting one (67-75°) and soluble in a variety of solvents. The molecular

weight (1850 - 1900), combined with elemental analysis, indicated that the polymer contained approximately 18 xylylene units.

In a second experiment a mixture of m-xylylene dibromide and a large excess of trimethylchlorosilane was reacted with the magnesium in tetrahydrofuran. From the reaction mixture we isolated bis(trimethylsilyl)-m-xylylene in 32% yield. A second component was also isolated from the reaction mixture that was identified as 3,3'-bis(trimethylsilylmethyl)bibenzyl, F.



F

The same technique when applied to p-xylylene dichloride and o-xylylene dibromide yielded the respective isomers of bis(trimethylsilyl)xylylene.

The physical properties of these three isomers are summarized in Table I and the infrared absorption spectra are reproduced in Figures 1, 2, and 3.

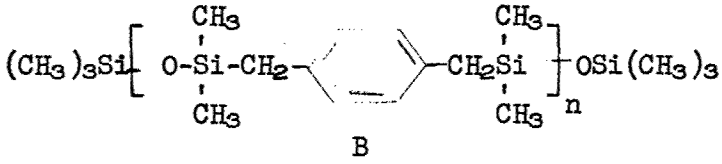
TABLE I

Isomer	Melting Point (°C)	Boiling Point (°C)	Pressure (mm)	d_4^t	n_D^{20}
ortho	----	75-6	0.55	0.8686^{25}	1.4950
meta	----	73-4	0.60	$0.8595^{24.7}$	1.4919
para	61-5	73-4	0.30	----	----

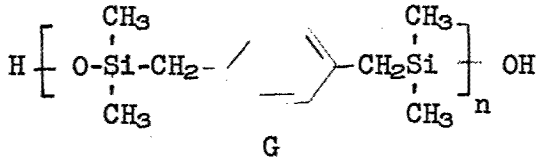
Having found a successful method for preparing the common building unit of polymers A and B, our next efforts were directed towards the synthesis of the polymerizable intermediate, D, bis(dimethylchlorosilyl)-p-xylylene. By reacting mixtures of p-xylylene dichloride and dimethyldichlorosilane, D, was obtained as a white crystalline solid, m.p. 74-7°; b.p. 113-122°C/ (0.25-0.35 mm) and in 33% yield (for infrared absorption spectrum see Figure 4). Several attempts to prepare the m-isomer from m-xylylene dibromide were unsuccessful and unidentified mixtures of compounds resulted.

The polymerization of D, to the polysilane A, necessitated the coupling of D with p-xylylene dihalide and the possibilities of obtaining homogeneous linkages in the polymer were considered unfavorable in view of the fact that a bibenzyl derivative, F, was obtained in the preparation of bis(trimethylsilyl)-m-xylylene.

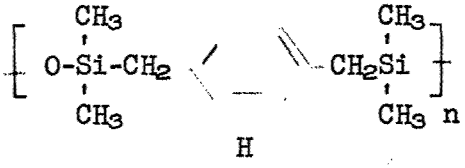
On the other hand, the polymerization of,D, to the polysiloxane could yield only homogeneous linkages although a maximum of four types of polymer could result, assuming the polymerization was conducted in the presence of trimethylchlorosilane as a terminating group. The possibilities are B, G, H, and I.



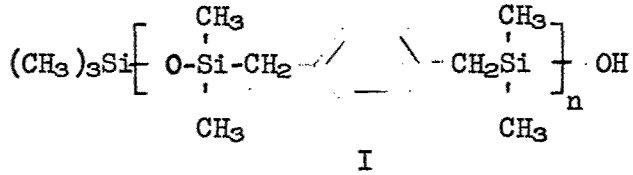
B



G



H



I

Several small-scale, preliminary polymerizations were made prior to polymerizing a relatively large scale batch. The molecular weights of these polymers varied from 700-1100 and the elemental analysis indicated mixtures. The increase in molecular weight was not concomitant with an increase in refractive index and this was interpreted as further indication of mixtures of cyclic and linear polymers. No significant differences were noted in the infrared absorption spectra of the polymers (see Figure 5 for spectra of poly-p-xylylyltetramethylsiloxane).

The results of these polymerizations are summarized in Table II.

TABLE II

Polymerization of Bis(dimethylchlorosilyl)-p-xylylene (D)

Mole ratio of reactants		Polymer		
D	$(CH_3)_3SiCl$	d_4^{25}	n_D^{20}	Mol. Wt.
1*	1	0.9583	1.4968	1102
1**	2	0.9583	1.4954	702
1***	3	0.9468	1.4890	902
1****	1	0.9586	1.4991	965

* Components dissolved in xylene and stirred into large excess of water.

** Water (1/2 mole) in dioxane added to D dissolved in dioxane followed by addition of $(CH_3)_3SiCl$.

*** Mixture of components in toluene added to large excess of water.

**** Large batch run in which mixture of components in toluene added to large excess of water. Material represents residue after stripping polymer at 200° (0.05 mm).

Further characterization and elaboration of the structure of the polymers was not possible due to the expiration date of the contract on the project.

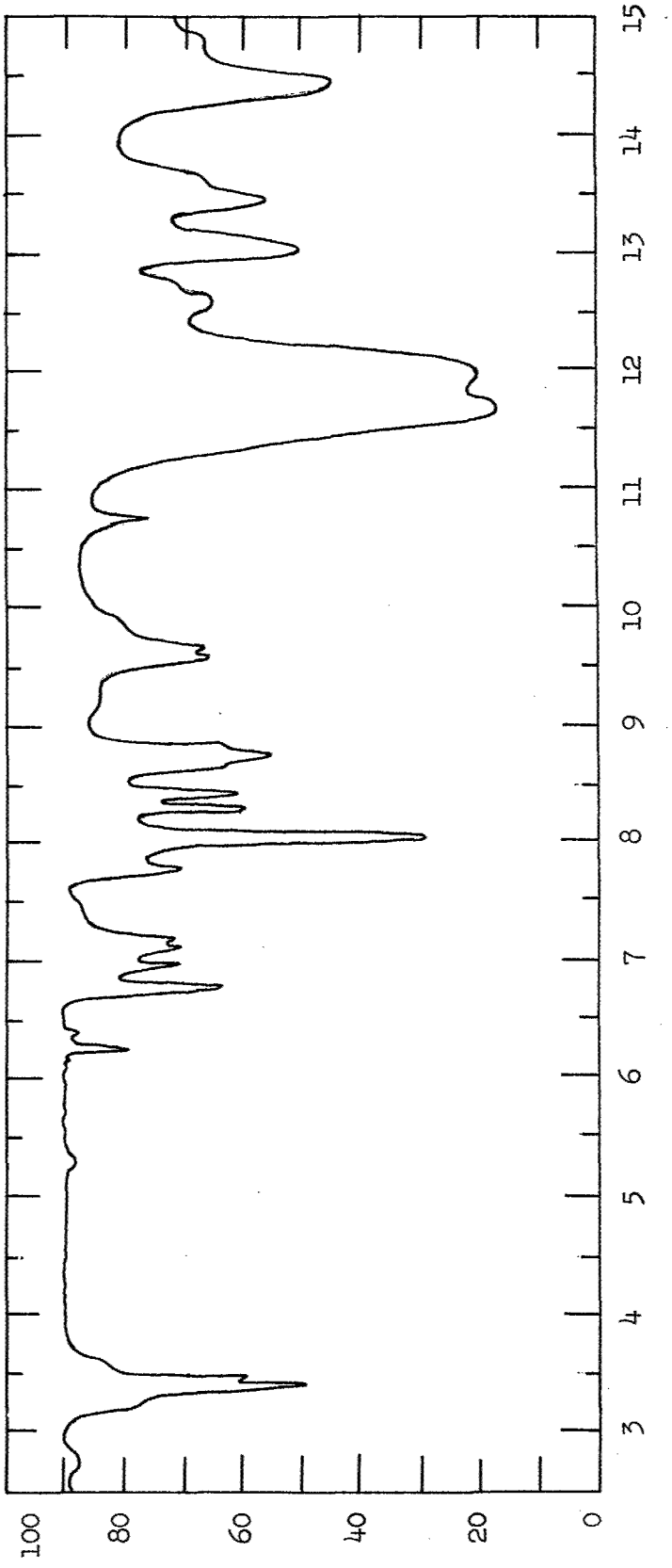


Fig. 1 Bis(trimethylsilyl)-o-xylylene

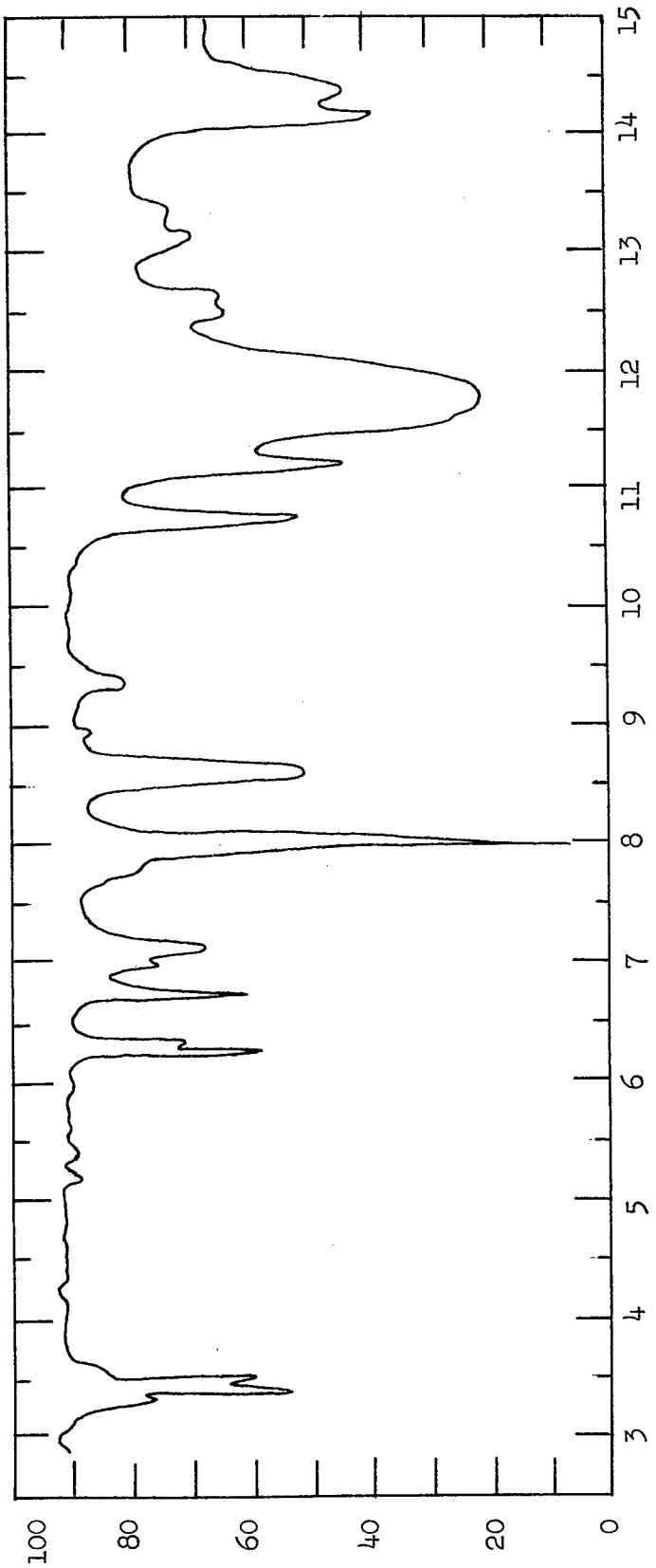


Fig. 2 Bis(trimethylsilyl)-m-xylylene

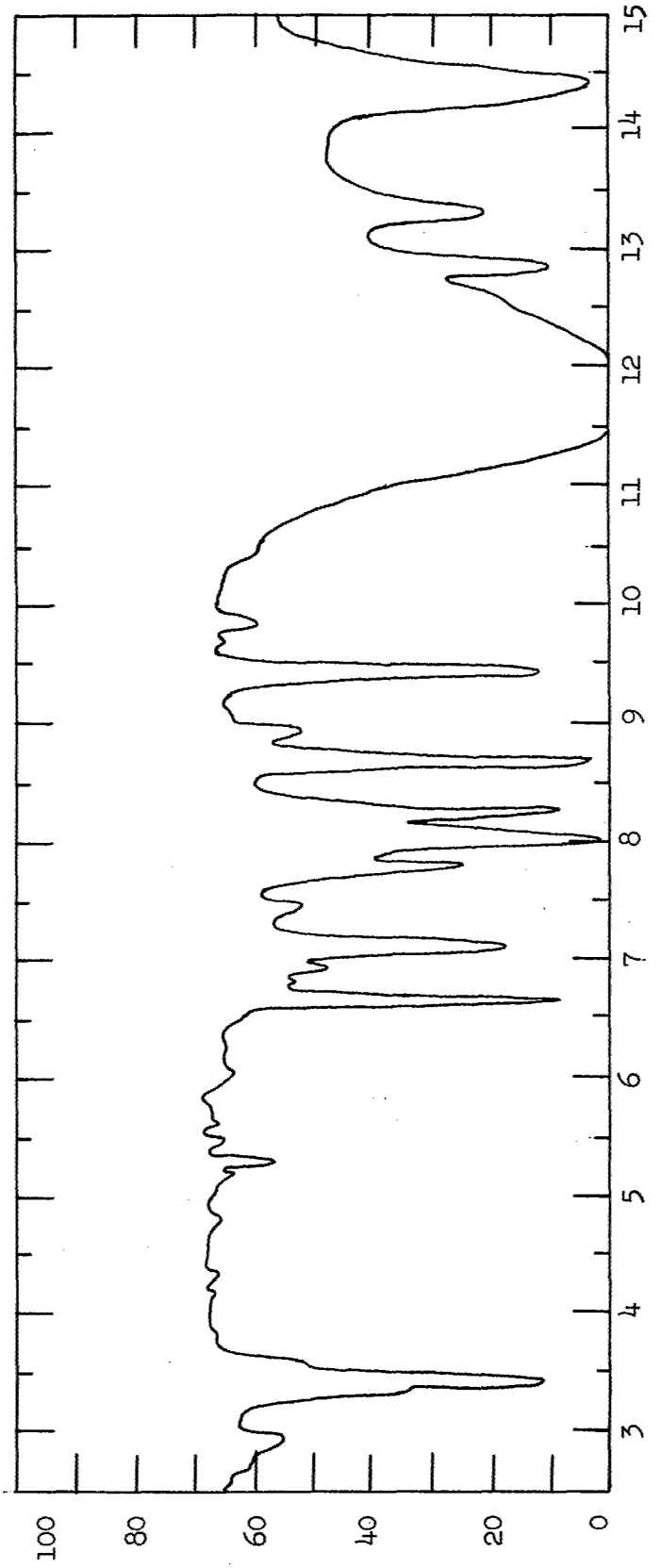


Fig. 3 Bis(trimethylsilyl)-p-xylylene

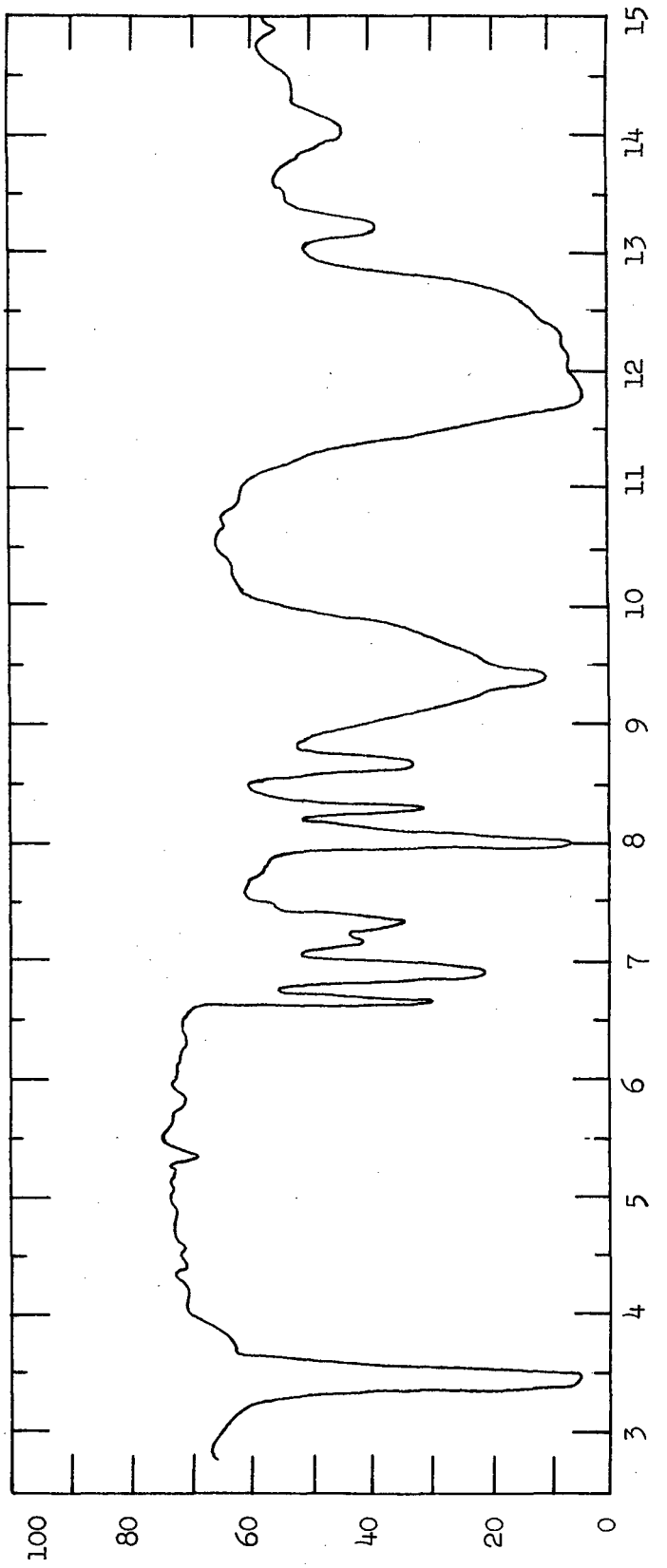


Fig. 4 Bis(dimethylchlorosilyl)-p-xylylene

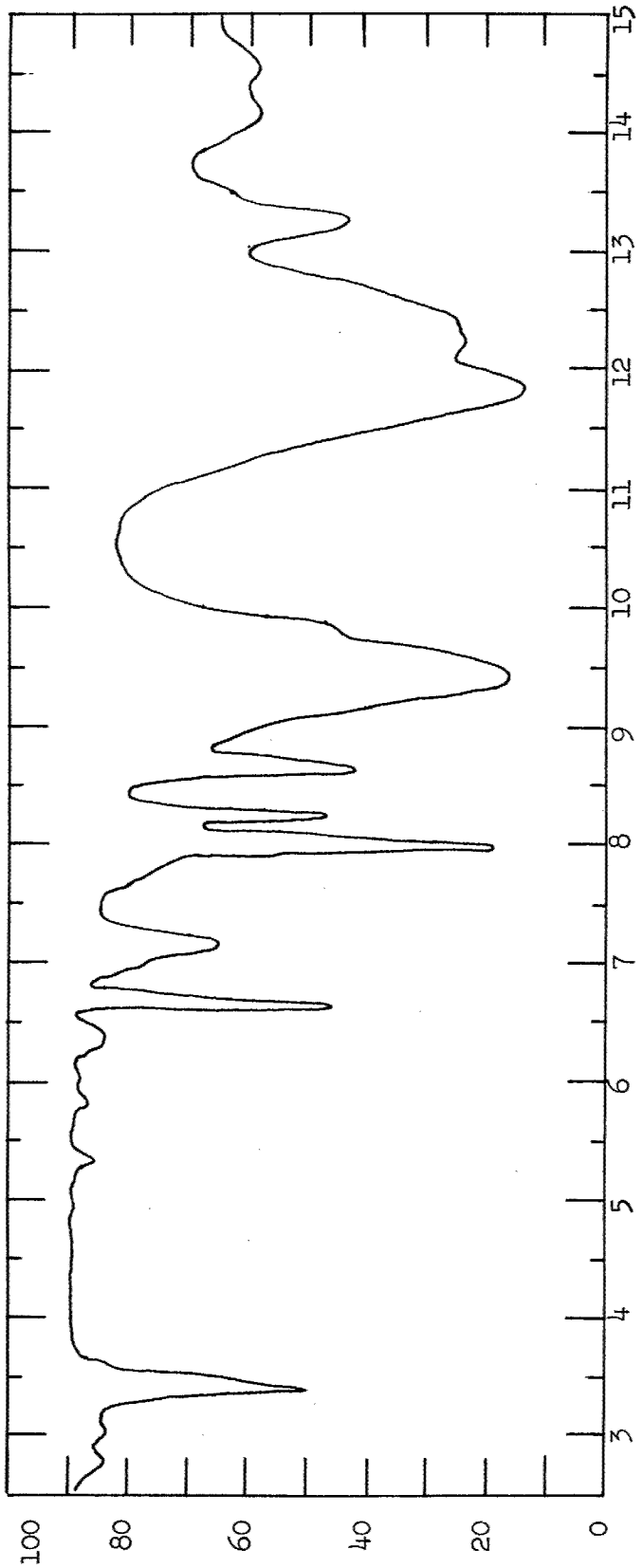


Fig. 5 Poly-p-xylylyltetramethylsiloxane

REFERENCES

(1) Gilman, H., and Goodman, J. J., J. Org. Chem., 22, 45 (1957).

(2) Mann, F. G., and Stewart, F. H. C., J. Chem. Soc., 2826, 2832 (1954).

(3) Hersh, J. M., U. S. Patent 2,615,033 (1952).

POLYMERS CONTAINING TIN

E. C. Evers

University of Pennsylvania

The following research is concerned with the synthesis of polymeric substances possessing the -Sn-X-Sn- skeleton where X may be an element, such as S, or a group such as $-CH_2-$. This study has been underway for only a few months and is largely exploratory; it has been concerned primarily with the development of synthetic methods and procedures. The preparation of compounds involving the -Sn-O- linkage is not being emphasized in view of the considerable attention being given to such bondings by other investigators. An example are those found in the stannosiloxanes.[1,2]

I. REAGENTS

The general preparative method for forming -Sn-X-Sn-linkages has been through the action of a bifunctional halide on an alkali metal salt of the type Na_2SnR_2, where R is an alkyl or aryl group.

The alkali metal tin salts are most conveniently prepared in liquid ammonia.[3] On adding sodium to a solution of R_2SnCl_2 in ammonia, the initial product is the insoluble polymerized free group R_2Sn, which is formed in accord with the equation

$$R_2SnCl_2 + 2Na = R_2Sn + 2NaCl$$

On further addition of metal the yellow precipitate dissolves, forming a deep red colored solution. In the case of the methyl compound, at least, the free group $(CH_3)_2Sn$ appears to dissolve on the addition of one atom of sodium per atom of tin. Evidently reaction takes place according to the equation[3]

$$2(CH_3)_2Sn + 2Na = NaSn(CH_3)_2Sn(CH_3)_2Na$$

---

(1) Andrianov, K. A., Ganina, T. N., and Khrustoleva, E. N., Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk., 798 (1956).
(2) Koenig, P. E., Astia Document No. AD142285, 50 (1958).
(3) Kraus, C. A., and Greer, W. N., J. Am. Chem. Soc., 47, 2568 (1925).

Further addition of sodium then results in the destruction of the Sn-Sn bond. A quantity of sodium equivalent to the tin then reacts according to the equation

$$NaSn(CH_3)_2Sn(CH_3)_2Na + 2Na = 2NaCl + 2Na_2Sn(CH_3)_2$$

Since the solutions are very opaque and colored deeply red it is virtually impossible to determine the end-point of the reaction visually; accordingly, measured quantities of the reactants are used and the solutions are stirred for approximately an hour to insure complete reaction. Identical procedures have been used to prepare $(n\text{-}B_4H_9)_2SnNa$, $(C_6H_5)_2SnNa$ and $(CH_3)_2SnNa_2$.

It may be of interest to note here that tin possesses a considerable capacity toward catenation when at least two of its sp^3 orbitals are occupied by alkyl groups. For example, the following reactions may be carried out in liquid ammonia,[3]

$$2NaSn(CH_3)_2Sn(CH_3)_2Na + Br_2Sn(CH_3)_2 =$$

$$NaSn(CH_3)_2Sn(CH_3)_2Sn(CH_3)_2Na + 2NaBr$$

$$Na_2\left[Sn(CH_3)_2\right]_3 + 2(CH_3)_3SnBr = (CH_3)_3Sn\left[(CH_3)_2Sn\right]_3Sn(CH_3)_3$$

The product, dodecamethylstannopentane, is an oily liquid soluble in ether and benzene. Its physical and chemical properties have not been investigated, other than to establish its molecular weight in benzene.

Although liquid ammonia is a very suitable solvent in which to prepare the alkali metal tin salts and to study their chemistry, it is not suitable when employing acid halides as reagents. Consequently this solvent limits the study to reactions involving metal halides which do not ammonolyze, as $(CH_3)_2SnBr_2$, or to hydrocarbon derivatives which undergo very slow reaction with ammonia, as CH_2Br_2.

In searching for aprotic solvents in which to dissolve and perhaps prepare disodium tin salts and to effect their reaction with acid halides, our attention turned to the polyethers, 1,2-dimethoxyethane (DME) and tetrahydrofurane (THF). Both solvents were found to give blue solutions of potassium metal, as does ammonia, attesting to their resistance toward reduction; but the solutions were extremely dilute. Sodium and lithium were not soluble. It did not prove practical, therefore, to prepare solutions of the tin salts directly in these solvents. Rather it was found more convenient to prepare the salts in liquid ammonia, than to add the polyether and evaporate the ammonia. The salt, $Na_2Sn(C_6H_5)_2$, was the most soluble, yielding deep red solutions in the polyethers at room temperature. It also appeared to yield the most stable solutions; in fact it was possible to obtain the salt in the dry state and to redissolve it without apparent decomposition. In contrast, the methyl derivative, $Na_2Sn(CH_3)_2$, underwent destructive degradation when prepared in the dry state.

In testing the suitability of a particular solvent the disodium salt was treated with methylene chloride, a reagent which proved to react satisfactorily and reproducibly in liquid ammonia, as described below. The appearance, yield and analysis of the resulting products were then compared with those obtained from liquid ammonia. DME with $Na_2Sn(C_6H_5)_2$ proved to be the best combination. Yields were lower and analyses were less satisfactory with THF or when $Na_2Sn(CH_3)_2$ was employed.

Unfortunately acid halides also attack the polyethers. However, reaction with solvent is often not rapid, while that with the sodium salts appears to proceed instantaneously. The relative rates of the two reactions therefore determines the usefulness of a particular solvent. DME seems more resistant to attack by acid halides than THF and the former has been employed in most of our recent studies.

II. THE STANNOETHYLENES

Polymeric stannoethylenes having the general formula R_2SnCH_2, where R is an alkyl or aryl group, may be prepared using either liquid ammonia or polyethers as solvent. The reaction is

$$R_2SnNa_2 + CH_2Cl_2 = R_2SnCH_2 + 2NaCl$$

Evaporation of the solvent after filtration leaves colorless to slightly yellow oils or glasses.

1. $(CH_3)_2SnCH_2$.- Dimethylstannoethylene was first prepared by Kraus and Greer[3]. We have repeated their synthesis and have verified their findings. When freshly prepared the product is obtained as an oily liquid which slowly solidifies on standing, suggesting further polymerization. The molecular weight of the freshly prepared material determined cryoscopically in benzene suggests a polymerization number of roughly six. Determinations have not been made on aged products. The substance undergoes slow hydrolysis on contact with water at room temperature with the evolution of methane. After two hours contact hydrolysis was approximately ten percent complete if reaction proceeds according to the equation

$$(CH_3)_2SnCH_2 + H_2O = (CH_3)_2SnO + CH_4$$

Heating for two hours at 300° under vacuum produced a black solid. Small quantities of both condensable and non-condensable gases were formed together with a small amount of crystalline solid which melted in the range 115-120°.

According to Kraus and Greer[3] the polymer is attacked by both anhydrous hydrogen chloride and bromine. The former produces $(CH_3)_3SnCl$ and $(CH_3)_2SnCl_2$. Bromine reacts fairly readily, but the expected products, CH_2Br_2 and $(CH_3)_2SnBr_2$ are not recovered; instead, CH_3Br is obtained together with other unidentified products. Although not well characterized, the chemical properties suggest we have the compound $(CH_3)_2SnCH_2$ in polymerized form. Typical analyses for Sn gave 72.20 and 72.55 percent Sn.

Calculated for $(CH_3)_2SnCH_2$, 72.93 percent Sn.

2. $(n\text{-}C_4H_9)_2SnCH_2$.-n-Dibutylstannoethylene, like the methyl compound, is obtained as a very viscous oil which gradually solidifies to a glassy solid on standing. A typical analysis gave 47.85 percent Sn; calculated, 48.00 percent Sn. The physical and chemical properties of the material have not been studied.

3. $(C_5H_5)_2SnCH_2$.-Diphenylstannoethylene was prepared in THF. Filtration, followed by removal of solvent in vacuo at 65° produced a clear resinous substance. Analysis gave 39.92 percent Sn; calculated, 41.40 percent Sn. This substance like the methyl and butyl compounds is soluble in benzene and ether.

4. $(C_6H_5)_2SnC(C_6H_5)_2$.-Tetraphenylstannoethylene was prepared in DME by treating $(C_6H_5)_2SnNa_2$ with $(C_6H_5)_2CCl_2$. The resulting product was a gummy solid from which it was extremely difficult to remove residual solvent in vacuo.

III. REACTIONS INVOLVING ACID HALIDES

Some progress has been made toward the synthesis of polymers employing $(C_6H_6)_2SnNa_2$ in combination with the acid halides $COCl_2$, $(CH_3)_2SiCl_2$ and SO_2Cl_2. These reactions appear to proceed best using DME as solvent.

1. $COCl_2$. - The product from the reaction of $COCl_2$ with $(C_6H_5)_2SnNa_2$, using either DME or THF as a solvent, is a bright yellow solid, which appears crystalline. The appearance of the product is not changed upon using an excess of $COCl_2$ or an amount equivalent to the disodium salt. It is sparingly soluble in ether and practically completely soluble in benzene. The product also contains some chlorine which appears to concentrate in the ether soluble fraction. It is interesting to note that the chlorine is no longer strongly acidic in that it is not readily removed by treatment with water, although this behavior may be due in part to the insolubility of the polymer in water. When a benzene solution of the substance is treated with water a small fraction of the chlorine is removed. A quantitative determination can only be made by fusion with sodium peroxide. A typical analysis follows: Sn, 39.5%; Cl, 2.07%. Calculated for $(C_6H_5)_2SnCO$; Sn, 39.6%.

The molecular weight of the product whose analysis is given above, determined cryoscopically in benzene, was 1268. This molecular weight would correspond approximately to a polymerization number of 4. If, however, a polymerization number is calculated on the basis that terminal groups are -SnCOCl, then the number would be roughly 12. These results suggest that a mixture of substances are present which conceivably might be separated by fractional extraction or precipitation. On the other hand it must be noted that molecular weights of the order of magnitude of 1200, determined cryoscopically, are suspect since small amounts of low

molecular weight impurity would render them unreliable. The substance melts at approximately 180° with some decomposition.

2. $(CH_3)_2SiCl_2$.- A bright yellow solid is obtained on treating $Na_2Sn(C_6H_5)_2$ with an excess of $(CH_3)_2SiCl_2$ in THF. The product is insoluble in ether, soluble in THF and slightly soluble in water. The aqueous solution gives an acid reaction and a positive test for chloride ion. The following analysis was obtained: found; mixed oxides, SnO_2 + SiO_2, 55.7%; Cl, 14.7%. Calculated for $(C_6H_5)_2Sn\left[Si(CH_3)_2Cl\right]_2$: mixed oxides, 58.9%; Cl, 15.4%. Although the analysis for chlorine and mixed oxides are each approximately 6% low, the results suggest that reaction with excess $(CH_3)_2SiCl_2$ proceeds essentially as follows

$$Na_2Sn(C_6H_5)_2 + 2(CH_3)_2SiCl_2 = (C_6H_5)_2Sn\left[(CH_3)_2SiCl\right]_2 + 2NaCl$$

When approximately stoichiometric quantities of dimethyldichlorosilane and the tin salt are combined in DME somewhat different results are obtained. The product is a yellow solid which appears physically similar to that obtained in the preceeding reaction, but the chlorine content is substantially lower. Values ranging from 2 to 5% have been obtained. The chlorine is not removed by hydrolysis on treatment with water but may be determined after fusion with sodium peroxide.

The product does not melt below 250° but commences to discolor at about 200° in a sealed tube in vacuo.

3. SO_2Cl_2.- When an excess of SO_2Cl_2 was added to a solution of $Na_2Sn(C_6H_5)_2$ in THF a chocolate colored precipitate was obtained. Filtration gave a clear solution. During evaporation of the solvent, the solution gradually acquired color and finally there was left a black viscous residue. This material contained only 19.7% Sn; calculated for $(C_6H_5)_2SnSO_2$, 35.3% Sn. Evidently there was considerable reaction between the product and solvent or, what is more likely, between the SO_2Cl_2 and solvent. THF was found to react vigorously with SO_2Cl_2; DME on the other hand does not react rapidly and this solvent will be employed in future experiments.

IV. INTERACTION OF $(CH_3)_2SnS$ AND SULFUR

Some effort has been made to prepare polymeric systems based on the -Sn-S- backbone. While our results here have not been encouraging, a brief summary of our results seems appropriate. Essentially we have endeavored to combine sulfur with dimethyltin sulfide under various conditions. When reaction does occur there is obtained mixtures of SnS_2 and SnS together with the volatile sulfides $(CH_3)_2S$ and $(CH_3)_2S_2$.

Dimethyltin disulfide may be prepared conveniently by treating an aqueous solution of dimethyltin dichloride with hydrogen sulfide. The product is a white solid, insoluble in water, which melts at 147-148°. The compound is trimeric $\left[(CH_3)_2SnS\right]_3$ in benzene solution as determined cryoscopically.

The sulfide is quite stable when heated in either vacuo or in air. A sample heated to 250° in vacuo showed no evidence of decomposition; the melting point after cooling was 147°. When heated in air to 275°, the melting point was lowered to 142°. Oxygen was not absorbed by the compound from air at one-half atmosphere pressure when heated to 250° in a sealed tube.

There is no evidence for reaction between sulfur and dimethyltin sulfide below a temperature of 225°. At 250° the addition of sulfur causes immediate formation of black, solid SnS. With larger proportions of sulfur SnS_2 is also produced in addition to volatile methyl sulfides.

SYNTHESIS AND EVALUATION OF SILOXANYLFERROCENES

by

R. L. Schaaf
P. T. Kan

Wyandotte Chemicals Corporation

SYNTHESIS AND EVALUATION OF SILOXANYLFERROCENES

R. L. Schaaf
P. T. Kan

Wyandotte Chemicals Corporation

Abstract.

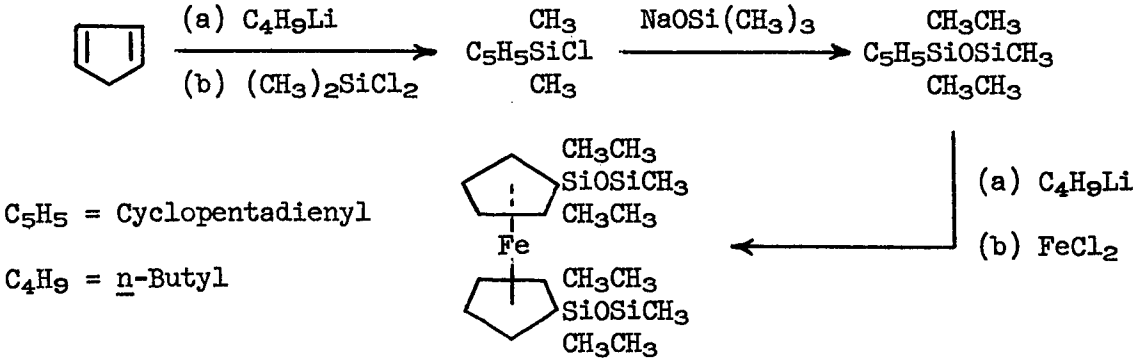
The objective of this work was the synthesis of materials suitable for use as high-temperature lubricants, hydraulic fluids and/or dielectric component potting materials. Nine candidate siloxanylferrocenes were prepared and the thermal stability, viscosity and fluid range determined. Effort was made, unsuccessfully, to prepare polymeric siloxanylferrocenes from difunctional silicon-substituted ferrocenes, from a bridged disiloxanylferrocene, and from bis(cyclopentadienyl)siloxanes. During this work 21 silicon-substituted cyclopentadienes and 22 silicon-substituted ferrocenes were synthesized.

Introduction.

The program at Wyandotte Chemicals Corporation, underway since March 1957, has as its objective the synthesis of thermally stable substituted ferrocenes for consideration as dielectric materials and as base stocks for Air Force extreme-temperature hydraulic fluids and lubricants. Inasmuch as ferrocene, or bis(cyclopentadienyl)iron (II), has been shown to be stable at temperatures up to 470°C (1), the possibility existed that appropriate substitution on ferrocene would furnish substances which would possess good thermal stability and by virtue of the substitution would have other desirable properties not present in ferrocene itself, in particular a fluid range of 0 to 1000°F. In view of the thermal stability of siloxane linkages in certain fluids, siloxane-substituted ferrocenes were logical candidates for study. No siloxanylferrocenes have been described in the literature, although considerable work has been reported concerning the chemistry of ferrocene and its derivatives (2, 3, 4).

General Approaches:

A major part of the work was devoted to the development of flexible routes to siloxanylferrocenes. The following reaction scheme for the synthesis of 1,1'-bis(pentamethyldisiloxanyl)-ferrocene, the first siloxanylferrocene prepared, is typical of reactions investigated during initial studies.



C_5H_5 = Cyclopentadienyl

C_4H_9 = n-Butyl

This first candidate material was too volatile (b.p. 360°C) for simple thermal tests at 366°C (690°F), but the second, 1,1'-bis(3-phenyltetramethyldisiloxanyl)-ferrocene, was found to possess good stability at 366°C under nitrogen, and was a liquid at 25°C. Investigation was then directed toward synthesis of compounds similar in structure to the phenyl derivative, first with the preparation of the corresponding 3-p-biphenylyl and 3-dichlorophenyl compounds. The analogous phenyltrisiloxane and phenyltetrasiloxane were then synthesized in order to determine the effect of increased chain length on thermal stability. Further modification of the side chains was accomplished by the synthesis of 1,1'-bis[1,1-dimethyl-3-phenyl-3,3-di(n-decyl)disiloxanyl]-ferrocene and 1,1'-bis(1,1-dimethyl-3,3,3-triphenyldisiloxanyl)-ferrocene. The effect of additional groups on the ferrocene nucleus was briefly examined through the synthesis of x,x'-dimethyl-1,1'-bis(3-phenyltetramethyldisiloxanyl)-ferrocene, prepared from methylcyclopentadiene.

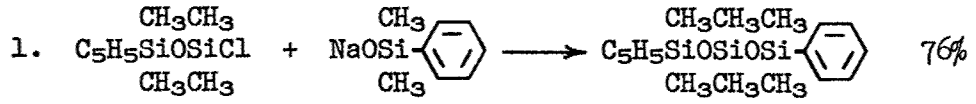
A major portion of the work concerned efforts to synthesize polymeric siloxanylferrocenes in which the ferrocene nucleus was part of the polymer backbone. Such polymers, if of low-molecular weight, were to be considered primarily for fluid applications, whereas solid high-molecular-weight products were to be tested as dielectric materials.

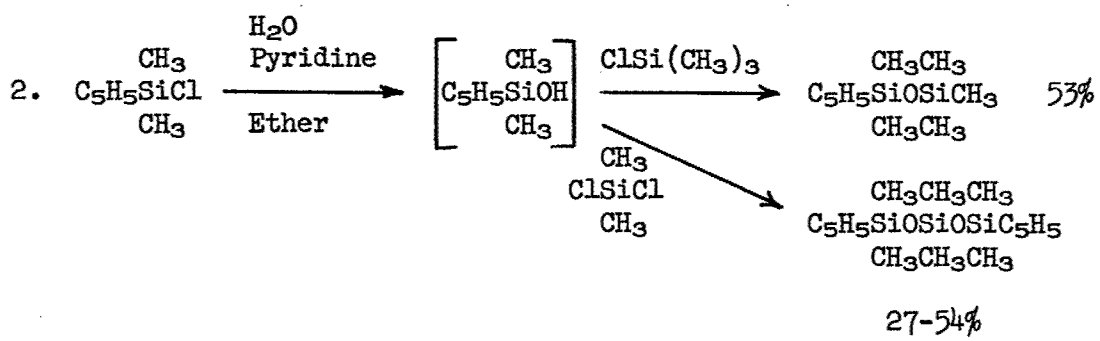
A synthetic approach which provided a route to a variety of silicon-substituted ferrocenes involved cleavage of the siloxanyl group in the bridged compound, 1,3-(1,1'-ferrocenylene)-tetramethyldisiloxane. For example, two candidate siloxanylferrocenes prepared via this cleavage were 1-phenyldimethylsilyl-1'-(3-phenyltetramethyldisiloxanyl)-ferrocene and 1,5-bis(1'-phenyldimethylsilyl-1-ferrocenyl)-hexamethyltrisiloxane.

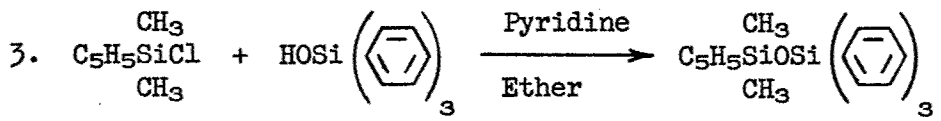
Cyclopentadienylsilanes and Cyclopentadienylsiloxanes.

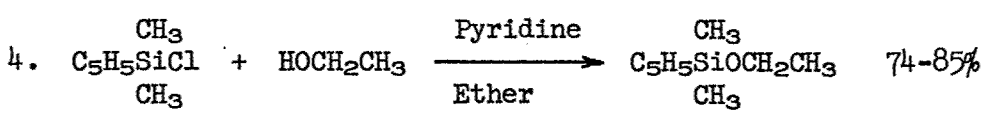
The reaction of cyclopentadienyllithium with dimethyldichlorosilane was found to give the desired cyclopentadienyldimethylchlorosilane in 53-60% yields. By reactions of this type were prepared 1-cyclopentadienyl-3-chlorotetramethyldisiloxane, 1-cyclopentadienyl-5-chlorohexamethyltrisiloxane, cyclopentadienylmethyldichlorosilane, and (methylcyclopentadienyl)dimethylchlorosilane.

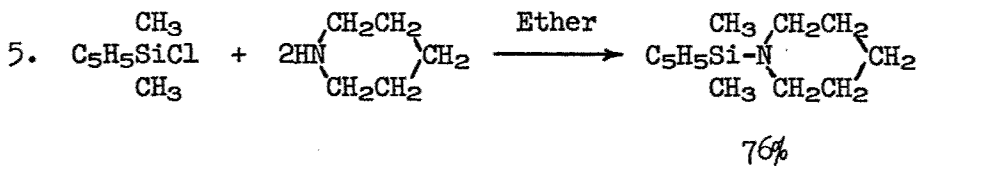
These cyclopentadienylchlorosilanes and cyclopentadienylchlorosiloxanes were converted to other cyclopentadienyl silicon compounds by a variety of methods, as shown by the following representative reaction schemes:











By using reactions of the types 1 to 5 there were prepared 1-(methylcyclopentadienyl)-3-phenyltetramethyldisiloxane, crude 1-cyclopentadienyl-3-(p-biphenylyl)-tetramethyldisiloxane, crude 1-cyclopentadienyl-1,1-dimethyl-3-phenyl-3,3-di(n-decyl)disiloxane, and the analytically pure compounds 5 to 17, Table I.

Pentachlorophenyldimethylchlorosilane was desired for the synthesis of 1-cyclopentadienyl-3-pentachlorophenyl-1,1,3,3-tetramethyldisiloxane. Addition of pentachlorophenylmagnesium chloride in tetrahydrofuran to a two-fold excess of dimethyldichlorosilane in toluene gave instead bis(pentachlorophenyl)dimethylsilane (44%).

TABLE I

CYCLOPENTADIENYLSILANES AND CYCLOPENTADIENYLSILOXANES

C_5H_5-R

No.	R	Yield	No.	R	Yield
1	CH_3 -SiCl CH_3	53-69%	10	$CH_3C_6H_5$ -SiOSiC_6H_5 $CH_3C_6H_5$	57%
2	CH_3CH_3 -SiOSiCl CH_3CH_3	36-57%	11	CH_3CH_3 -SiOSi-C_5H_5 CH_3CH_3	53%
3	$CH_3CH_3CH_3$ -SiOSiOSiCl $CH_3CH_3CH_3$	40%	12	$CH_3CH_3CH_3$ -SiOSiOSi-C_5H_5 $CH_3CH_3CH_3$	27-54%
4	CH_3 -SiCl Cl	41%	13	CH_3 -SiOCH_2CH_3 CH_3	74-85%
5	CH_3CH_3 -SiOSiCH_3 CH_3CH_3	53%	14	CH_3CH_3 -SiOSiOCH_2CH_3 CH_3CH_3	80%
6	CH_3CH_3 -SiOSiC_6H_5 CH_3CH_3	80%	15	$CH_3CH_3CH_3$ -SiOSiOSiOCH_2CH_3 $CH_3CH_3CH_3$	76%
7	CH_3CH_3 -SiOSi-$C_6H_3Cl_2$ CH_3CH_3	46%	16	OCH_2CH_3 -SiOCH_2CH_3 CH_3	86%
8	$CH_3CH_3CH_3$ -SiOSiOSi-C_6H_5 $CH_3CH_3CH_3$	76%	17	CH_3 CH_2CH_2 -Si-N CH_2 CH_3 CH_2CH_2	76%
9	$CH_3CH_3CH_3CH_3$ -SiOSiOSiOSi-C_6H_5 $CH_3CH_3CH_3CH_3$	61%			

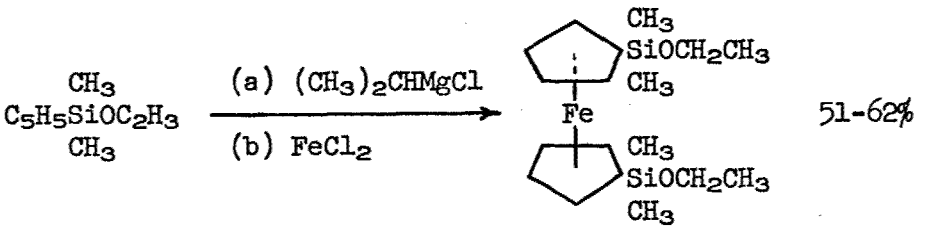
The substituted cyclopentadiene compounds mentioned in this section have not been reported in the literature, with the exception of cyclopentadienyldimethylchlorosilane and cyclopentadienylmethyldichlorosilane. These two chlorosilanes have been reported in a patent on cyclopentadienylsilanes (5) but the boiling point given for the former is much too high for the

monomer, and the boiling point of the diacetoxy derivative of the latter, used for identification, is also abnormally high.

Symmetrical Silicon-substituted Ferrocenes.

Cyclopentadienylsilanes and cyclopentadienylsiloxanes which did not contain an ethoxy, piperidino, or a second cyclopentadienyl group were converted to ferrocenes by treatment successively with n-butyllithium and ferrous chloride, reagents used effectively for the conversion of trimethylsilylcyclopentadiene to 1,1'-bis(trimethylsilyl)-ferrocene (6). By this method were synthesized x,x'-dimethyl-1,1'-bis(3-phenyltetramethyldisiloxanyl)-ferrocene and compounds 13 and 1 to 8, Table II.

The conversion of cyclopentadienyldimethylethoxysilane to the corresponding ferrocene posed a particular problem in that ethoxysilanes are known to react with alkyllithium and Grignard reagents to displace the ethoxy group (7). After attempting this conversion with varying degrees of success by employing n-butyllithium (under various conditions), as well as phenyllithium and ethylmagnesium bromide, it was found that treatment of the cyclopentadienyl compound successively with isopropylmagnesium chloride and ferrous chloride furnished the ferrocene, compound 9, Table II, in 51-62% yields.

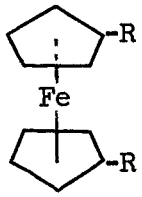


Compounds 11 and 12, Table II, were also prepared by this method. When applied to 1-cyclopentadienyl-5-ethoxyhexamethyltrisiloxane, however, no ferrocenyl products were obtained; on the other hand, with butyllithium and ferrous chloride, compound 10, Table II, was obtained analytically pure in 23% yield. The corresponding disiloxane, 1-cyclopentadienyl-3-ethoxytetramethyldisiloxane, with n-butyllithium and ferrous chloride gave the desired ferrocene in crude form, but from the elemental analyses, it appeared that some replacement of ethoxy groups by n-butyl groups had also taken place.

1,1'-Bis(dimethylchlorosilyl)-ferrocene was prepared in crude form in 62% yield by the action of hydrogen chloride on a solution of 1,1'-bis(dimethylpiperidinosilyl)-ferrocene in ether.

TABLE II

SYMMETRICAL SILICON-SUBSTITUTED FERROCENES



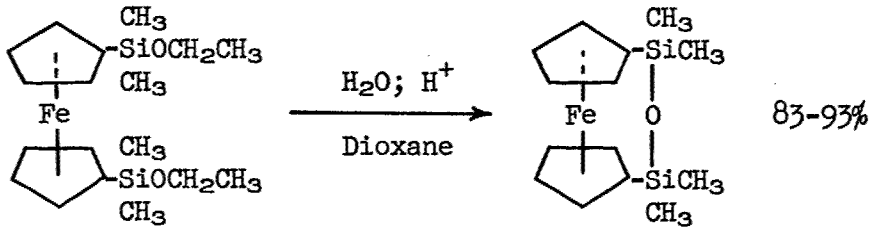
No.	R	Yield	No.	R	Yield
1	CH_3CH_3 $-SiOSiCH_3$ CH_3CH_3	41%	8	$CH_3C_{10}H_{21}$ $-SiOSi-C_6H_5$ $CH_3C_{10}H_{21}$	12%
2	CH_3CH_3 $-SiOSiC_6H_5$ CH_3CH_3	58%	9	CH_3 $-SiOCH_2CH_3$ CH_3	62%
3	CH_3CH_3 $-SiOSiC_{12}H_9$ (a) CH_3CH_3	23%	10	$CH_3CH_3CH_3$ $-SiOSiOSiOCH_2CH_3$ $CH_3CH_3CH_3$	23%
4	CH_3CH_3 $-SiOSiC_6H_3Cl_2$ CH_3CH_3	47%	11	OCH_2CH_3 $-SiOCH_2CH_3$ CH_3	57%
5	$CH_3CH_3CH_3$ $-SiOSiOSiC_6H_5$ $CH_3CH_3CH_3$	50%	12	CH_3 CH_2CH_2 $-Si-N$ CH_2 CH_3 CH_2CH_2	69%
6	$CH_3CH_3CH_3CH_3$ $-SiOSiOSiOSiC_6H_5$ $CH_3CH_3CH_3CH_3$	36%	13	CH_3 $-SiCH_2Cl$ CH_3	39%
7	$CH_3C_6H_5$ $-SiOSiC_6H_5$ $CH_3C_6H_5$	31%			

(a) p-Biphenylyl.

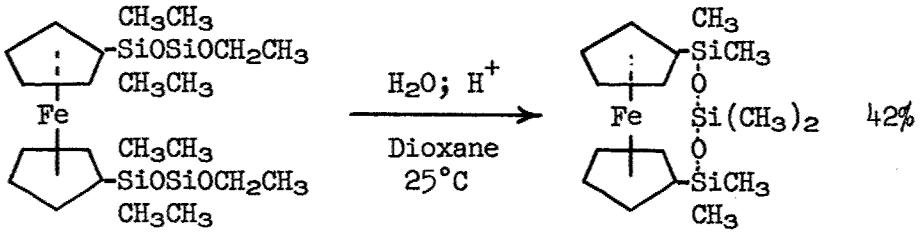
Approaches to Polymeric Siloxanylferrocenes.

1. When 1,1'-bis(dimethylethoxysilyl)-ferrocene in dioxane was treated with a two-fold excess of water and an acid catalyst at room temperature, the bridged compound, 1,3-(1,1'-ferrocenylene)-tetramethyldisiloxane was

formed in 83-93% yields. When ethanol was the solvent and the mixture was refluxed, the bridged compound was again formed (84% yield).



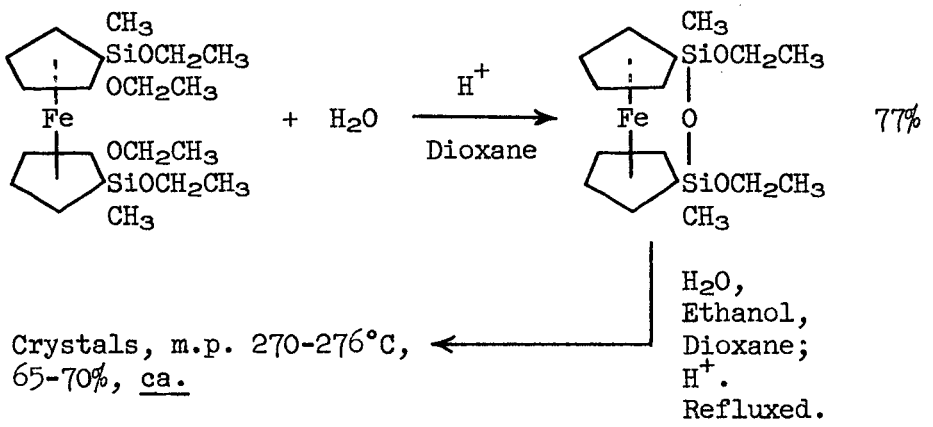
Hydrolysis of crude 1,1'-bis(3-ethoxytetramethyldisiloxanyl)-ferrocene in dioxane at 25°C yielded a bridged compound but not 1,7-(1,1'-ferrocenylene)-octamethyltetrasiloxane; instead, 1,5-(ferrocenylene)-hexamethyltrisiloxane was isolated in 29% yield, or 42% yield based on unrecovered starting material. The only other ferrocene isolated contained hydroxyl groups



according to infrared analysis, and it was suspected that this material may have formed during isolation via chromatography on alumina, inasmuch as chromatography of pure 1,1'-bis(dimethylethoxysilyl)-ferrocene on alumina also gave a hydroxy compound. On standing, the latter hydroxy compound went over to 1,3-(1,1'-ferrocenylene)-tetramethyldisiloxane. In a second experiment, hydrolysis was conducted in ethanol at 75°C, and in this case the bridged disiloxane, 1,3-(1,1'-ferrocenylene)-tetramethyldisiloxane, was isolated in crude form in 45% yield. Catalysis of this hydrolysis reaction by sodium bicarbonate in dioxane was ineffective.

Results from hydrolysis of the ethoxytrisiloxane, 1,1'-bis(5-ethoxyhexamethyltrisiloxanyl)-ferrocene, were inconclusive, but from the low yield of non-volatile material isolated it appeared that degradation of the siloxane chain may also have occurred here.

Hydrolysis of 1,1'-bis(methyldiethoxysilyl)-ferrocene with one mole of water in dioxane in the presence of acid catalyst at 25°C for 6 days gave 1,3-(1,1'-ferrocenylene)-1,3-dimethyl-1,3-diethoxydisiloxane in 77% yield. When the latter was refluxed in aqueous ethanol-dioxane with an acid catalyst, a hydroxyl-free solid, m.p. 270-276°C, was isolated in about 65-70% yield. Hydrolysis of these ethoxy compounds at 25°C in ethanol gave 10-20% yields of this solid, 25-35% yields of a hydroxy compound, and viscous mixtures of orange oil and solid, the infrared spectra of which showed strong hydroxyl bands.

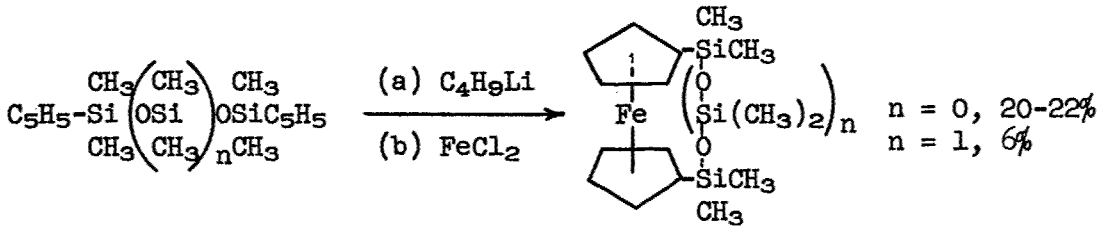


2. Silicones have been prepared by the loss of ethyl chloride from a mixture of a diethoxysilane and a dichlorosilane in the presence of a catalyst such as ferric chloride (7). In an exploratory experiment 1,1'-bis(dimethylethoxysilyl)-ferrocene was heated with two equivalents of a monochlorosilane, namely phenyldimethylchlorosilane, and a catalytic amount of ferric chloride. Ethyl chloride was evolved, but the major product was 1,3-(1,1'-ferrocenylene)-tetramethyldisiloxane (58%) and not 1,1'-bis(3-phenyltetramethyldisiloxanyl)-ferrocene.

3. Homopolymerization of cyclic siloxanes by the action of strong catalysts is a common method for the preparation of polymeric siloxanes (7). The bridged ferrocene, 1,3-(1,1'-ferrocenylene)-tetramethyldisiloxane, is a cyclic siloxane, but application of methods known to polymerize commercial siloxanes did not affect this compound.

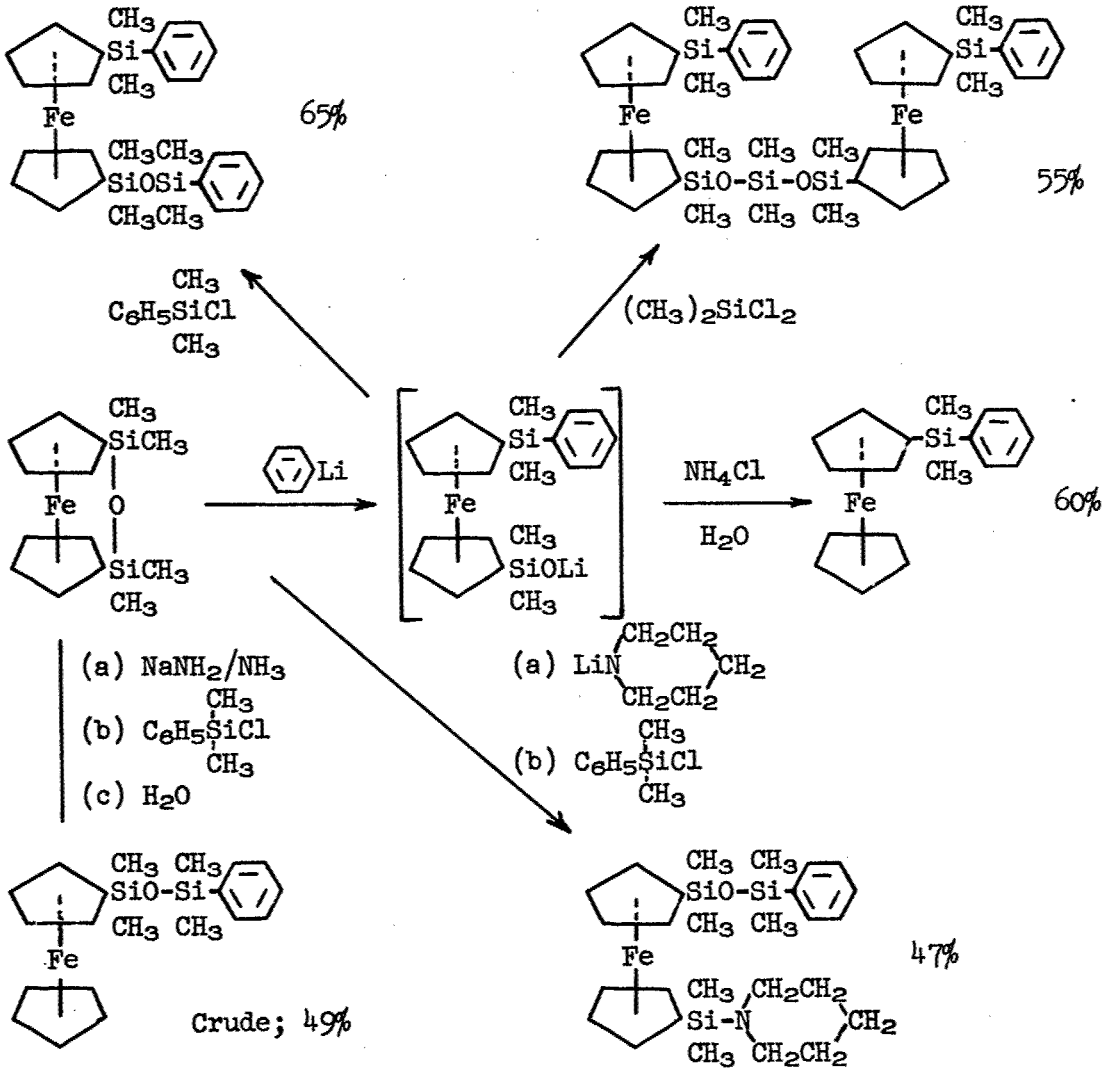
4. The conversion of bis(cyclopentadienyl)siloxanes to ferrocenes could conceivably give bridged compounds, polymers, and/or, in the event of incomplete reaction, 1,1'-bis(cyclopentadienylsiloxanyl)-ferrocenes. When the conversion was tried with 1,3-bis(cyclopentadienyl)-tetramethyldisiloxane, the only ferrocene isolated was the bridged compound (20-22%). In another experiment the same bis(cyclopentadienyl)-disiloxane was treated with one equivalent of butyllithium followed by half an equivalent of ferrous chloride in an effort to form 1,1'-bis(3-cyclopentadienyltetramethyldisiloxanyl)-ferrocene, and the product, without isolation, was then treated with butyllithium and ferrous chloride as before in order to afford polymers. In this instance the crude bridged compound, 1,3-(1,1'-ferrocenylene)-tetramethyldisiloxane, was isolated in 20% yield, and, in addition, significant amounts of lower-boiling liquid and higher-boiling residue were obtained; further investigation of the residue was unfruitful, and it is not known whether this was polymeric siloxanylferrocenes, poly(cyclopentadienylsiloxanes), or lithium silanolates formed by siloxane cleavage.

From the reaction of the trisiloxane, 1,5-bis(cyclopentadienyl)-hexamethyltrisiloxane, with two equivalents of butyllithium and one of ferrous chloride, the bridged compound 1,5-(1,1'-ferrocenylene)-hexamethyltrisiloxane was isolated in 6% yield; the major high-boiling fraction isolated (b.p. 220-240°C/0.07 mm.), was believed to be a mixture of a cyclic dimer and 1,1'-bis(5-cyclopentadienylhexamethyltrisiloxanyl)-ferrocene (20-25% yield).



Silicon-substituted Ferrocenes From 1,3-(1,1'-Ferrocenylene)-1,1,3,3-tetramethyldisiloxane.

Routes to a variety of candidate siloxanylferrocenes were developed via cleavage of the siloxane linkage in 1,3-(1,1'-ferrocenylene)-tetramethyldisiloxane. In the following reaction scheme, work completed in this area at the writing of this report is summarized. The reactions of certain siloxanes with phenyllithium (8) and with sodamide (9) have been described in literature.



Miscellaneous.

Attempts to prepare compounds containing $SiCH_2Si$ or $SiCH_2SiOSi$ linkages from 1,1'-bis(chloromethyldimethylsilyl)-ferrocene were unsuccessful. The chloromethyl compound reacted with magnesium in tetrahydrofuran, presumably to form the di-Grignard reagent, but failed to react with the lithium derivative of diphenylamine.

Work toward synthesis of aryloxycyclopentadienes for the preparation of aryloxyferrocenes was deferred when it was noted that the reaction of cyclopentenyl chloride with sodium phenolate had given o-cyclopentenylphenol rather than phenoxycyclopentene (10). In this reaction, the cyclopentenyl group migrated much more readily than an allyl group (Claisen rearrangement). It would be expected, therefore, that 1-phenoxycyclopentadiene, in which the ether is doubly activated, would be a particularly unstable compound.

1,5-Bis(p-biphenylyl)-hexamethyltrisiloxane was prepared in 28% yield by conversion of p-biphenylyldimethylchlorosilane to the corresponding silanol, and treatment of the silanol, without isolation, with half a mole of dimethyldichlorosilane. An effort was made to prepare 4,4'-bis(3-phenyltetramethyldisiloxanyl)-biphenyl by the reaction of 4,4'-bis(dimethylchlorosilyl)-biphenyl with sodium phenyldimethylsilanolate. However, attempts to repeat a known procedure for the preparation of the bis(chlorosilyl)biphenyl compound led to a very impure product, the melting point of which was considerably above the literature value (11).

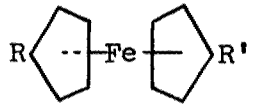
Physical Tests.

Thermal Stability. The thermal stability of candidate siloxanylferrocenes was determined by measuring the weight loss of samples during 10 hrs. at 366°C (690°F) under pure nitrogen, and noting changes in viscosity and infrared spectra. Results are shown in Table III. Although compound 9 showed the least weight loss of the ferrocenes tested, the large increase in viscosity during the test suggested some structural changes had taken place. In contrast to the disiloxane, 1, and the trisiloxane, 2, the corresponding tetrasiloxane, compound 3, lost appreciable weight during the test. Addition of a methyl group to each ring of the ferrocene nucleus of compound 1 resulted in decreased thermal stability (see compound 4, Table III).

Compounds 6 and 7, Table III, are similar in structure to compound 1 but certain of the methyl groups on the side chains of 1 have been replaced by phenyl groups (compound 6) or n-decyl groups (compound 7). These substitutions resulted in a decrease in thermal stability. The dichlorophenyl compound (5, Table III), decomposed vigorously at 366°C yielding ferrocene as one of the products.

TABLE III

THE THERMAL STABILITY AND FLUID RANGE OF CANDIDATE SILOXANYLFERROCENES



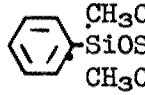
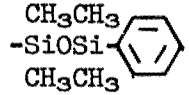
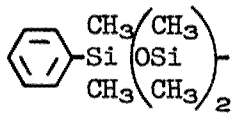
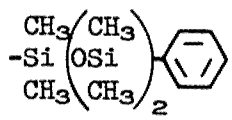
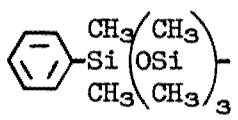
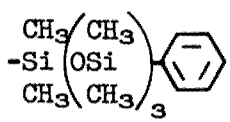
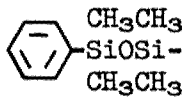
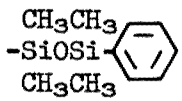
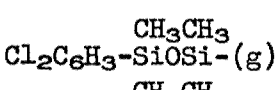
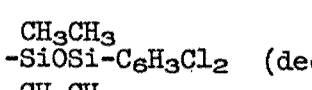
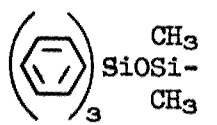
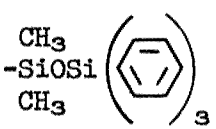
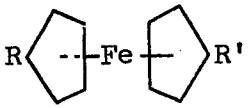
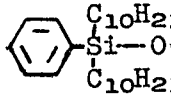
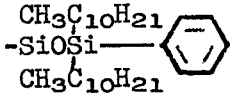
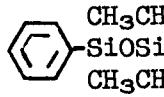
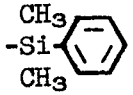
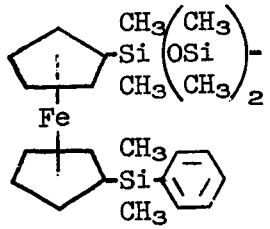
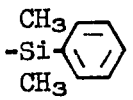
No.	R	R'	Micro B.p., °C	Pour Point, °C	Loss, %	Viscosity, cs., At 100°F Before	Viscosity, cs., At 100°F After	Comments
1			460	-31(a)	0.5 0.5(b)	21.7	23.5(c)	0.04% Deposit
2			463	-40	0.4	16.8	17.8	No deposit
3			471	-57	2.2 2.6(d)	17.2 17.2	(e) 16.8(c)	3.8% Deposit 0.05% Deposit
4	 (f)		446	-22	1.1	30.8	31.0(c)	0.1% Deposit
5	 (g)		(dec.)	5	11.0	335	(e)	Confined explosion
6			--	(h)	1.0	--	--	Residue, m.p. 125-140°C

TABLE III

THE THERMAL STABILITY AND FLUID RANGE OF CANDIDATE SILOXANYLFERROCENES



No.	R	R'	Micro B.p., °C	Pour Point, °C	Loss, %	Viscosity, cs., At 100°F Before	Viscosity, cs., At 100°F After	Comments
7			(dec.)	(i)	3.0 3.4(j)	79.8	104	No deposit
8			460	-23	0.5	32.4	46.3	No deposit
9			455	-12	0.2	185	300	No deposit

(a) M.P. 19-20°C. (b) After 18 hrs. (c) Determined on filtered residue. (d) Sample additionally purified by chromatography on alumina before tested. (e) Viscous. (f) In addition to R and R', there is a methyl group on each ring of the ferrocene nucleus. (g) $C_6H_3Cl_2$ = x,x-dichlorophenyl. (h) M.p. 148.5-150°C. (i) Insufficient sample. (j) After 12.5 hrs.

The infrared spectra of the residues from compounds 1, 2, 8, 9 and chromatographed 3, Table III, were the same as spectra of the pure samples, except that in each case weak bands appeared at 1204-1199 $cm.^{-1}$, 918-915 $cm.^{-1}$, and 910-907 $cm.^{-1}$. Similar bands in the spectrum of the residue from compound 6 were very weak and the remainder of the spectrum was essentially unchanged. The spectrum of the residue from compound 9 showed a new weak band at 951 $cm.^{-1}$. No changes in spectra were noted during tests on compounds 4, 7, and un-chromatographed 3.

At 425°C ± 5°C, the weight loss by compound 2, during 10 hrs. under nitrogen was 5.9%, with a viscosity change from 16.8 cs. to 21.1 cs. The distillate was a mixture of ferrocene crystals and a liquid, not a ferrocene, shown by infrared analysis to a phenylsiloxane having Si-H bonds; the residue contained a small amount of insoluble material. Compound 9 at 430°C ± 5°C for 10 hrs. under nitrogen lost 17% in weight, but despite this large loss, the residue showed only a small deposit and could be poured at 25°F; one decomposition product was ferrocene.

The weight loss by 1.0150 g. of 1,5-bis(4-biphenylyl)-1,1,3,3,5,5-hexamethyltrisiloxane during 10 hrs. at 366°C under pure nitrogen was 0.0002 g. (0.02%). The residue melted 79.5-82°C, compared with 81.5-83°C when pure.

Fluid Range. The micro boiling point and pour point of each of the candidate siloxanylferrocenes are given in Table III. Of the compounds which had shown good thermal stability at 366°C, compound 2, 1,1'-bis(5-phenylhexamethyltrisiloxanyl)-ferrocene, showed the widest liquid range (503°C or 905°F). The melting point of compound 1, Table III, was 50°C above the pour point. The other compounds in Table III, unless otherwise noted, did not crystallize during refrigeration for 1 to 10 months.

The micro boiling points given in Table III may actually be a "decomposition point", although there was no indication of this during the measurement itself. The "micro boiling point" of compounds 1 and 9 were very close, but when distilled for isolation, compound 1 boiled at 200-208°C/0.05 mm. and compound 9 at 283-285°C/0.03 mm. As stated above, compound 9 lost considerable weight during a thermal test at 430°C.

Viscosity at 400°F and 700°F. Values for the viscosity of compound 1, Table III, at 400°F and 700°F were 1.5 cs. and 0.50 cs., respectively, and for compound 2 were 1.55 cs. and 0.53 cs., respectively. These determinations, however, were not made in the complete absence of oxygen, and inasmuch as solids formed during measurements, the accuracy of these values is questionable.

Conclusions.

By proper choice of substituents, liquid siloxanylferrocenes can be prepared which have boiling points above 450°C and which show good thermal stability during 10 hrs. at 366°C under nitrogen. The best candidate material synthesized to date (March 1959) is 1,1'-bis(5-phenylhexamethyltrisiloxanyl)-ferrocene, liquid range -40°C to 463°C, a compound which at 366°C

under nitrogen lost 0.4% in weight during a 10 hr. period, and at 425°C lost 5.9% in weight in 10 hrs.

In the systems tested, trisiloxanes were as thermally stable as similar disiloxanes and passed thermal stability tests at 366°C. On the other hand, a tetrasiloxane showed some instability at 366°C. A candidate material prepared from methylcyclopentadiene offered no advantage over those prepared from cyclopentadiene.

High-molecular-weight polymeric siloxanylferrocenes apparently cannot be formed by a simple route due to a strong tendency toward formation of low-molecular-weight bridged compounds.

References.

1. Rosenblum, M., Ph.D. Thesis, Harvard University, August 1953.

2. Pauson, P. L., Quart. Rev. (London), 9, No. 4, 391-414 (1955).

3. Fischer, E. O., Angew. Chem., 475-82 (1955).

4. Rausch, M., M. Vogel, and H. Rosenberg, J. Chem. Ed., 34, 268 (1957).

5. Martin, R. W., U. S. 2,667,501, Jan. 26, 1954; (C.A. 49, 2493 (1955)).

6. Goldberg, S. I., D. W. Mayo, M. Vogel, H. Rosenberg and M. Rausch, in press.

7. Rochow, E. G., An Introduction to the Chemistry of Silicones, John Wiley & Sons, Inc., 2nd Edition, New York (1951).

8. Gilman, H., H. N. Benedict, and H. Hartzfeld, J. Org. Chem., 19, 419 (1954).

9. Hyde, J. F., O. K. Johannson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager and N. P. Roche, J. Am. Chem. Soc., 75, 5615 (1953).

10. Braun, J. V., and M. Kuhn, Ber., 60, 2551 (1927).

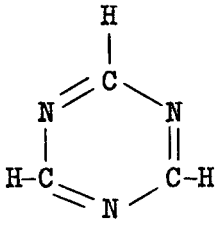
11. Baum, G., J. Org. Chem., 23, 480 (1958).

Organosilicon Derivatives of Inorganic "Benzenoid" Compounds

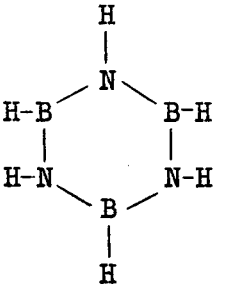
by Dietmar Seyferth

Department of Chemistry
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

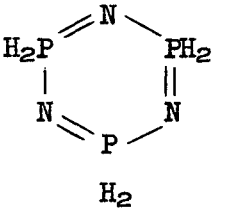
It was the purpose of this research to synthesize organometallic derivatives of inorganic "benzenoid" compounds in which the metal atom of the substituent group is linked directly to a ring atom. Parent compounds of the inorganic benzene analogs would be:



1,3,5-triazine

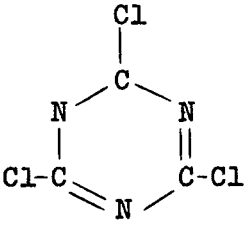


borazene



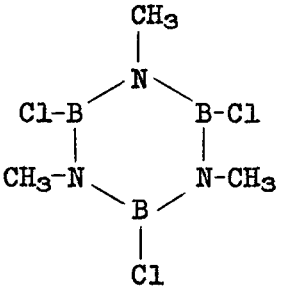
phosphinazine

Suitable derivatives of these compounds are either available commercially or are relatively easy to prepare:



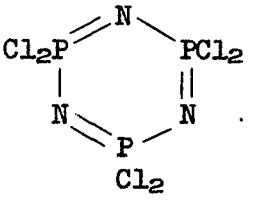
I

cyanuric chloride



II

B,B',B"-trichloro-N,N',N"-trimethylborazene



III

trimeric phosphonitrilic chloride

Grignard and Wurtz alkylations of I, II and III have been reported in the literature,[1] and it seemed possible that reagents such as triphenylsilyllithium[2] and triethyltinlithium[3] might react with I, II or III to produce compounds of the type desired.

This paper reports the results of experimental work carried out by Dr. H. P. Kögler in the period September 15, 1958 to March 1, 1959.

Attempts to effect silylation of cyanuric chloride with triphenylsilyllithium were not successful. Addition of ϕ_3SiLi in tetrahydrofuran to $(ClCN)_3$ gave a 44% yield of hexaphenyldisilane. A small amount of solid, apparently polymeric, which contained carbon, hydrogen, nitrogen and silicon, was also obtained. This solid did not melt or decompose below 380°. Attempts to effect Wurtz coupling between triphenylchlorosilane and $(ClCN)_3$ were equally unsuccessful.

The reaction of ϕ_3SiLi with phosphonitrilic chloride trimer also resulted in a 55% yield of hexaphenyldisilane, while attempted Wurtz coupling of triphenylchlorosilane with $(NPCl_2)_3$ gave small yields of tetraphenylsilane and the starting materials and/or their hydrolysis products. The reaction of ϕ_3SiCl and $(NPCl_2)_3$ in the presence of zinc metal also yielded small amounts of tetraphenylsilane. Solid products containing carbon, hydrogen, phosphorus, nitrogen, silicon and chlorine were obtained from the reaction of $(NPCl_2)_3$ with trimethylchlorosilane in the presence of magnesium metal in tetrahydrofuran solution. The elemental ratios of these solid water-insoluble products (C:H:P:N:Si:Cl = 1.3:5.2:1.02:1:1:0.5) did not permit even the assignment of a tentative structure.

---

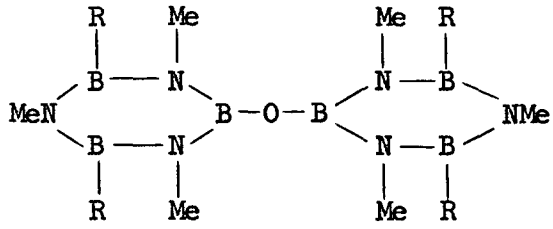
(1) I. (a) Hendrich and Hardtmann, U. S. P. 1,911,689 (1933); C. A., 27, 3952 (1933).
(b) Ostrogovich, Chem. Ztg., 36, 738 (1912).
(c) Klason, J. prakt. Chem. (2), 35, 82 (1887).
(d) Krafft, Ber., 22, 1759 (1889).
II. (a) Hohnstedt and Haworth, Abstr. of Papers, 132nd A. C. S. Meeting, September 1957.
(b) Ryschkewitsch, Harris and Sisler, J. Am. Chem. Soc., 80, 4515 (1958).
(c) Groszos and Stafiej, J. Am. Chem. Soc., 80, 1357 (1958).
III. (a) Rosset, Compt. rend., 180, 750 (1925); Bull Soc. Chim. [4], 37, 518 (1925).

(2) Gilman and Lichtenwalter, J. Am. Chem. Soc., 80, 608 (1958).

(3) Gilman and Rosenberg, J. Am. Chem. Soc., 75, 2507 (1953).

It may be noted that Burg and Caron[4] were not able to methylate $(NPCl_2)_3$ with methyllithium, and that Gilman and coworkers[5] in a broad study of the action of ϕ_3SiLi on inorganic halides were not able to isolate any compounds containing Si-other metal (including P) bonds. These negative results which came to our attention while our work was in progress, as well as our uniformly unsuccessful experiments, prompted us to shift our attention to substances in which the silicon atom is bound to a ring atom via a methylene group or an oxygen atom. This work, still in progress, has been carried out using B,B',B"-trichloro-N,N',N"-trimethylborazene as the cyclic starting material.

Trimethylsilylmethylmagnesium chloride reacted readily with $(ClBNMe)_3$ in refluxing diethyl ether solution, giving B,B',B"-tris-(trimethylsilylmethyl)-N,N',N"-trimethylborazene, m.p. 63-64°, in 44% yield. This compound was first obtained as a distillable oil which crystallized on standing. It proved to be quite stable thermally and resistant to hydrolysis. When a slight deficiency of Grignard reagent was inadvertently used, the trisubstituted borazene was accompanied by small yields of what appeared to be



(R = Me_3SiCH_2)

which was obtained as an oil which crystallized on standing (m.p. 95-96°). This compound also appeared to be quite stable thermally, and structures of this type seem worthy of further study.

Attempts to prepare B,B',B"-trivinyl-N,N',N"-trimethylborazene by reaction of vinylmagnesium chloride with $(ClBNMe)_3$ were not successful. Only polymeric materials were obtained.

---

(4) Burg and Caron, J. Am. Chem. Soc., 81, 836 (1959).

(5) Gilman, Gaj and Marrs, Progress Report, September 30, 1958, Contract No. AF 33(616)-3510.

SILOXANES

L. W. Breed
Midwest Research Institute

In any attempt to extend the useful range of silicone plastics to 1000°F., not only must an increase of thermal stability range be considered, but also the improvement in the rigidity of the polymers at the elevated temperatures.

Limitations in the thermal stability of silicones are not well defined because of the frequent confusion of thermal stability with thermal-oxidative stability. Purely thermal instability is reflected in rearrangement of siloxane linkages, and may occur above 350°C. By heating resins prepared from methyltrichlorosilane and dimethyldichlorosilane between 350°C and 600°C., Scott obtained two-thirds of the original hydrolysis products as volatile materials which were identified as various cyclic compounds[1]. Thermal-oxidative instability, however, may occur at lower temperatures and involves cleavage of carbon silicon bonds with the resultant loss of organic groups. Depending on the organic group attached to silicon, decomposition may become significant at temperatures above 250°C. Totally phenylated resins are considerably more stable and may show small weight losses at greater temperatures. Most considerations of thermal stability discussed in the literature involve the latter type of instability.

Greater limitations are imposed on the use of silicones because of their lack of strength at high temperatures. Up to half the flexural strength and flexural modulus of elasticity (rigidity) is lost when laminates prepared from these resins and glass fabric are heated from room temperature to 500°F. (260°C.). This type of instability, which reflects a loss in rigidity in the polymer system, is frequently referred to as a "thermoelastic" property.

Any thermal-oxidative changes should result in additional cross-linking in the polymer and yield more rigid materials: thermal decomposition should cause permanent changes in the polymer properties. However, the laminates exhibit a loss in strength at elevated temperature (500°F.) and regain their original strength on cooling to room temperature.

Stearic factors in silicone systems may be of importance in contributing to instability in any of several ways: the formation of cyclic structures with resultant loss of effective functionality of the monomers; the density or packing of polymer chains as it may contribute to heat susceptibility; and the failure of all silanol groups to condense.

The completeness of cure of silicone resins is important in determining their strength properties. Prolonged exposure of these polymers to elevated temperatures results in an increase in the rigidity or a recovery of part of the original strength. Also, a considerable part of the rigidity of silicone laminates at 500°F. is imparted to the material during a "post-curing" operation in which the material is heated at 500°F., for 2 or 3 days. The largest number of these silanol groups stearically capable of condensation may be removed during a postcure, but others may remain uncondensed. If this factor is important in contributing to silicone instability, it should be considered as a stearic problem in polymer formation rather than as a matter of intrinsic instability of the polymer itself.

The size and space relationships of substituents on the polymer chain may increase or decrease the probability of interchain bonding. Also, the density or packing of the chains may permit more or less group or molecular freedom, which would suggest an effect on heat susceptibility. Such a relationship was described in some recent work which claimed that more stable materials are formed from methyl monomers if four-membered rings were formed and from ethyl monomers if three-membered rings were formed[2].

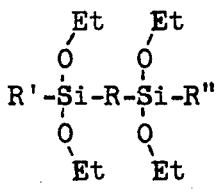
The change in properties of silicone resins at elevated temperatures is probably related, directly or indirectly with the possibility of polymerization through intermediate cyclic siloxanes rather than between linear siloxane chains. Low molecular weight cyclic materials have been isolated in the partial hydrolysis of methyltriethoxy- and ethyltriethoxysilane[3]. Polymerization through either type of intermediate would be expected to yield a different product. If the cyclic structures are the primary intermediate, the formation of numerous small rings would reduce the effective functionality of the monomer system.

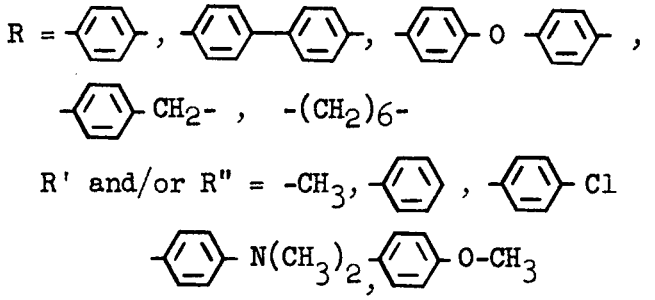
The problem in preparing silicon-containing resins stable above 500°F involves improving the rigidity of the polymer systems throughout the temperature range while maintaining or extending the thermal stability limit of the materials. The method selected for investigating this problem has been the preparation of silicon-containing resins which would be expected to have different structural characteristics than the materials prepared from conventional silane monomers.

Taking into consideration the factors already outlined, structural modifications were effected in the polymers through the use of selected monomers and selected methods of preparation of resins and polymers from silicon-containing monomers. In some cases the rigidity of the resultant systems has been examined by determining the ultimate flexural strength and flexural modulus of elasticity of glass fabric laminates prepared from the new resins.

Synthesis of Monomers

The main group of monomers chosen for examination in new polymer systems are described by the following formula:



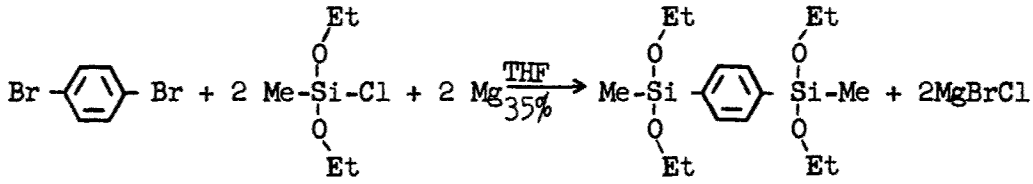


The initial research carried out in finding methods for preparing compounds with this type of chemical structures was discussed at the last Contractor's Conference in October, 1957. From the information presented at that time and on the basis of more recent work, a series of these compounds has been prepared, and some have been used in the preparation of new resins. The variety of methods required in these syntheses reflects some of the problems encountered in the preparation of monomers.

In order that the structure of each monomer would be known with some certainty, the method chosen for the preparation of these compounds utilized the condensation of an intermediate mono- or di-organometallic with the required silane. Because of the variation in the reactivity of the possible organic dihalides and their organometallic intermediates, as well as the condensing silane, the method of synthesis of most of the compounds had to be selected individually. It is obvious that if the method is not judiciously chosen, the reaction of a di-organometallic compound and a polyfunctional silane may lead to the quantitative production of highly polymeric materials. This possibility has even greater importance as the number of hydrolyzable groups attached to the silicon is increased, and is very important where trialkoxysilanes are used. There is only one example in the literature of a di-silane prepared by these methods which contains four functional groups, symmetrically placed.

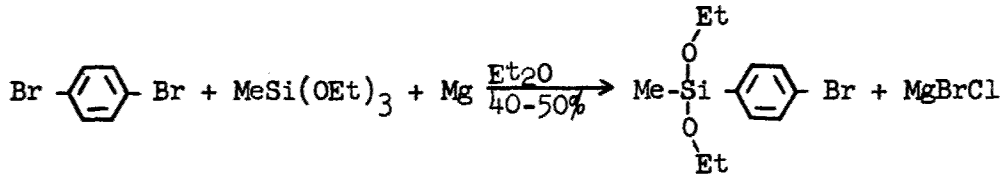
This material was obtained in a small yield as the secondary product of the described preparation[4].

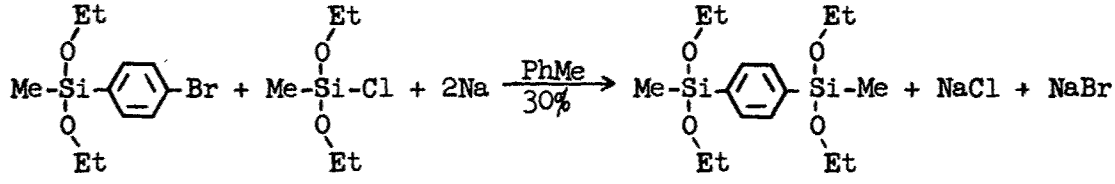
The most generally successful method found for the preparation of these monomers has been the condensation of the arylene-di-Grignard reagent formed in tetrahydrofuran with the appropriate mixed chloro-alkoxysilane. Typical of this method is the preparation of 1,4-bis-(methyldiethoxysilyl)benzene. When the reaction is carried out in such a way that the Grignard reagent condenses with the silane as soon as it is formed (concomitant addition of reactants), the product is obtained consistently in a 35 per cent yield in molar quantities.



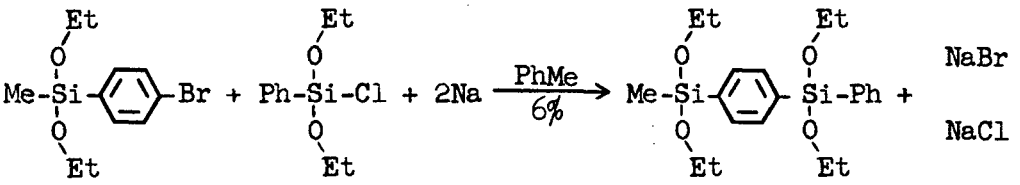
In most of the syntheses to be discussed, the use of the mixed chloro-alkoxysilane is essential, since materially lower yields are obtained if either the trichloro- or trialkoxysilanes are used.

This same compound was prepared by an alternate, two-step procedure. An intermediate, p-bromophenylmethyldiethoxysilane, could be prepared from p-dibromobenzene by condensation of the Grignard reagent formed in ether with methyltriethoxysilane according to the known procedures[5,6]. Conversion to the required monomer in a 30 per cent yield was achieved by condensation of the intermediate with methylchlorodiethoxy-silane in the presence of sodium in refluxing toluene.

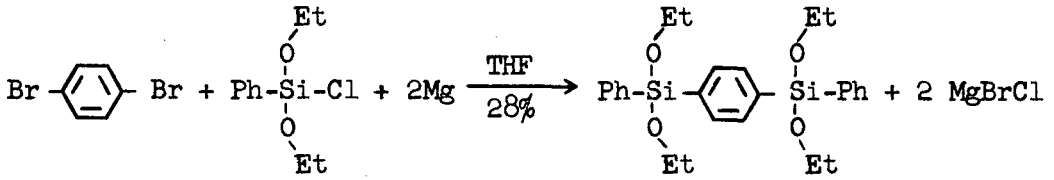




The unsymmetrical monomer, 1-methyldiethoxysilyl-4-phenyldiethoxysilylbenzene, was prepared by condensation of the same intermediate with phenylchlorodiethoxysilane, but in considerably reduced yield.



Although the phenylated silanes gave lower yields in the sodium condensation, no such limitation was effective in the syntheses making use of the di-Grignard reagents in tetrahydrofuran. By the latter procedure, 1,4-bis(phenyldiethoxysilyl)benzene was prepared in a 28 per cent yield from phenylchlorodiethoxysilane and p-dibromobenzene.

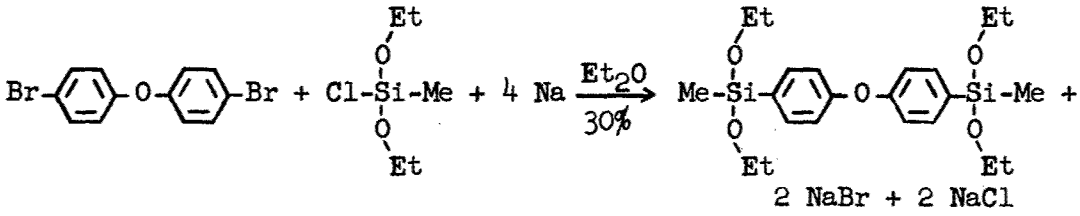


Carbon-functional derivatives of 1,4-bis(phenyldiethoxysilyl)benzene were also prepared in a similar manner. These monomers included the p-chlorophenyl, p-dimethylaminophenyl, and the p-anisyl derivatives, and they were obtained in yields of 27, 44, and 44 per cent, respectively. It may be noted that the substitution of the negative group para to silicon substantially improved the yields. Mixed chloro-alkoxysilanes were also used in these preparations, but in the case of the p-anisyl and p-N,N-dimethylamino derivatives it appeared that the trialkoxysilane would have functioned equally as well.

The required chloroalkoxysilanes in each case were prepared by the ethoxylation of the corresponding phenyltrichlorosilanes, and were obtained in good yields in all cases with the exception of the p-N,N-dimethylamino derivative. Here a lower yield was obtained primarily because of the failure to effect solubility of the p-N,N-dimethylaminophenyltrichlorosilane. Yields of 30 to 40 per cent were obtained in converting p-bromochlorobenzene, p-chloroanisole, and p-N,N-bromodimethylaniline to the corresponding trichlorosilanes. The Grignard synthesis was used in all three preparations with diethyl ether as the solvent in the first example and tetrahydrofuran as the solvent in the other two.

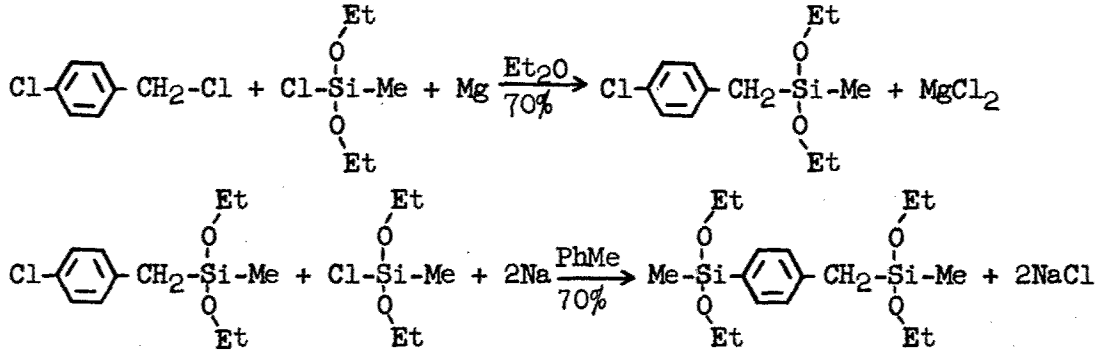
A suitable method of preparation was most difficult to find for the biphenyl derivatives. A number of variations of procedures involving sodium intermediates, lithium intermediates, and Grignard reagents were attempted with no success. Difficulties encountered in these syntheses apparently were related to two factors; the insolubility of 4,4'-dibromobiphenyl in non-polar solvents, and the lack of reactivity of the intermediate metallo-organic reagents toward chlorosilanes. It was found, however, that 4,4'-bis(methyldiethoxysilyl)biphenyl could be prepared through the di-Grignard reagent prepared into tetrahydrofuran, provided that the tetrahydrofuran was replaced with a higher boiling solvent (toluene) to effect condensation with the chlorosilanes. Even with this procedure, yields were not consistent, the highest being about 23 per cent, and substantial amounts of p-biphenylymethyldiethoxysilane were generally obtained along with the required product.

4,4'-Bis(methyldiethoxysilyl)phenylether was prepared by condensing 4,4'-dibromophenylether with methylchlorodiethoxysilane in the presence of sodium in ethyl ether. The yield was 30 per cent.



Substitution of phenylchlorodiethoxysilane for methylchlorodiethoxysilane. in this preparation failed to give 4,4'-bis(phenyldiethoxysilyl)phenylether. Instead, only a small yield of p-bromophenoxyphenylmethyldiethoxysilane was obtained.

α, p-Bis-(methyldiethoxysilyl)toluene was best obtained in a two-step procedure. α, p-Dichlorotoluene was converted to p-chlorobenzylmethyldiethoxysilane in a 70 per cent yield by treating the Grignard reagent of α,p-dichlorotoluene in ether with methylchlorodiethoxysilane. p-Chlorobenzylmethyldiethoxysilane gave α,p-bis(methyldiethoxysilyl)-toluene in a 70 per cent yield by a condensation with methylchlorodiethoxysilane in the presence of sodium in refluxing toluene.



Attempts to prepare this monomer through a one-step procedure involving the di-Grignard reagent in tetrahydrofuran were unsuccessful and gave only the bibenzyl derivatives.

The di-Grignard reagent of 1,6-dibromohexane, prepared by a known method[7], was coupled with methyltriethoxysilane to give 1,6-bis-(methyldiethoxysilyl)hexane in a yield of 43 per cent.

$$Br\text{-}(CH_2)_6\text{-}Br + 2\ Mg \xrightarrow{Et_2O} BrMg\text{-}(CH_2)_6\text{-}MgBr$$

$$BrMg\text{-}(CH_2)_6\text{-}MgBr + 2\ MeSi(OEt)_3 \xrightarrow[43\%]{} MeSi(OEt)_2\text{-}(CH_2)_6\text{-}Si(OEt)_2\text{-}Me + 2\ MgBrCl$$

In this case, the use of the mixed chloroalkoxysilane was unsatisfactory and failed to give the desired product. A different product was obtained by coupling this di-Grignard reagent with methylchlorodiethoxysilane, but it was not identified.

When mixed chloroalkoxysilanes were used in any of the preceding syntheses, these compounds were obtained by the partial alcoholysis of the corresponding chlorosilanes. The compounds obtained and used, however, did not represent pure materials. In the case of alkylsilanes, distillation of the reaction products through an Oldershaw column with 15 plates did not give a plateau at the boiling point of the expected product. Rather, a gradual rise in the head temperature was observed, and the product was collected over about a five degree range. Additional material was collected at a higher temperature. Examination of these fractions by vapor phase chromatography indicated that there were at least five components which could not be further resolved. The concentration of the component present in the largest amount (methylchlorodiethoxysilane) was estimated at about 79 mole per cent. From a knowledge of the properties of these type systems, the remainder of the components represented methyltriethoxysilane, methyldichloroethoxysilane, and various siloxanes. From similar distillations, fractions were selected which had slightly high neutralization equivalents for use in coupling with Grignard reagents. If the amount of methylethoxydichlorosilane in the system could be minimized, the other extraneous components would serve mainly as inert diluents in the syntheses.

The use of mixed alkylchloroalkoxysilanes with more than one chlorogroup in similar preparations was not satisfactory if the silane was prepared by alkoxylation. For example, in an attempt to prepare

dichlorodiethoxysilane, the distillation fraction having the closest neutralization equivalent contained only about 76 mole per cent of the required silane along with at least four other components that could be resolved. These other components, which included chlorotriethoxysilane and ethoxytrichlorosilane, would materially reduce the yield in any coupling reactions with metallo-organic reagents.

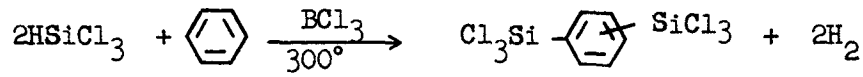
The alcoholysis of phenylchlorosilanes, however, gave well defined products in good yields. Elementary analysis, neutralization equivalents, and behavior on distillation indicated that the products of alcoholysis were not nearly so complex and that fairly well defined materials were obtained.

Silicone Resins

Correlation of changes in monomer structure with changes in polymer structure involves a somewhat obscure relationship. The monomers are separated by two chemical steps from the materials whose characteristics are of interest. Monomers must first be converted into resins which are soluble in organic solvents, usually by hydrolysis procedures, then cured into insoluble polymers by means of heating the resins in the presence of an appropriate catalyst. The chemistry of each of these transformations was of interest in regards to the manner in which they affected the structure and rigidity of the finished polymer. Each transformation involves a series of variables which may be important in determining the structure of the finished polymer. Some study of these variables was necessary so that the effects of changing monomer structure would not be obscured in the intermediate chemical transformation.

Considerable amounts of monomers are required for procedures conventionally used in determining rigidity of polymer systems--flexural strength and flexural modulus of elasticity. The preparation of the glass fabric laminates generally used in these procedures requires several hundred grams of a 50 per cent resin solution. For this reason the preliminary work in examining hydrolysis and curing parameters was carried out using conventional monomers, phenyltrichlorosilane and methyltrichlorosilane, and commercially available resins.

Also, in the initial examination of the composition and structural parameters of resin systems containing bis-silylarylenes, monomers which are somewhat more readily available were used. These materials which may be prepared by similar methods to those used in the production of phenylchlorosilanes could, in some cases, be purchased.



A modification of this synthesis which is also described in the literature was used for the preparation of a pentafunctional monomer, phenyldichlorosilyl-trichlorosilyl-benzene[8].

Throughout the evaluation phase of the program described in this report, the determination of the flexural properties of silicone-glass fabric laminates was used as a criterion of polymer rigidity. This method is disadvantageous in not being directly related to any fundamental chemical property of the system, requiring large amounts of materials, being time-consuming, and limited by a large number of variables which are difficult to control. However, the method has received a degree of standardization and relates to the end use of the materials. As will be pointed out, certain refinements were made in the procedure so that smaller amounts of materials were required. However, in the current work, a method is being sought by which resin samples may be screened more expeditiously.

1. Hydrolysis procedures - Conventional toluene-isopropyl alcohol-aqueous hydrochloric acid systems were not satisfactory for the conversion of experimental monomers to resins, since this procedure frequently led to gellation. On the basis of several hundred small scale experiments which studied hydrolysis temperature, types of solvents, monomer concentration, acid catalyst concentration, and the amount and kind of alcohol used in the hydrolysis, a suitable procedure was selected. This method, which essentially involved the addition of sufficient ethyleneglycol diethylether to the hydrolysis system to bring the solvents into a single phase, gave resins from commercially available silanes that were satisfactory in the preparation of glass fabric laminates. Laminates prepared from these control resins had essentially the same strength as those prepared from commercial resins. Although very dilute hydrolysis could probably have been used, limitations on a practical basis made the latter procedure undesirable.

Not all the monomers which were prepared have yet been evaluated in resin systems. Following the new procedure resins were prepared from the following new monomers: 1,4-bis(methyldiethoxysilyl)benzene, 4,4'-bis-(methyldiethoxysilyl)phenylether, α,p-bis(methyldiethoxysilyl)toluene, and 1,6-bis(methyldiethoxysilyl)hexane. Also a variety of resins were prepared based on mixtures of phenyldichlorosilyl-trichlorosilyl-benzene with phenyl- and/or methyltrichlorosilane, as well as other compositions

which contain similar types of monomers. In some cases it was necessary to remove solvents from the resin solution under reduced pressure to avoid gellation. Of the monomers hydrolyzed, only 4,4'-bis(methyldiethoxysilyl)biphenyl failed to yield a soluble resin.

The study of the hydrolysis procedure as it relates to the structure of finished polymers was limited to one set of experiments. It is known that equilibration of cyclic polysiloxanes with basic catalysts isomerizes these materials to structures which are primarily linear. This suggests that if a silicone resin is treated with a suitable catalyst, structural changes may be effected which minimize cyclic siloxane formation in the material.

A series of laminates were prepared from a series of silicone laminating resins which had been equilibrated with dilute solutions of various catalysts; sodium carbonate, sodium bicarbonate, acetic acid, and hydrochloric acid. The flexural strength of each laminate was determined and the results analyzed by the methods of statistical analysis. Although the laminate strength increased with increased basicity of the catalyst, these differences were not statistically significant.

2. Lamination (curing) parameters - A somewhat more thorough study was made of the curing variables in the lamination procedure for silicone resins as it relates to the formation of more rigid polymers in silicone-glass fabric laminates. The details of this series of experiments are described in a recent publication[2]. In this study 128 laminates were prepared from a commercially available silicone laminating resin. Several levels of each of the parameters important in the fabrication of silicone-glass fabric laminates were selected, and an experiment was designed which was a 1/32 replicate of a $2^9 \times 2^4$ factorial. Among the variables studied were precure time and temperature, laminating time, temperature and pressure, and postcure time and temperature, as well as the amount of resin picked up by the fabric during impregnation and the number of plies in the laminate. All laminates were tested for ultimate flexural strength at room temperature, as well as at 500°F. after 1/2 hour at the latter temperature, and the results were analyzed by statistical methods.

Examination of the significant main effects and significant interactions between the variables indicated the variables which primarily determined the over-all strength of the laminate were those that were concerned with the completeness of cure. The highest level of laminating

temperature, post-cure temperature, and laminating time always gave the strongest laminates, both at room temperature and at elevated temperatures. Making a generalization about the factors associated with the retention of a greater part of rigidity when laminates are heated to an elevated temperature is somewhat more complicated, but strength retention did seem to depend on the factors which allow greater resin flow and a more even cure across the thickness of the laminate during the curing operation.

Although significant differences in strength were found between laminates having different numbers of plies, no significant interactions were found between this and the other variables. Therefore, for subsequent tests, thinner laminates were prepared, usually only 4 x 4 in. sq., with the consequent economy of considerable experimental resin.

Also, in laminate preparation from experimental resins, only those variables found important in these experiments were examined to optimize the properties of the polymers. The general significance of the results of these experiments was to emphasize the importance of bringing the polymerization reactions as near to completion as possible.

3. Disilylarylene polymers - In the case of resins prepared entirely from the experimental monomers (see above), the changes in structure of the polymers obtained by hydrolysis followed by conventional curing processes were too radical in most cases to give satisfactory materials. Those materials prepared from 1,4-bis(methyldiethoxysilyl)benzene and α,p-bis(methyldiethoxysilyl)toluene were too brittle; those from 1,6-(methyldiethoxysilyl)hexane, which can cyclize intramolecularly, too soft. The only resin of this type which gave a satisfactory material was prepared from 4,4'-bis(methyldiethoxysilyl)phenylether, and the results of tests performed on laminates prepared from this resin are detailed in Table I.

The samples for these tests were prepared from 6-ply laminates (ca. 1/16 in. thick) which would be expected to have a greater flexural strength than 12-ply, 1/8-in. laminates. Therefore, for purposes of comparison, the results of similar tests of 6-ply laminates prepared from a commercial laminating resin are reported.

It may be noted in Table I that the proportion of the strength retained when the laminate from the experimental resin was heated to an elevated temperature was greater, and that small changes in strength were noted when the samples were heated at higher temperatures for longer times.

Because the preparation of resins entirely from experimental monomers produced composite materials in which the polymer structure was so radically changed that the materials could not be evaluated by the usual procedures, other compositions were prepared from mixtures of the experimental monomers with methyl and/or phenyltrichlorosilane as diluents. In mixed systems such as these, a large number of variables can be of importance. Several of these variables were examined, and the results of three of these investigations are shown in Figs. 1,2, and 3. In these experiments the phenyldichlorosilyl-trichlorosilyl-benzene was used as the experimental monomer because of the large number of individual laminates that had to be prepared.

The first variable--functionality--was examined in the following manner: Phenyldichlorosilyl-trichlorosilyl-benzene was treated with various quantities of methylmagnesium bromide to give a monomer having any desired functionality. Monomers with various functionalities were used to prepare resins in which 80 mole per cent of the composition was derived from phenyltrichlorosilane. Fig. 1 demonstrates that an optimum value for the average functionality was close to 4.0.

Also, a series of resins were prepared to find the best amount of bis-silylarylene to be included in experimental resins. In this group phenyldichlorosilyl-trichlorosilyl-benzene was reduced to an average functionality of 4.0 with methylmagnesium bromide, then used to prepare resins containing various mole percentages of phenyltrichlorosilane. The results of this experiment are illustrated in Fig. 2. The strength of the laminates at both room temperature and 500°F. increased rapidly as the mole percentage of phenyltrichlorosilane approached 90. A maximum value would be reached between 90 and 100 per cent, since resins prepared entirely from phenyltrichlorosilane did not have good strength properties.

In a third group of experiments, mixtures of phenyl- and methyltrichlorosilane in resin compositions similar to those in the previous group were investigated. The results are shown in Fig. 3 and illustrate that there is no particular advantage in including any methyltrichlorosilane in the composition. Although the 500°F. strength was essentially unchanged, the room temperature strength decreased with increasing concentrations of methyltrichlorosilane.

The results of testing laminates prepared from resins in which the optimum levels of these three variables are approximated are shown in Table II. Again results from laminates similarly prepared from commercial resins are shown for purposes of comparison. The experimental resin in this case was prepared from a monomer mixture containing 90 mole per

cent phenyltrichlorosilane and phenyldichlorosilyl-trichlorosilyl-benzene reduced to an average functionality of 4 with methylmagnesium bromide. Although the results of determining the flexural modulus of elasticity are not shown, the 6-ply laminates show a sharp increase in flexural modulus at 800°F. The embrittlement at this temperature reflects a chemical instability, but this limitation is not effective in the thicker laminates. At 500°F. the flexural moduli of the commercial materials are about 1.5 to 1.8 x 10^6, while the modulus of the experimental material is 25 to 50 per cent greater at these temperatures.

Conclusions

Monomer systems which would be expected to impart different structural characteristics to silicone polymers have been investigated. Specifically, alkylene and arylene disilane monomers have been synthesized and used in formulating resin compositions. This type of monomer may be prepared by the procedures described in this paper and obtained in a chemically pure form in adequate yields for the preparation of experimental materials. Improvement in polymer rigidity has been observed in silicones containing these monomers, but there are severe limitations on composition and structural variables when these monomers are incorporated into new resins by conventional hydrolysis procedures. The conditions used in the preparation of resins and curing them into thermosetting polymers appear important in determining the rigidity of the final polymer system. Methods of establishing polymer structure other than the hydrolysis of silane monomers are currently being examined, in the attempt to prepare thermally stable silicon-containing resins. A convenient method of evaluating polymer properties other than the preparation laminates is also needed.

TABLE I

Test Temp. (°F)	Aging Time (hr.)	4-Bis(methyldiethoxy-silyl)phenylether FS	Commercial Silicone Laminating Resin FS
Room temp.		28,600	42,800
	1/2	16,200	16,600
500	100	16,100	13,200
	200	14,000	14,700
	1/2	15,800	13,000
575	100	15,600	15,500
	200	15,500	14,400
	1/2	14,000	9,900
650	100	15,000	11,700
	200	13,600	12,100

TABLE II

Test Temp. (°F)	6-Ply		12-Ply	
	Experimental Resin	Commercial Resin	Experimental Resin	Commercial Resin
Room temp.	39,300	38,900	25,800	32,400
500	22,900	17,000	16,000	13,800
575	19,200	13,700	16,100	11,700
650	21,400	12,200	16,300	9,900
725	19,500	14,700	15,100	10,600
800	18,000	--	14,200	10,800

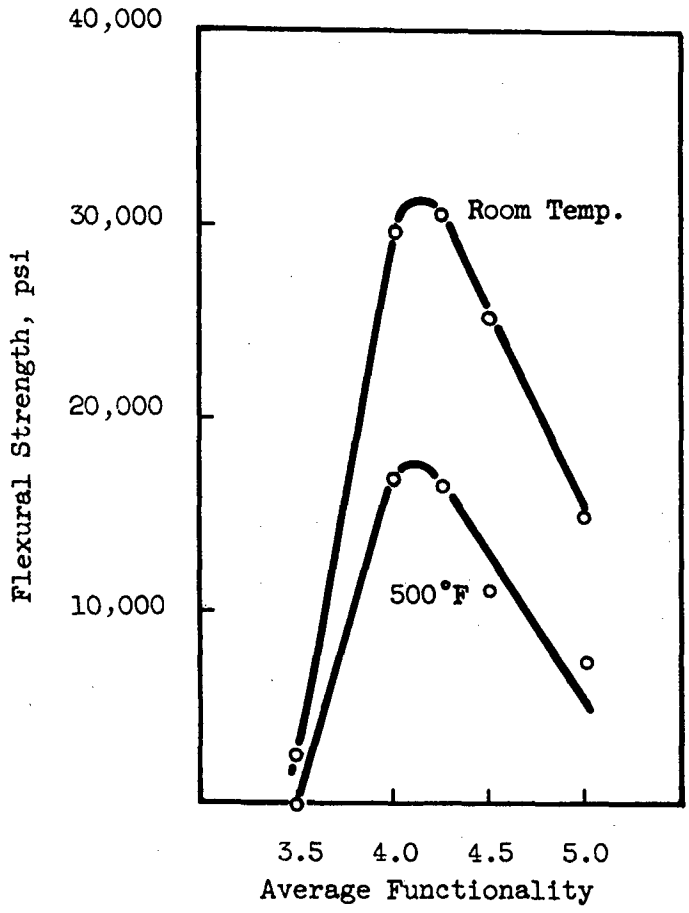


Fig. 1 - Effect of Average Monomer Functionality on Strength of Experimental Resins

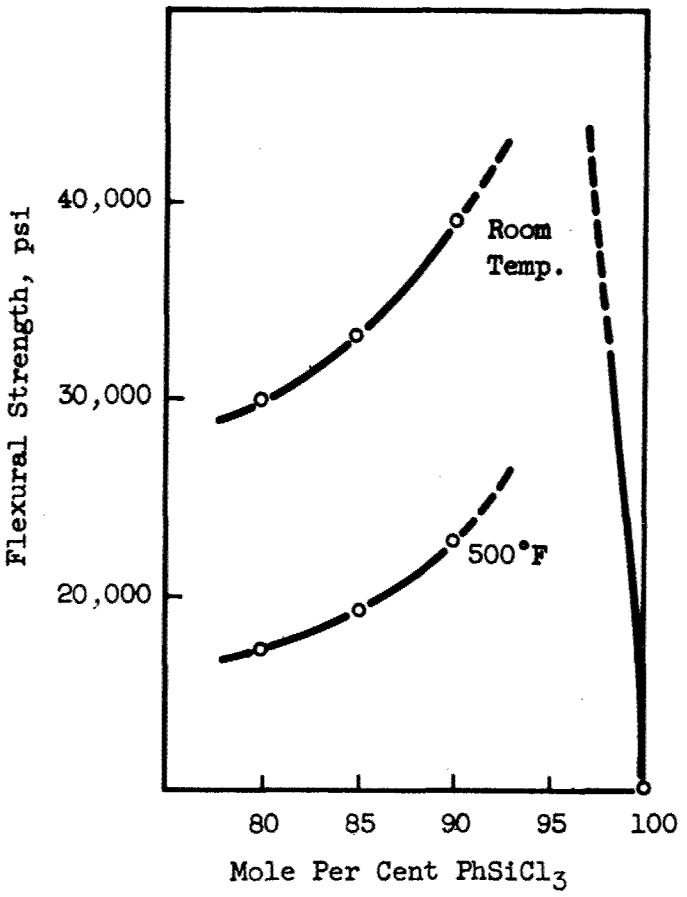


Fig. 2 - Effect of Increasing the Concentration of $PhSiCl_3$ on the Strength of Experimental Compositions

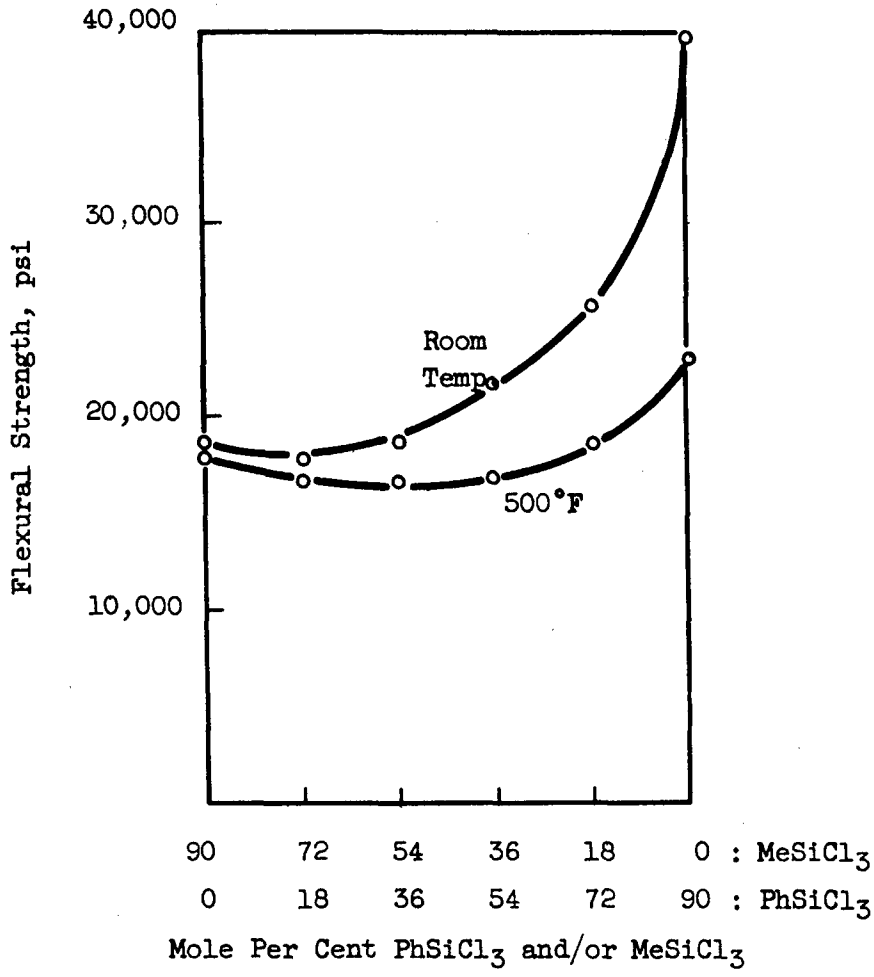


Fig. 3 - Effect of Various Concentration of $MeSiCl_3$ and $PhSiCl_3$ in Experimental Compositions on Laminate Strength

Bibliography

1/ Scott, D.W., J. Am. Chem. Soc., 68, 356-8 (1946).

2/ Sokolov, N.N., Zhur. Obshchei Khim., 28, 2578-82 (1958) C.A. 53-3037b.

3/ Sprung, M. M., and Grunther, F.O., J. Am. Chem. Soc., 77, 3990-3996; 77, 3996-4002 (1955).

4/ Gainer, Gordon C., U.S. Patent 2,709 692, May 31, 1955.

5/ Burkhard, C.A., J. Am. Chem. Soc., 68, 2103 (1946).

6/ Gainer, G.C., U.S. Patent 2,709,692, May 31, 1955

7/ Kreuchunas, A., J. Am. Chem. Soc., 75, 3339-44 (1953).

8/ Clark, H.A., U.S. Patent 2,557,782, June 19, 1951.

9/ Breed, L.W., Christie, H., Bolze, L. and Baiocchi, F., SPE Journal, 15, 220-224 (1959).

THE PREPARATION OF CERTAIN HETEROCYCLIC POLYMERS BY CYCLIC POLYMERIZATION

George B. Butler
Department of Chemistry
University of Florida
Gainesville, Florida

ABSTRACT

A number of monomers containing silicon and phosphorus have been prepared which are functionally capable of undergoing polymerization by an alternating intramolecular-intermolecular mechanism to produce soluble, linear polymers. Monomers prepared include the following: diallyldimethylsilane, diallyldiphenylsilane, dimethallyldimethylsilane, diallylphenylphosphine, diallylphenylmethylphosphonium bromide and iodide, and diallylphenylphosphine oxide. The first three and the latter three monomers undergo free radical catalyzed polymerization to produce soluble polymers. The first two monomers produce soluble polymers by use of Ziegler catalysts. The polymer of diallyldiphenylsilane appears to be stable to temperatures in the range of 330°C. The other polymers show varying degrees of high temperature stability.

I. INTRODUCTION

The purpose of this research program is to investigate the possibility of producing new and useful heterocyclic polymers containing silicon, phosphorus, oxygen, sulfur, selenium, germanium, arsenic, tin, lead or zinc through use of monomers functionally capable of polymerization by an alternating intramolecular-intermolecular chain propagation. The synthesis of suitable monomers for polymerization studies is also a purpose of this research program.

II. HISTORY AND BACKGROUND INFORMATION

A study of polymerization of unsaturated quaternary ammonium salts begun in this laboratory several years ago [1] resulted in a rather unexpected observation. All compounds containing two allyl type double bonds, which based on previous concepts of olefin polymerization, would be expected to produce cross-linked polymers, resulted in the formation of linear water-soluble polymers [2]. Compounds containing more than two allyl type double bonds invariably led to cross-linked, water-insoluble polymers. Such polymers have been shown to be useful as ion exchange resins.

In an effort to explain this apparent anomaly, a mechanism involving an alternating intramolecular-intermolecular chain propagation was proposed [3,4,5,6]. In such a mechanism, a catalyst free radical attacks one double bond of the monomer. A second attack follows on the remaining double bond, since probability places it in the most

favorable position for further reaction, resulting in the formation of a six-membered piperidinium ring. Further free radical attack must then occur on a separate monomer molecule resulting in a covalent bond between the two monomer molecules, and in chain growth.

This proposed mechanism has been proven to be correct through establishment of the structure of the poly-(diallylammonium halides) [7]. The establishment of this mechanism of polymerization as a general one has been classified as the eighth major structural feature of synthetic high polymers to become established [8].

In a somewhat related case, Simpson, Holt, and Zeite [9] studied the structure of polydiallyl phthalate at the gel point and by calculations from values of residual unsaturation and degree of polymerization, concluded that at the gel point about 40% of the reacted monomer unit was used up in cyclization reactions and were, therefore, not available for further cross-link formation. In a later publication [10], these authors analyzed several other polydiallyl esters in a similar way, but only in the above case did cyclization appear to occur to any great extent. Such an intramolecular cyclization in the case of diallyl phthalate would lead to ten-, eleven-, twelve-membered, or even larger, rings. Such cyclizations are much less likely to occur than those which lead to five- or six-membered rings.

Further substantiation of the proposed mechanism has been obtained by C. S. Marvel and R. D. Vest [11] who reported the formation of soluble, non-cross-linked polymers containing cyclic units from diethyl α,α'-dimethylenepimelate and similar derivatives.

C. S. Marvel and J. K. Stille [12] reported the formation of linear, cyclic polymers by polymerization of 1,6-heptadiene and 1,5-hexadiene by use of Ziegler-type catalysts.

Acrylic anhydride has been shown to polymerize by this mechanism to produce a linear, soluble polymer containing methyleneglutaric anhydride units [13,14]. This polymer when hydrolyzed gave evidence that the resulting polyacrylic acid contained a high degree of stereospecificity at the asymmetric centers along the chain [13]. If the conformation of all the anhydride rings in the polymer is the same, then completely stereospecific polyacrylic acid should be obtained on hydrolysis, provided no racemization occurred during the process. Scale models of the polymeric anhydride indicate that there is less overlap in the model in which all of the bonds between the methylene groups and their respective rings are equatorial rather than axial. Polymerization and hydrolysis of methacrylic anhydride to the polymethacrylic acid in which no racemization can occur during hydrolysis, resulted in a product which showed a higher degree of stereoregularity than the polyacrylic acid [15].

In an attempt to prepare diacrylylmethane, Jones [16] obtained a polymer having repeating methylene dihydroresorcinol units, which he postulated as having been formed from the intermediate diacrylylmethane by the alternating intramolecular-intermolecular mechanism through anionic catalysis.

Allyl ether and allyl sulfide undergo cyclization to tetrahydropyran and tetrahydrothiopyran derivatives, respectively, when treated with chain transfer reagents under free radical conditions [17].

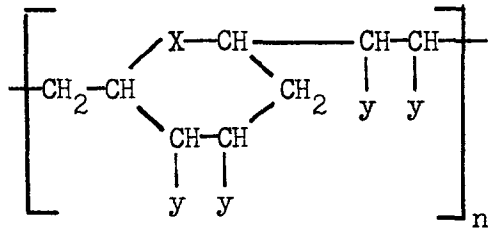
Alloocimene [18] was found to produce a soluble polymer in which two of the three double bonds had been consumed in the polymerization reaction. This can be the case only if cyclization has occurred.

Schuller [19] and coworkers have shown that diallyl monomers of various types produce soluble copolymers with acrylonitrile and acrylamide. Soluble polymers were obtained by Stille and Frey [20] by polymerization of 1,6-heptadiyne with complex metal catalysts. Evidence was presented to support a cyclic structure for these polymers.

All of the previously reported work involved studies of symmetrical dienes, or monomers in which the relative reactivities of the two double bonds in a given monomer were equal. Two papers [21,22] which were published before the cyclic polymerization mechanism was proposed included results on polymerization of allyl methacrylate. These results indicate, although inconclusively, that some cyclic polymerization may have occurred in this case. Crawshaw, Barnett and Butler [23] have shown that some cyclization occurs in unsymmetrical 1,6heptadienes, even though gelation occurs at high degrees of conversion. These authors reported on the polymers of allyl, crotyl and 3-butenyl methyl maleates and fumarates, and showed that considerable cyclization occurred in each case before gelation.

Polymerization of an unsymmetrical 1,6-heptadiene by this mechanism to produce cyclic recurring units may be considered to be quite analogous to a true copolymerization in which the relative reactivities of the two double bonds would control the ratio and order of monomer units in the resulting polymer chain. When both dissimilar double bonds are present in a single molecule, copolymerization results in cyclization and the reactivity ratios would control this degree of cyclization, however would also permit cross-linking.

It has been shown [24,25] that suitably selected monomer pairs can be copolymerized by a mechanism similar to that followed by 1,6-dienes to produce linear polymers having recurring six-membered heterocyclic rings, formed during the polymerization process. This copolymerization requires two types of monomers: Type I, a mono-olefin, and Type II, a 1,4-diene. Examples of monomer Type I which have been investigated and found to copolymerize with one or more examples of monomer Type II are maleic anhydride and fumaronitrile. Examples of monomer Type II which have been investigated and found to copolymerize with one or more examples of monomer Type I are divinyl sulfone, divinyl dimethylsilane, and divinyl ether. The heterocyclic copolymers have the following generalized structures:



x = O, SO_2, or $(CH_3)_2Si$

y = CN, or y - y = $-\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}-$

In view of the mounting evidence for the proposed mechanism, and the wide variety of monomer and catalyst systems to which it has been applied, there appears to be little or no doubt that it is correct. For example, dimethyldiallyl ammonium bromide, by virtue of the size of the methyl groups, thus forcing the two allyl groups into favorable positions for the cyclization, results in a higher degree of cyclization than does diallylamine hydrobromide. Diallylamine hydrobromide, by virtue of the size of the bromide ion.

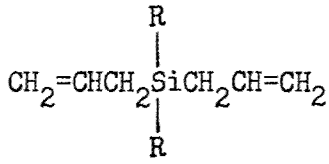
Substitution of nitrogen by other elements as listed above offers the possibility of a wide variety of new heterocyclic polymers having new and interesting properties.

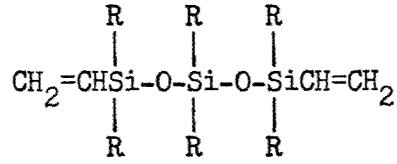
III. OUTLINE OF PROPOSED WORK AND SYNTHETIC APPROACH

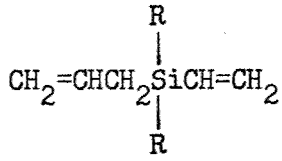
1. Monomer Synthesis

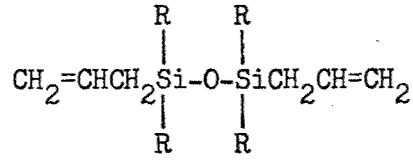
Monomers proposed for study in this program were compounds which were believed to be capable of forming cyclic structures during the polymerization process.

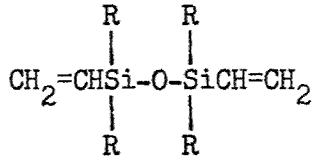
a. Monomers containing silicon

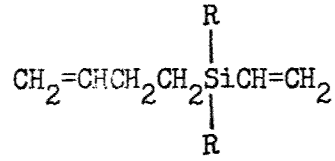












Because of the known tendency of siloxane compounds to form rings larger than six, due to the Si-O-Si bond angle, compounds functionally capable of forming larger rings during the polymerization process were also considered. The vinyl allyl silanes would be expected to lead to five membered rings.

Introduction of vinyl, allyl, or 3-butenyl groups into the silane or chlorosilane molecule can be done most readily by reaction of the appropriate Grignard reagent with the appropriate chlorosilane. The siloxanes can be synthesized by hydrolysis of the appropriate chloro- or ethoxylsilane, or by cohydrolysis with the appropriate dichloro- or diethoxysilane.

b. Monomers containing phosphorus

$(CH_2=CHCH_2)_2PRO$ $(CH_2=CHO)_2P(OR)$

$(CH_2{=}CHO)_2PO(OR)$ $\quad\quad$ $[(CH_2{=}CHCH_2)_2P(R)_2]^+X^-$

The following reactions have been considered as possible routes to the desired phosphine derivatives:

(1) Reaction of alkyl halides with compounds having a phosphorus to metal linkage: $NaPH_2 + RX \longrightarrow NaX + RPH_2$

(2) Reaction of Grignard reagents with halogen derivatives of trivalent phosphorus: $RPX_2 + 2\ RMgX \longrightarrow R_3P + 2\ MgX_2$

(3) Reaction of organic halogen derivatives with halogen derivatives of trivalent phosphorus, with metallic sodium: $PX_3 + 3\ RX + 6\ Na \longrightarrow R_3P + 6\ NaX$

(4) Reaction of Grignard reagents with compounds containing a phosphorus to hydrogen bond: $RPH_2 + 2\ R'MgX \longrightarrow RP(MgX)_2 + 2\ R'H$ and $RP(MgX)_2 + 2\ R''X \longrightarrow RPR''_2 + 2\ MgX_2$

(5) Reduction of the appropriate phosphine oxide or sulfide to the corresponding phosphine:

$R_3P{\rightarrow}O \xrightarrow{[H]} R_3P + H_2O$ and $R_3P{\rightarrow}S \xrightarrow{[H]} R_3P + H_2S$

The following reactions have been considered as possible routes to the desired phosphine oxide derivatives.

(1) Oxidation of tertiary phosphines: $R_3P + (O) \longrightarrow R_3PO$

(2) Isomerization of phosphinous esters: $R_2POR' + R''X \longrightarrow R_2R''PO + R'X$

(3) Reactions of Grignard reagents with halides and esters of phosphorus acids: $RP(O)Cl_2 + 2\ R'MgX \longrightarrow RP(O)R'_2 + 2\ MgXCl$ and $RP(O)(OR')_2 + 2\ R''MgX \longrightarrow RP(O)R''_2 + 2\ MgXOR'$

(4) Isomerization of alkyl phosphites followed by reduction to phosphine, and repeating process: $(RO)_3P + R'Cl \longrightarrow R'P(O)(OR)_2 \xrightarrow{[H]} R'P(OR)_2 + R'Cl \longrightarrow R'_2PO(OR) \xrightarrow{[H]} R_2P(OR) + R''Cl \longrightarrow R'_2R''P{\rightarrow}O$

c. Other monomers

Monomers resulting from replacement of silicon and phosphorus with other elements such as oxygen, sulfur, selenium, germanium, arsenic, tin, lead, and zinc are included in the scope of this project.

2. Polymerization Studies

Because of the widely divergent nature of the monomers being prepared and studied, it has been necessary to consider a wide variety of polymerization techniques and catalyst systems. For example, the silanes which are quite closely related to the hydrocarbons, lend themselves to polymerization by Ziegler catalysts. Because of the sensitivity of the phosphines to oxygen, considerable problems have been encountered,

effectively eliminating the use of oxygen containing polymerization catalysts of the peroxy type.

3. Polymer Characterization

Characterization of the resulting polymers includes molecular weight, degree of polymerization, solubility, melting or softening points, thermal stability, and other properties necessary for the complete elucidation of polymer structure.

IV. RESULTS AND CURRENT STATUS OF THE WORK

1. Monomer Synthesis

a. Silicon Compounds

(1) Preparation of Diallyldimethylsilane

$$CH_2=CH-CH_2-Br \xrightarrow[\text{dry ether}]{Mg} CH_2=CH-CH_2-MgBr$$

$$CH_2=CH-CH_2-MgBr + ClSi(CH_3)_2-CH_2-CH=CH_2 \longrightarrow$$

$$(CH_2=CH-CH_2)_2Si(CH_3)_2$$

(a) Preparation of Allyl Magnesium Bromide [16]

To a five-liter, three-necked flask, equipped with a reflux condenser, addition funnel and mechanical stirrer were added 3.5 moles of magnesium turnings (85 g) and 1.75 liters of absolute ether. The flask was flushed with dry nitrogen. One and seventy-five hundredths moles (212 g) of allyl bromide were weighed out and about 5 ml were added to the flask and stirred. When the ether began to reflux the flask was cooled with an ice bath and the remainder of the allyl bromide, diluted with an equal volume of absolute ether, was added dropwise over a period of nine hours. Throughout this time the flask was cooled with the ice bath. The solution was stirred for an hour and then two 1-ml portions of the solution were titrated with standard base. The solution was found to contain 1.65 moles of the Grignard reagent.

(b) Preparation of Diallyldimethylsilane

Ninety-four hundredths mole (126 g) of allyldimethylchlorosilane diluted with an equal volume of absolute ether was added slowly to the solution of 1.65 moles of Grignard reagent. The addition took one hour after which the mixture was stirred for 18 hours. The mixture was then hydrolyzed by pouring it over a mixture of ice and ammonium chloride solution. The ether layer was separated, and the water layer was washed twice with 100 ml portions of absolute

ether. The ether layers were combined and dried over $CaCl_2$ overnight. The ether was removed by distillation and then the silane was distilled through an 18-inch Vigreux column. The yield of diallyldimethylsilane was 99 g (78%). The physical constants were: b.p. 132°C, n_D^{20} 1.4399. The literature reports [27] b.p. 135°C, n_D^{20} 1.4420. Two preparations of this compound were made. The other in smaller quantity; the yield was 14.5 g (52%).

Diallyldimethylsilane has also been prepared in 76% yield by reaction of dimethyl dichlorosilane with allyl magnesium bromide.

(2) Preparation of Diallyldiphenylsilane

The preparation of allyl magnesium bromide here was the same as used for the diallyldimethylsilane. To a solution of 1.5 moles of allyl magnesium bromide was added 0.5 mole (126 g) of dichlorodiphenylsilane over a period of two hours. The mixture was stirred for 24 hours and then hydrolyzed by pouring over a mixture of ice and ammonium chloride. The ether layer was separated and the water layer washed twice with 100-ml portions of ether. The ether was removed by distillation and then the crude diallyldiphenylsilane was distilled under reduced pressure. The yield of diallyldiphenylsilane was 91 g (71%). The physical properties of the compound were: b.p. 134°C/1 mm, n_D^{20} 1.5738. The literature values [27]: b.p. 140.5°C/2 mm, n_D^{20} 1.5750. Yield, 62%.

Three preparations of this compound were made. The boiling points and index of refraction were the same for each preparation. The yields were 72% (22 g) and 71.5% (44 g).

(3) Preparation of Dimethallyldimethylsilane

(a) Preparation of Methallyl Magnesium Chloride

Into a 2-liter, 3-necked flask, equipped with a stirrer, reflux condenser and addition funnel were added 1.5 moles (36 g) of magnesium turnings and 500 ml of ether. Ninety-one grams (1 mole) of methallyl chloride were added slowly after the reaction had begun. The flask was cooled with ice during the addition which took three hours. Titration of 2 one-ml aliquots of the solution showed a yield of 0.6 equivalents of Grignard reagent.

(b) Preparation of Dimethallyl Dimethyl Silane

Twenty-five grams (0.02 mole) of dimethyldichlorosilane were added dropwise to the Grignard reagent over a period of one hour. Five hundred ml of ether was added at the end of the addition because the mixture became very thick. The mixture was hydrolyzed after 6 hours stirring and the ether layer dried. The ether was removed by distillation and the residue was distilled through an 18-inch column at reduced pressure.

Nineteen and four hundredths grams of dimethallyldimethyl silane was obtained for a yield of 60%. The physical constants were: b.p. 75-79°C at 25 mm, 167°C at 760 mm, n_D^{20} 1.4525.

A second preparation of this compound gave 24 g of the desired product for a yield of 71%. The physical constants of the product were: b.p. 72-75/22 mm, and n_D^{20} 1.4550.

(4) Attempted Preparation of Di(2-chloroallyl)dimethyl silane

(a) Preparation of Grignard reagent of 2,3-dichloropropane

Into a one-liter, three-necked flask was placed 400 ml of dry tetrahydrofuran and 18 g of magnesium turnings. A few drops of 2,3-dichloropropene were added and the mixture was heated to about 60°C and the reaction started. Forty-four grams of 2,3-dichloropropene was added slowly in order to keep the mixture refluxing. During the addition the flask was cooled with an ice bath. The addition took 6 hours. After the addition the mixture was stirred for an additional 2 hours.

(b) Reaction with Dimethyldichlorosilane

A solution of 0.14 equivalents of 2-chloroallylmagnesium chloride in tetrahydrofuran was prepared by the procedure given previously.

To the Grignard solution was added 7.8 g (0.06 mole) of dimethyldichlorosilane over a period of 1 hour. The mixture was stirred for 12 hours and was then hydrolyzed by pouring it over an ice-HCl solution. The tetrahydrofuran layer was separated and the water layer extracted with 100 ml of tetrahydrofuran. The organic layer was dried over anhydrous sodium sulfate.

The tetrahydrofuran was removed by distillation through an 18-inch Vigreux column. The distillation was continued. Only a very small amount of low boiling material was obtained in the distillation, but a large amount of tar remained in the pot. Attempts to identify some product in the residue failed.

b. Phosphorus Compounds

(1) Phosphine and Phosphonium Compounds

(a) Preparation of Diallylphenylphosphine

Allyl magnesium bromide was prepared as previously reported. To the Grignard reagent from one mole of allyl bromide in 600 ml of dry ether was added slowly at 5-10°C 45 g (0.25 mole) of phenyldichlorophosphine. The solution was then refluxed for one-half hour and cooled to 5°. One hundred grams of ammonium chloride in 500 g of water was added at 5-10° and the two layers separated. The organic layer was dried over anhydrous magnesium sulfate and filtered. The ether was removed at atmospheric pressure, and the product was distilled at reduced pressure. All operations were performed under a nitrogen atmosphere. B.p. 72-74/0.5 mm; 100-102/3 mm. Several runs were made. Yields ranged from 23-30%.

(b) Preparation of Diallylphenylmethylphosphonium Iodide

To a solution of diallylphenylphosphine in dry ether was added a slight excess of methyl iodide. The product

solidified on refluxing the oil with heptane. The melting point was found to be 80° after recrystallization from methyl ethyl ketone and ether.

(c) Residue from Diallylphenylphosphine Distillation

It was assumed that the residue from the phosphine distillation contained the corresponding oxide. The product distilled at 175°/4 mm.

(d) Preparation of Diallylphenylmethyl Phosphonium Bromide

Diallylphenyl phosphine was prepared as previously described and retained as the ether solution rather than being distilled. The dried solution was cooled to 0° and treated with methyl bromide for two hours, maintaining the temperature below 10°. A white solid was obtained after the solution had stood at room temperature for one hour. This solid was isolated and recrystallized from acetone-ether solution. The yield of diallylphenylmethyl phosphonium bromide was 53% based on starting phenyldichlorophosphine. The product melted sharply at 98-99° after drying for one week in a vacuum desiccator. The infrared spectrum of the compound shows the characteristic absorptions. Anal. Calcd. for $C_{13}H_{18}PBr$, % Br = 28.07; % P = 10.87. Found: % Br = 28.22; % P = 10.86.

(2) Phosphine Oxide Derivatives

(a) Attempted Reaction of Diethyl Ethylphosphonate with the Allyl Grignard Reagent

To a cooled (5°C) 0.5 molar solution (in 500 ml of anhydrous ether) of the allyl Grignard reagent (filtered free of magnesium and titrated to determine its strength) was added 16.7 g (0.1 mole) of diethyl ethylphosphonate during the course of 30 minutes. The entire reaction, including the addition period, was performed under nitrogen.

After the addition was complete, the ice bath was removed and the ether was caused to boil for 6 hours by means of a heat lamp. At the end of this time the flask was chilled with ice. To the cool mixture was added, with caution, 200 ml of saturated aqueous NH_4Cl solution. Eventually most of the solid which was present in the flask dissolved. Distillation of the organic layer gave back diethyl ethylphosphonate; the return was nearly quantitative.

When ether-benzene was used as the solvent system, again diethyl ethylphosphonate was recovered unchanged. The use of anisole as the solvent, in order to raise the temperature of the reaction medium, apparently invoked too strenuous conditions. Only very low boiling materials could be obtained from distillation of the organic layer. These materials were not studied.

All of the above conditions were repeated to verify the previous results.

(b) Attempted Reaction of Phenyl Dichlorophosphine Oxide with the Allyl Grignard Reagent

The Grignard reagent was prepared in the manner similar to that previously reported. The ingredients used were 18.0 g (0.75 g atom) of magnesium turnings, 30.2 g (0.25 mole) of allyl bromide, and 150 ml of anhydrous ether. Although the reagent was filtered before use, it was not titrated.

To the chilled Grignard reagent was added, with caution, a solution of 10.0 g (0.05 mole) of freshly distilled phenyl dichlorophosphine oxide in 20 ml of anhydrous ether. (The reaction was performed entirely under nitrogen.) Even at 5° C the reaction was vigorous and thus a slow drop rate was required. At the end of one half hour the addition was complete; a solid had settled in the bottom of the flask. The ether was caused to boil for another one-half hour by means of a heat lamp. The flask was cooled to 5° and 100 ml of 10% NH_4Cl was added cautiously. The mixture was allowed to stand overnight; nearly all of the precipitated solid had dissolved. The organic phase and two 70-ml ether extracts of the aqueous layer were dried over Na_2SO_4. Removal of the ether and benzene by distillation left a black tar-like oil which could not be vacuum distilled at 1.3 mm and 190°C.

(c) Attempted Reaction of Triisopropyl Phosphite with Allyl Bromide

This was an attempt to prepare diisopropyl allylphosphonate which had potentialities as an intermediate in the preparation of diallyl phosphorous compounds.

Sixty-seven grams (0.32 mole) of triisopropyl phosphite, 44.6 g (0.36 mole) of allyl bromide, and some carborundum chips were placed in a flask. After being heated under gentle reflux for 5 hours, the contents of the flask were distilled in-vaco. Two low-boiling fractions were removed and almost immediately the residue became a tacky solid. The material (probably polymeric) was dissolved in alcohol and chilled. No further work was done with this reaction.

A more clean-cut reaction would be anticipated if trimethylphosphite was used in place of the triisopropylphosphite. This was found to be the case as is seen below.

(d) Reaction of Trimethylphosphite with Allyl Bromide

The mixture, consisting of 62.0 g (0.50 mole) of trimethylphosphite, 70.0 g (0.57 mole) of allyl bromide, and some chips of porous plate, was held at reflux for 7 hours. Distillation, in vaco, of the reaction mixture gave a small forerun followed by a clear liquid which boiled at 45°/1.3 mm; yield 40 g (53%). A thorough literature search established that dimethyl allylphosphonate is known [30]. The boiling point reported was 90-92°/13 mm; n_D^{22} 1.4271. Observed: n_D^{20} 1.4320.

(e) Attempted Reaction of Dimethyl Allylphosphonate with Thionyl Chloride

This was an attempt to prepare allyl phosphonic dichloride [$CH_2{=}CHCH_2P(O)Cl_2$].

A flask containing 5 g (0.033 mole) of dimethyl allylphosphonate and 19 g (0.16 mole) of thionyl chloride was placed on a steam bath. After being boiled for 2 hours, the contents of the flask were subjected to distillation in vaco. Only the two starting materials were found in the distillates or residue.

(f) Preparation of Allyldichlorophosphine Oxide

To a suspension of 66.7 g (0.5 mole) of $AlCl_3$ in 137.5 g (1.0 mole) of phosphorus trichloride was added, cautiously, 19.8 g (0.25 mole) of freshly distilled allyl chloride. The addition required one-half hour and was done at room temperature. The resulting orange mixture was allowed to cool to room temperature. The flask was chilled with dry ice for 8 hours at the end of which time a solid had precipitated. The clear supernatant liquid was decanted, and the solid residue was again cooled as before; two hundred ml of methylene chloride were then added to dissolve the solid. To the resulting, chilled solution was added, with caution, 81 g (4.5 moles) of water. The mixture which formed was stirred at room temperature for one-half hour; during this time a white solid precipitated in the flask. About 200 ml additional methylene chloride was added to the flask (it was again chilled with dry ice). The cold mixture was filtered quickly, and the organic phase was separated and fractionated. A fraction boiling at 45-51°/1.3 mm was collected, yield 4.0 g. The reported boiling point is 55°/3 mm.

As the yield of this material was so low another route to the intermediate is being sought.

(g) Reaction of Diphenyl Phenylphosphonate with the Allyl Grignard Reagent

The Grignard reagent was prepared in a manner cited earlier.

Preparation of the Grignard reagent from 26.8 g (1.2 g atom) of magnesium turnings, 60.5 g (0.5 mole) of allyl bromide, and 270 ml of anhydrous ether was done at 5°C; it required 2-1/2 hours. To the chilled (5°C) reagent (filtered free of magnesium) was added a solution of 15.5 g (0.05 mole) of diphenyl phenylphosphonate in 100 ml of anhydrous benzene. The addition was made in a period of 1-1/2 hours. This entire process including the remainder of the reaction was performed under nitrogen.

The dark colored mixture was allowed to warm to room temperature, and then it was heated to boiling by means of a heat lamp. At the end of 5-1/2 hours, the flask was chilled with an ice bath. With caution, 200 ml of 10% aqueous NH_4Cl solution was added dropwise. Most of the solid material dissolved. An additional 100 ml of ether was added to the flask. The cold organic layer was separated and washed 3 times with 50-ml portions of 10% NaOH. The organic solvents were removed by distillation and the residual oil was distilled in vaco. Following a small forerun a liquid distilled at 169°/1.3 mm and partially solidified in the condenser. The solid was nearly colorless; it appeared to be very hygroscopic and was stored in a vacuum desiccator over P_2O_5. The compound melted at 40-42.5° (approximately). The infrared

spectrum suggests the presence of a double bond (1641 cm^{-1}), a phosphorus-oxygen bond (1150-1220 cm^{-1}, broad) and other bands which could be assigned to the structure below:

$$(CH_2{=}CHCH_2)_2\overset{\nearrow O}{P}\text{-}\phi$$

The odor of both the water layer and the acidified base extracts suggested the presence of phenol, the expected by-product.

Several preparations of this compound have been carried out. It was found that an 8-10 molar excess of the allyl Grignard reagent gave the highest yields, namely 20-35%. Anal. Calcd. for $C_{12}H_{15}PO$; %C = 69.90; %H = 7.28; %P = 15.05. Found: %C = 69.33; %H = 7.41; %P = 14.53.

(h) Preparation of Dimethylphosphonic Acid and Diethylphosphonic Acid

Dimethylphosphonic acid and diethylphosphonic acids have been prepared in similar fashion as follows. It is hoped that they can be converted to the diphenyl alkylphosphonates which in turn can be treated with the allyl Grignard reagent to give the tertiary phosphine oxides.

Diisopropyl methylphosphonate (or diethyl ethylphosphonate) was hydrolyzed with boiling concentrated hydrochloric acid over a 16-hour period. The mixture was treated with a benzene-toluene mixture, and the water was azeotroped from the reaction flask; this required 24-36 hours. The acids (impure) are white crystalline solids and will be converted to their acid chlorides. The phosphonates were obtained by treating the alkyl phosphite with the corresponding alkyl halide in an Arbuzov rearrangement.

2. Polymerization Studies

a. Silicon Compounds

(1) Polymerization of Diallyldimethylsilane

(a) Peroxide Initiated Polymerization at 100°C

Into a test tube were placed 1 g (60 drops) of diallyldimethylsilane and 0.1 g (8 drops) of di-tert butyl peroxide. The test tube was heated in a steam bath for four days but little polymerization occurred.

(b) Peroxide Initiated Polymerization at 140°C

Into a tube were placed 2 g (120 drops) of dimethyldiallylsilane and 0.2 g (16 drops) of di-tert butyl peroxide. The tube was fitted with a reflux condenser and placed in a three-necked, one-liter flask fitted with a reflux condenser and thermometer well. The tube was maintained at 140°C by refluxing xylene in the lower flask. After 24 hours the heat was turned off and the polymer scraped out of the tube. It was a soft white solid.

The polymer was refluxed with benzene overnight but was only slightly soluble and very little polymer could be obtained by treating the benzene filtrate with methanol.

Another similar reaction was run in which the tube containing the silane and the peroxide was heated for 48 hours. The polymer obtained was a yellow rubbery solid. It was insoluble in benzene and several other common solvents.

Polymerizations of diallyldimethylsilane have been run with 0.1% and 0.25% di-tert-butyl peroxide. The temperature was maintained for 60 hours and the polymers recovered were both soluble in benzene. Reprecipitation of the polymers gave a soft sticky white polymer. The polymerization with 0.1% peroxide, however, gave only a very small amount of recoverable polymer.

(c) Ziegler Catalyst Polymerizations

A number of polymers have been obtained by polymerization of diallyldimethylsilane with aluminum triethyl and titanium tetrachloride as catalyst. A molar ratio of aluminum triethyl to titanium tetrachloride of 4:1 was used, and heptane was used as solvent. The catalyst was prepared by adding the aluminum triethyl and titanium tetrachloride to dry heptane in a dry box. The monomer was then added to this mixture, and the solution removed from the dry box and placed in an oven at 60°C. Other polymerizations have been run at temperatures up to 85°C, and for periods up to 48 hours. Other polymerizations have been carried out in a three-necked stirred flask. All operations were carried out under a nitrogen atmosphere.

The polymers were hydrolyzed by pouring into methanol. The polymer coagulated and was filtered. It was then washed with methanolic HCl, and with water, and then dried. The polymers were all soluble in benzene. Only a small amount of the polymer in each case was insoluble. They were purified by reprecipitation from the benzene solutions by addition to rapidly stirred methanol.

The highest yield yet obtained is 25%. The melting points of these polymers were between 115° and 145°, and decomposition begins at 220-300°.

(2) Polymerization of Diallyldiphenylsilane

(a) Peroxide Initiated Polymerization

A reaction similar to (1-b) above was run with 3 g (120 drops) of diallyldiphenylsilane and 0.2 g (16 drops) of di-tert-butyl peroxide. The reaction was continued for 24 hours at 140°C. The polymer obtained was a hard brown solid, and was soluble in benzene. It was purified by reprecipitation from the benzene solution by the addition of methanol. The purified polymer was a light tan solid, and became soft between the temperatures 152-168°C and began to decompose at 320°C. At the decomposition temperature it was a very viscous liquid. Other physical properties of the polymer are being determined.

The diallyldiphenylsilane was also polymerized using only 0.1% of the peroxide. The temperature of the solution was maintained at 140°C for 48 hours and a white solid polymer was obtained which was soluble in benzene. It was purified in the same manner as the other polymer. Its melting points were similar to the first (soften, 150-165°C) and it started to decompose at 315°C.

(b) Ziegler Catalyst Polymerizations

Five polymers of diallyldiphenylsilane have been prepared with aluminum triethyl and titanium tetrachloride catalyst systems. Yields have been in the range of 30-60%, the melting points of the polymers were between 130 and 190°, and decomposition usually begins at 290° to 330°.

(c) Other Catalyst Systems

Attempts have been made to polymerize diallyldiphenylsilane with a catalyst system of V_2O_5 and boron trimethyl [31]. A small amount of solid polymer was obtained using the same procedure as was used with the aluminum triethyl titanium tetrachloride system. No physical properties have yet been obtained for this polymer.

(3) Polymerization of Dimethallyldimethylsilane

Three attempts have been made to polymerize dimethallyldimethylsilane with the aluminum triethyl, titanium tetrachloride catalyst system. None of these attempts gave any polymer. It has been noted in the literature that this type of catalyst is not effective for polymerization of α-olefins with branching closer than the 3 or 4 carbon [32].

b. Phosphorus Compounds

(1) Phosphine and Phosphonium Compounds

No attempt has been made to polymerize the diallylphenyl phosphine.

Diallylphenylmethylphosphonium iodide, m.p. 80°, appears to be converted to a polymer, m.p. 170-180°, upon heating on a steam bath as a solution in ethanol and carbon tetrachloride. The polymer is precipitated as a light tan solid upon addition of ether.

Diallylphenylmethylphosphonium bromide was polymerized in an oven under N_2 at 68° over a period of three days as a solution of 67% in H_2O. The catalyst was 2.1% t-butyl hydroperoxide. The product was isolated by dissolving in a small amount of absolute EtOH and precipitation with dry acetone. The solid obtained was filtered in a dry box. The product is a tan solid which darkens at 230° slightly and melts with some decomposition over 270°.

(2) Phosphine Oxide Compounds

Diallylphenylphosphine oxide was polymerized by use of free radical initiators.

Benzoyl peroxide was found to give the best yield of polymer; 3% by weight of this initiator was used. When a small run of 0.5 grams of the monomer was used, an 86% conversion to polymer was obtained in 48 hours. The polymerization was done in bulk at 80° and in an atmosphere of nitrogen. The polymerization mixture was poured into dry ether from which the polymer separated as a white

solid. The polymer was dissolved in a minimum amount of alcohol and precipitated with dry ether. To insure removal of the monomer, the polymer was extracted with boiling benzene (it is only very slightly soluble in benzene) for 24 hours. The purified polymer is light brown in color and melts in the range 210-225° without decomposition. The melt appeared to be stable up to 265° where some decomposition appeared to take place. It is soluble in alcohol and dimethylformamide.

An attempted solution polymerization in benzene with t-butyl hydroperoxide for more than 4 days at 60° did not succeed. The oxide was recovered near quantitatively. The monomer is soluble in benzene to a limited extent.

BIBLIOGRAPHY

1. G. B. Butler and R. L. Bunch, J. Am. Chem. Soc. 71, 3120 (1949).
2. G. B. Butler and F. L. Ingley, J. Am. Chem. Soc. 73, 895 (1951).
3. Fifth Quarterly Progress Report, Atomic Energy Commission Contract Number AT-(40-1)-1353, September 15, 1953, p. 3.
4. Ion Exchange Conference, Gordon Research Conferences, June 15, 1955. Program published in Science 121, 576 (1955).
5. Chem. and Eng. News, March 11, 1957, pp. 22-24.
6. G. B. Butler and R. J. Angelo, J. Am. Chem. Soc. 79, 3128 (1957).
7. G. B. Butler, A. Crawshaw, and W. L. Miller, J. Am. Chem. Soc. 80, 3615 (1958).
8. F. C. McGrew, J. Chem. Ed. 35, 178 (1958).
9. W. Simpson, T. Holt and R. Zeite, J. Polymer Sci. 10, 489 (1953).
10. W. Simpson and T. Holt, J. Polymer Sci. 18, 335 (1955).
11. C. S. Marvel and R. D. Vest, J. Am. Chem. Soc. 79, 5771 (1957).
12. C. S. Marvel and J. K. Stille, J. Am. Chem. Soc. 80, 1740 (1958).
13. A. Crawshaw and G. B. Butler, J. Am. Chem. Soc. 80, 5464 (1958).
14. J. F. Jones, J. Polymer Sci. 33, 15 (1958).
15. A. Crawshaw and G. B. Butler, Unpublished Work.
16. J. F. Jones, J. Polymer Sci. 33, 7 (1958).
17. W. S. Friedlander, Paper Number 29, p. 18N, Division of Organic Chemistry Abstracts, A.C.S. Meeting, San Francisco, April, 1958.
18. J. F. Jones, J. Polymer Sci. 33, 513 (1958).
19. W. H. Schuller, J. A. Price, S. T. Moore, and W. M. Thomas, J. Chem. Eng. Data 1, 0000 (1959).
20. J. K. Stille and D. A. Frey, Paper Number 43, p. 17S, Division of Polymer Chemistry Abstracts, A.C.S. Meeting, Boston, Mass., April, 1959.
21. E. R. Blout and B. E. Ostberg, J. Polymer Sci. 1, 230 (1946).
22. S. G. Cohen, B. E. Ostberg, D. B. Sparrow, and E. R. Blout, J. Polymer Sci. 3, 269 (1948).
23. A. Crawshaw, M. D. Barnett, and G. B. Butler, Paper Number 47, p. 17S, Division of Polymer Chemistry Abstracts, A.C.S. Meeting, Boston, Mass., April, 1959.
24. G. B. Butler, Paper Number 15, p. 6R, Division of Polymer Chemistry Abstracts, A.C.S. Meeting, San Francisco, April, 1958.
25. G. B. Butler, Paper Number 77, p. 32T, Division of Polymer Chemistry Abstracts, A.C.S. Meeting, Chicago, September, 1958.

26. Preparation of Allyl Magnesium Bromide obtained from Peninsular ChemResearch, Inc.
27. A. D. Petrov, V. F. Mironov, and V. G. Glukhovtsev, Syntheses of Diallylsilanes, Izvest, Akad Nauk S.S.S.R. Otdel Khim Nauk 1954, 1123, C.A. 49, 7510i.
28. Kosolapoff, Organo-phosphorus Compounds, Wiley 1958; Chap. 2, p. 10.
29. Jones, Davies, et al., J. Chem. Soc. 1947, 1446.
30. C.A. 46, 7517e (1952).
31. J. Furvkawa and T. Tsurûta, J. Polymer Sci. 28, 227 (1958).
32. J. K. Stille, Chem. Revs. 58, 541 (1958).

PERFLUOROALKYL AMIDINE POLYMERS

by
Henry C. Brown
University of Florida

INTRODUCTION

Work in the area of the perfluoroalkylamidine polymers began several years ago with the study of the addition reactions of the perfluoroalkylnitriles. At that time, it was found that these nitriles would add ammonia to form the stable amidine structure as shown in Fig. 1.

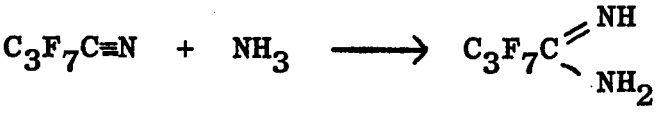


Fig. 1

For formation of polymers the most interesting reaction of the perfluoroalkylamidines is the condensation which proceeds with the liberation of ammonia and subsequent cyclization to form the substituted symmetrical triazine as shown in Fig. 2.

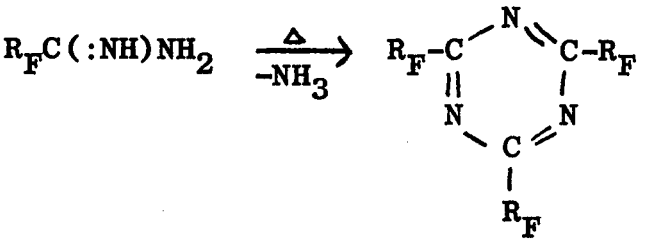
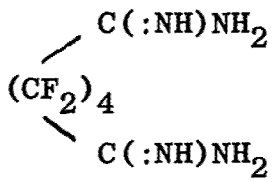


Fig. 2

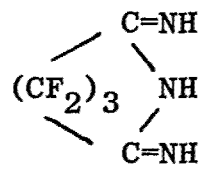
These substituted triazines, in which R_F=C_2F_5, C_3F_7, etc., have been described previously. They show thermal stability well above 300°C. and are particularly resistant to strong oxidizing mineral acids at elevated temperatures.

Since both the chemical and thermal stability of the perfluoroalkyl substituted triazines were impressive, the next step in this research was the attempt to incorporate this stable structure into a polymer molecule. For this purpose, perfluoroglutarodinitrile and perfluoroadipodinitrile were synthesized and reacted with ammonia. The reaction of perfluoroadipodinitrile with ammonia produced the expected

diamidine structure, I. However, perfluoroglutarodinitrile, in its reaction with ammonia, formed a cyclic product which resulted from the addition of only one mole of ammonia per mole of dinitrile. This cyclic product, II, has been termed perfluoroglutaroimidine.



I



II

Fig. 3

Both of these ammonia addition products underwent a typical condensation reaction to liberate ammonia and produce hard, infusible, thermally stable resins. These polymers are quite stable when heated in air at 350°C. for 24 hours. They show a small initial weight loss, but no change in physical shape or color. A sample was heated rapidly on an exposed metal block to a block temperature of 540°, which was held for 10 minutes, with no sign of charring, although the polymer was apparently losing weight under these conditions.

Although a complete structure determination of these polymers has not been made, it appeared that condensation to form triazine rings had taken place and that the final structure was a network of triazine rings connected at three points by $-CF_2-$ chains, the whole molecule being very large and very highly crosslinked.

The next step in this work was the reaction of the perfluoroalkyldiamidines with a perfluoroalkylmonoamidine. This work showed that copolymers could be prepared from the di- and mono- amidines and that these exhibit a great variety of physical properties ranging from viscous liquids to elastomeric solids. Thermal stability similar to that described for the homopolymers is retained by the copolymers.

If the network type of structure is accepted for the homopolymer, then the copolymer may have the structure shown in Fig. 4, where x and y depend on the particular diamidine

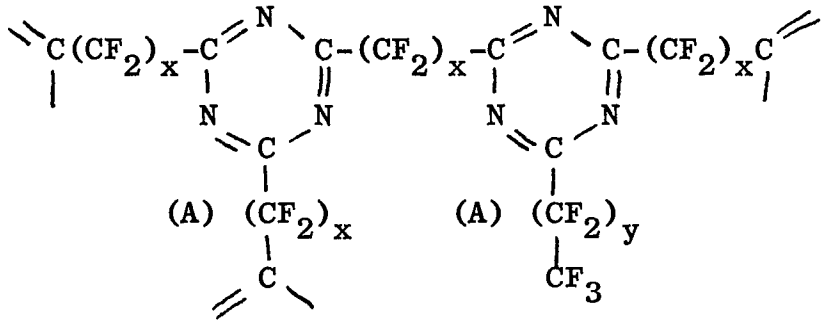


Fig. 4

or monoamidine used. The structural groups at A may continue the polymer structure if formed by the diamidine or be a terminal group if formed by the monoamidine.

The objectives of the present project, which began in June 1958, are several: (1) A study of the basic properties of the polymers from the condensation reactions of the amidines and imidines, this study to include molecular weight determination, fractionation of the soluble polymers, investigation of the possibilities of crosslinking soluble polymers, etc. (2) New methods of synthesis of this basic type of polymer structure or modification of the present polymers. (3) A study of the possibilities of catalytic polymerization of perfluoroalkylnitriles. (4) New monomer nitriles which, if they are incorporated into polymer structures, may modify the known properties of the present polymers.

SOLUTION COPOLYMERIZATION

As mentioned above, it was found in the early work on this polymer series that both viscous liquids and elastomeric solids could be prepared by copolymerization of perfluoroglutaroimidine and perfluorobutyramidines in a melt of these two monomers. The characteristics of the final polymer depend on the mole ratio of the monomers. Liquid polymers could also be obtained by copolymerization of the same two monomers in a solvent. Early work on the present project showed that the liquid polymers prepared in Kel-F polymer oil were soluble in methylethylketone, as were the liquid polymers from the melt polymerization, and that the liquid polymers prepared in solution had a higher molecular weight, as determined by their intrinsic viscosity, than similar polymers prepared by the melt polymerization. The elastomeric solids prepared by a melt copolymerization are insoluble and presumably have a loosely linked network structure. Since it is highly desirable for purposes of polymer structure study that the polymer be soluble, the polymerization studies in Kel-F polymer oil have been extended.

The first of a series of polymerizations carried out in Kel-F polymer oil was made with a molar ratio 1.00 to .050, perfluoroglutarimidine to perfluorobutyramidine. This polymer was separated from the Kel-F oil media by precipitation with methylene chloride and was subsequently dried at 90°C. under reduced pressure. After this treatment the polymer product was not soluble in methylethylketone or in Kel-F polymer oil and was also infusible.

A series of copolymerizations was, therefore, carried out with monomer ratios of 1.00 to 0.60, 1.00 to 0.70, and 1.00 to 0.80, perfluoroglutaroimidine to perfluorobutyramidine. At the completion of these polymerizations, as judged by the cessation of ammonia evolution, the three polymer solutions were clear and yellow-brown in color. These polymer products were separated from the Kel-F oil with the use of a methyl alcohol-water mixture and benzene. After the removal of the solvents the polymers were heated under reduced pressure for 16 hours at 194°. All of the resulting products were dark brown, brittle solids. The products obtained by this separation procedure from the mixture with a 1.00 to 0.6 ratio of monomers was no longer soluble or fusible and, therefore, solution viscosities could not be determined. Although this product is not fusible and is brittle at room temperature, it becomes plastic and somewhat rubbery when heated.

The remaining two polymer samples gave soluble polymers by the above separation procedure. Intrinsic viscosities were determined in methylethylketone and gave a value for the most viscous one of .09.

These polymers are therefore of low molecular weight. However, their IR spectra shows the characteristic absorption assigned to the C=N group in conjugated cyclic systems and the triazine ring is obviously a basic structural unit.

These soluble copolymers are being studied further for possible crosslinking mechanisms applicable to this polymer system.

The polymerization reaction with monomer mixtures containing smaller amounts of the monoamidine, which gave polymer products soluble in the Kel-F oil at the completion of the condensation reaction, but which were insoluble after the separation procedure is also of interest and will be investigated in greater detail.

CATALYTIC POLYMERIZATION OF PERFLUOROALKYLDINITRILES

Previous work on the fluorocarbon triazine type of polymer has been concerned principally with the study of the condensation reactions of perfluoroalkylamidines and imidines. An investigation has now been begun of the effect of small amounts of other materials on the polymerization of the perfluoroalkyldinitriles. Preliminary work has begun with the following materials in catalytic amounts: ammonia, aluminum chloride, boron trifluoride and benzoyl peroxide.

As a control for the catalytic study, a sample of perfluoroglutarodinitrile was heated in a sealed Pyrex tube at 200°C. for 20 hrs. This procedure produced somewhat less than 2% polymer with the remainder of the dinitrile unchanged. The infrared spectra of this polymer, however, does show the characteristic perfluoroalkyl triazine absorption. A similar experiment at 350°C. for 13 hours produced 11% of solid polymer. These products were somewhat resilient when removed from the tube, but became hard on continued heating in air. The appearance of the original polymer is more that of a swollen gel which loses liquid on further heating rather than a compound which had undergone further reaction. It is possible that a low molecular weight polymer, for example, a cyclic trimer, was formed in this reaction and absorbed by the more highly polymerized fraction.

In the presence of 0.09 mole % benzoylperoxide at 300° for 23 hours perfluoroglutarodinitrile yielded 67% solid polymer. This product is similar in appearance to that obtained with the dinitrile alone, but was produced in much higher yield. The infrared spectra of this polymer shows little change on heating the product at 300° for 72 hours, but the polymer becomes hard. The spectra shows absorption in the region previously assigned to the C=N conjugated cyclic triazine ring and also a small but definite absorption in the C≡N group. The thermal stability at 300° of this product is characteristic of the normal polymer of perfluoroglutaroimidine. An initial weight loss of about 12% occurs but the rate of weight loss decreases thereafter to a value of 0.021% per hour at the end of 192 hours heating at 300°C.

The first polymerization of perfluoroglutarodinitrile in the presence of ammonia was carried out with less than 0.10 mole % of ammonia present. At a temperature of 200° for 14 hours only a trace of solid was produced. At 300° for 3 hours the reaction yielded 56% of yellow-white, slightly resilient polymer that became hard on further heating in air at 300°.

A second run with 0.13 mole % ammonia yielded 83% solid, insoluble polymer. The thermal stability of this product

was somewhat greater than that of the product produced with benzoyl peroxide. After 193 hours at 300° in air the polymer had lost a total of 10.3% in weight with an average rate during the last 48 hours of 0.010% per hour. Infrared spectra of this original product shows absorption for C≡N and C=N cyclic as well as a weak band at 5.6 to 5.7 microns that could be due to C=NH or C=O. The C=NH assignment seems more probable.

A preliminary study of the polymerization of perfluoroglutarodinitrile with small amounts of ammonia in the presence of Kel-F oil has also been made. The purpose of this experiment was the investigation of the possibility of forming a soluble polymer in solution in the Kel-F oil. Under the conditions used, most of the polymerization took place in the gas phase. However, a small amount of tacky soluble polymer was isolated by diluting a Kel-F oil with carbon tetrachloride. This tacky polymer was partially soluble in methylethylketone and its presence gives some indication that a soluble homopolymer can be produced. The polymer from the upper portion of the reaction tube was yellow-white and somewhat resilient. It resembles the polymer previously described prepared from the dinitrile with ammonia with no solvent media present.

Aluminum chloride undoubtedly promotes a homopolymerization of perfluoroglutarodinitrile and this reaction occurs at a much lower temperature (approximately 150°C.) than the one in the presence of ammonia. The nature of this polymer product is not clear at the present time. This reaction was carried out in the usual sealed glass tube and the polymerization apparently took place in the liquid phase since the polymer is formed as one solid hard lump in the bottom of the tube. This product is insoluble and on heating a solid piece at 300° for 72 hours, remains unchanged in appearance. A pulverized sample, however, lost considerable weight when heated under similar conditions. Since the concentration of aluminum chloride catalysts in this experiment was quite high, this weight loss is perhaps due to subliming residual catalyst. In other properties, resistance to acid attack, etc., this polymer is similar to previously reported homopolymers of perfluoroglutarodinitrile.

The infrared spectra of the aluminum chloride polymer product is complicated by the presence of the residual catalyst. The presence of the triazine ring is definitely indicated but the presence of unreacted C≡N groups is in doubt.

NEW THERMALLY STABLE POLYMERS

C. S. Marvel

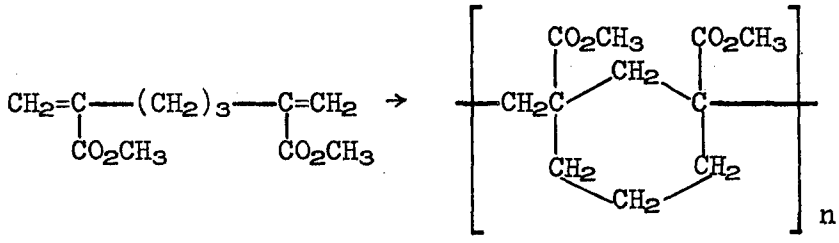
University of Illinois

Several approaches to the problem of preparing thermally stable polymers have been tried in our laboratory but I would hesitate to say that we have prepared a new polymer which really fits the name.

The general type of polymers which we have been studying includes those with recurring cyclic units both aromatic and aliphatic, chelates of polymeric Schiff bases, polymeric basic beryllium carboxylates and polymeric phthalocyanines. Each will be discussed briefly.

Polymers with Recurring Cyclic Units

At the 1957 conference we reported briefly on the preparation of a polymer containing alternate methylene and cyclohexylene units which was prepared by the intermolecular-intramolecular process of Butler to yield a high molecular weight glassy type of product (I) with



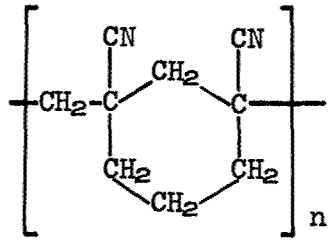
I

fair stability at 300°. This type of cyclic polymerization has been extended to the case of the corresponding dinitrile to give a product which has thermal stability which is far greater than that of polyacrylonitrile or polymethacrylonitrile.

α,α'-Dimethylenepimelonitrile was prepared from the corresponding pimelic acid derivative. α,α'-Dimethylenepimelic acid was converted to the acid chloride with thionyl chloride and then to the amide by the action of cold concentrated ammonia in an overall yield of 80%. Dehydration was effected in a 62.5% yield by treating a pyridine solution of the amide with benzenesulfonyl chloride at moderate temperatures.

α,α'-Dimethylenepimelonitrile polymerized in dimethylformamide solution and in emulsion systems to produce a polymer which was soluble in hot dimethylformamide and which had an inherent viscosity of 0.655. The infrared spectrum indicated that a small amount of the monomer units was incorporated by a noncyclic process and the remaining

double bonds are hanging from the chain; however, the spectral and solubility data were in agreement with the cyclic structure (II) as the major recurring unit of the polymer.

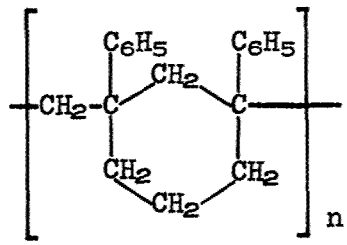


II

Poly-α,α'-dimethylenepimelonitrile did not change color until heated to temperatures above 275°. This is in sharp contrast to the thermal stability of poly-methacrylonitrile which undergoes thermal discoloration at 140°.[1] Poly-α,α'-dimethylenepimelonitrile turned red at 300° and jet black at 325° over a period of three hours but the thermally degraded polymer contained about 80% of the original nitrogen content.

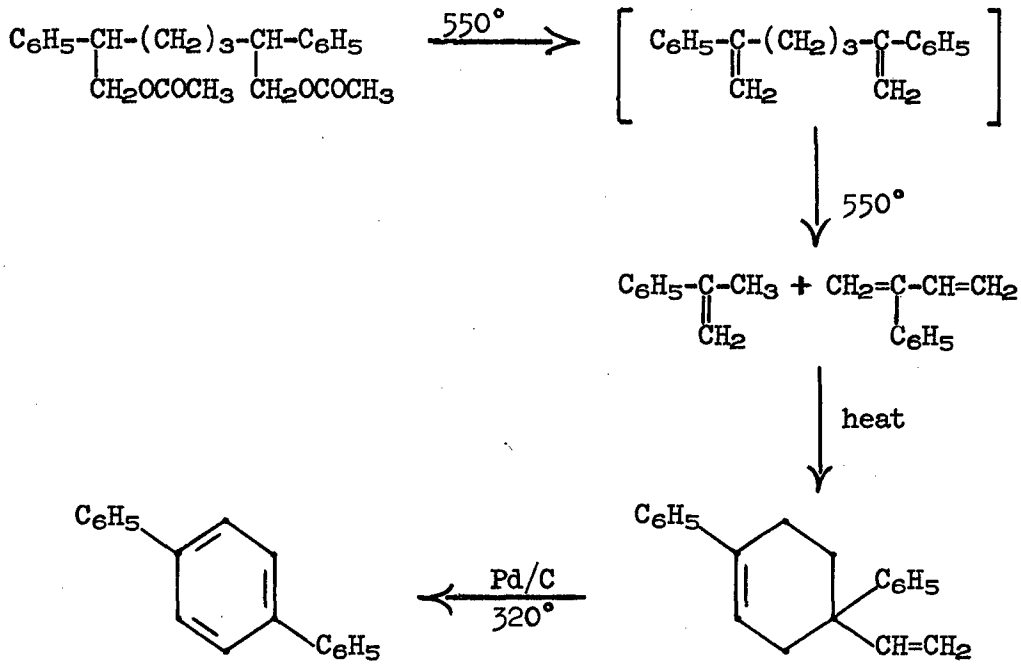
α,α'-Dimethylenepimelamide polymerized in dimethylformamide solution to yield, in high conversion, a polymer which is insoluble in the hot dimethylformamide solvent. The infrared spectrum of this polymer is not helpful in determining the amount of residual unsaturation because of the overlap of the amide carbonyl and carbon-carbon double bond absorptions; terminal methylene absorption (928 $cm.^{-1}$ in the monomer) was not present in the polymer. It is possible that the amide nature of the polymer, rather than primary bond-crosslinking, rendered the polymer insoluble.

In this same group of polymers we have now prepared a polymer (III) by the method described below but as yet we have not had time to determine its properties.

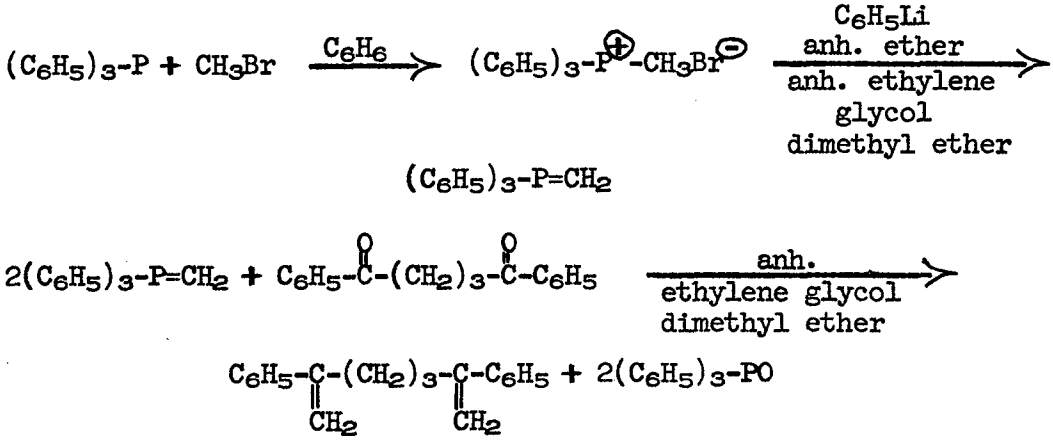


III

The first attempts to synthesize the monomeric 2,6-diphenylheptadiene-1,6 by the pyrolysis of 2,6-diphenyl-1,7-diacetoxyheptane gave us a very unexpected cleavage of the carbon chain to yield α-methylstyrene and 2-phenylbutadiene-1,3.



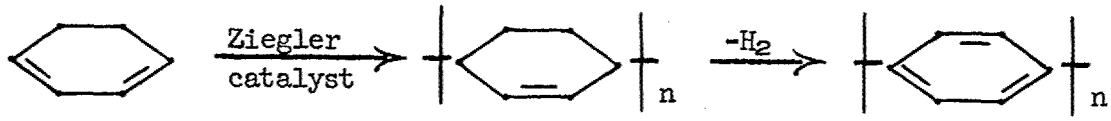
After two attempts to prepare 2,6-diphenylheptadiene-1,6 by means of the Wittig reaction[2] applied to 1,3-dibenzoylpropane in diethyl ether-tetrahydrofuran failed, a third attempt was successful, yielding 18.7 g. (48%) of pure diene when the reaction was carried out in ethylene glycol dimethyl ether as solvent.



The polymerization of 2,6-diphenylheptadiene-1,6 by free radical catalysts has not gone well but a good polymerization reaction has been achieved by use of Ziegler catalysts to give a polymer which is soluble, free of unsaturation and fairly high melting (180°).

Two attempts have been made to obtain polymers with aromatic units as the main recurring unit. In the first, cyclohexadiene was

polymerized with Ziegler catalysts to yield a polymer with recurring cyclohexene units.



IV V

These cyclohexadiene polymers (IV) were rather low molecular weight with inherent viscosities in the 0.11 to 0.14 range. They softened near 200°.

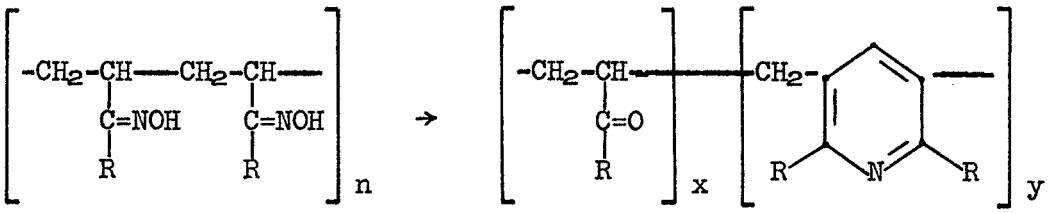
Attempts to dehydrogenate these polymers to give para-polyphenylenes (V) have not been highly successful. However, when the cyclohexadiene polymer was heated with chloranil in refluxing xylene a tan-brown insoluble polymer was obtained. The infrared absorption spectrum of this material was almost identical to a spectrum of p-quaterphenyl. The absorption maxima corresponding to aromatic C-H stretching (3035 $cm.^{-1}$) and C=C skeletal inplane vibrations (1603, 1575 and 1486 $cm.^{-1}$) were very nearly identical with those of p-quaterphenyl. The maximum at 1006 $cm.^{-1}$, characteristic of para aromatic substitution, also corresponded very closely. The most intense absorption maximum in the infrared spectrum of the p-polyphenyl was that occurring at 811 $cm.^{-1}$ which can be assigned to para aromatic substitution. Absorption maxima at 765 $cm.^{-1}$ and 695 $cm.^{-1}$ in the spectra of the impure polyphenyl correspond to out-of-plane deformation vibrations of five adjacent carbon-hydrogen bonds. The presence of these monosubstituted aromatic absorption maxima could be explained only by the end rings of the polyphenyl molecule. The possibility of phenyl side groups in the polymer does not seem likely in view of x-ray diffraction studies. The spectrum of the crude polyphenyl also showed absorption maxima corresponding to O-H stretching (3500 $cm.^{-1}$) and $-CH_2-$ stretching (2925 and 2860 $cm.^{-1}$), showing that although partial aromatization had occurred, some tetrachlorohydroquinone and unaromatized poly-1,3-cyclohexadiene were also present in the tan-brown material. Analysis of the material showed 80.32% carbon, 5.81% hydrogen and 8.90% chlorine. The presence of chlorine was assumed to be due to the tetrachlorohydroquinone impurity, and appropriate correcting calculations were made to arrive at an empirical formula of $(C_6H_{5.4})_x$ for the polymer. Since poly-1,3-cyclohexadiene has the formula $(C_6H_8)x$ and polyphenyl has the formula $(C_6H_4)x$, it appeared that about 65% of the theoretical amount of hydrogen necessary for complete aromatization had been lost by the polymer. From the analysis it was estimated that the tan-brown product contained 15% tetrachlorohydroquinone, 30% unaromatized poly-1,3-cyclohexadiene and 55% polyphenyl.

Although heating the impure polyphenyl for several hours at 450° under nitrogen removed the tetrachlorohydroquinone and destroyed

the unaromatized poly-1,3-cyclohexadiene, this treatment also caused some carbonization to occur. A black powder was obtained, the infrared spectrum of which was identical to that of the brown material before heating, except for the absence of maxima corresponding to the tetrachlorohydroquinone and unaromatized poly-1,3-cyclohexadiene impurities. The weight of the material lost during the heating experiment corresponded almost exactly to the quantities of tetrachlorohydroquinone and unaromatized polymer which had been calculated to be present in the impure polyphenyl. The black powder, which did not melt when heated to 530°, was indicated by analysis to be composed of about 90% polyphenyl and 10% carbon. Although the black material was very stable under a nitrogen atmosphere, it was slowly destroyed by heating in air at temperatures above 300°. This instability of the aromatized polymer at high temperatures may be attributed to oxidation of isolated unsaturation or unaromatized sections of the polymer. The polyphenyl appeared to be relatively stable in air at 230-240°, since heating the material at this temperature for 72 hours failed to cause a loss in weight. A 3% gain in weight over the 72-hour period was observed, due probably to oxidation. It appears that any polyphenyl prepared by dehydrogenation of poly-1,3-cyclohexadiene must be completely aromatized, since any isolated unsaturation or unaromatized sections of the polymer would be susceptible to oxidation at high temperatures.

A second scheme designed to introduce aromatic type rings into the polymer chain involved the application of the Knoevenagel ring closure of 1,5-dioximes to pyridines, to two polyvinyl ketones.

The first work was done on polymethyl vinyl ketone following the approach of Marvel and Levesque.[3] Then the reaction was applied to the polymer of phenyl vinyl ketone.



VIa. R = CH_3 VIIa. R = CH_3

b. R = C_6H_5 b. R = C_6H_5

Conversion of high molecular weight polymethyl vinyl ketone to polymethyl vinyl ketoxime (VIa) was effected by use of a modification of the procedure of Marvel and Levesque.[3] Treatment of this material with an ethanolic hydrogen chloride solution produced a copolymer of methyl vinyl ketone and 2,6-dimethylpyridine units (VIIa) containing 76.2 mole per cent of pyridine units. From polymethyl vinyl ketoximes of inherent viscosity 3.2 to 3.6 in dimethyl sulfoxide,

copolymers were obtained which possessed inherent viscosities in chloroform of 0.11 to 0.14. Infrared spectra of the copolymer in chloroform revealed pertinent absorption bands at 1708 (C=O), 1599, 1562 cm.$^{-1}$, and a weak shoulder at 1500 cm.$^{-1}$ (pyridine C=C and C=N bands). In addition a band of very weak intensity was noted at 3300-3160 cm.$^{-1}$ (-OH). The results of the elemental analysis eliminate the possibility of this absorption being due to the hydroxyl group of a residual oxime or an aldol condensation, and suggest the observed band was again due to residual water. This is consistent with the hygroscopic nature of the copolymer and the frequently low carbon analyses. The possibility of amide formation by rearrangement of the oxime functions under the conditions of the ring closure was excluded by treatment of the copolymer with 20% sulfuric acid at reflux temperature. The infrared spectrum of the material isolated from this reaction was identical at all significant points with the spectrum of the starting material. Comparison of the ultraviolet spectrum of the copolymer with spectra reported for a number of methyl substituted pyridines provided additional evidence for the presence of a recurring pyridine unit in the polymer. The general shapes of the curves were quite similar, a bathochromic shift being observed with increasing alkyl substitution. An average neutralization equivalent of 117.0 for the basic unit of the copolymer was obtained by titration of the polymer with perchloric acid in a non-aqueous system; this represents a 1.8% deviation from the theoretical value of 119.1.

Since the practicality of this route to a pyridine-containing polymer had been successfully demonstrated by the preparation of copolymer VIIa, it was desirable to extend this series of reactions to the analogous aromatic system, i.e. to polyphenyl vinyl ketoxime. As a preliminary to this work, an examination of the ring closure reaction was carried out on a comparable monomeric system. It was found that 2,6-diphenylpyridine could be prepared from the dioxime of 1,3-dibenzoylpropane in a yield of about 97.5%; therefore, it was evidently feasible to extend this reaction to polyphenyl vinyl ketoxime.

The first point of attack in this phase of the work involved a series of experiments designed to uncover the optimum conditions for the preparation of high molecular weight polyphenyl vinyl ketone. Solution polymerization of phenyl vinyl ketone initiated by benzoyl peroxide or azo-bis-isobutyronitrile produced polymers with inherent viscosities in the range 0.11 to 0.26. With a potassium persulfate system emulsified with Triton X-301, polymers of inherent viscosity 0.14 to 0.17 were obtained at temperatures of 5° to 55°. The addition of silver nitrate to this system as an activator raised the inherent viscosity range to 0.21-0.30 for experiments carried out at 5°. Similar results were obtained with a potassium persulfate-ORR soap system containing 5% of emulsifier and 0.37% of initiator; polymers prepared by this procedure possessed viscosities of 0.16 to 0.31. Lowering

the initiator concentration to 0.2% and raising the soap concentration to 7.5% changed the viscosity range to 0.41-0.65.

Under ionic conditions, low molecular weight material was obtained with a number of initiator systems. Physically, these polymers varied from tacky semi-solids to powders while the inherent viscosities ranged from 0.03 to 0.10. Comparison of the infrared spectra of the soluble polymers with spectra of authentic samples of polyphenyl vinyl ketone indicated the polymers were similarly constituted.

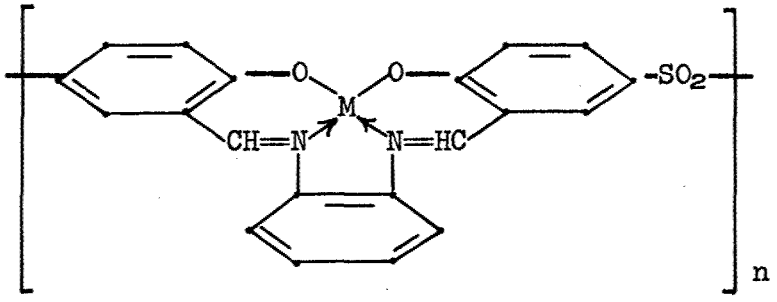
A sample of the higher molecular weight polyphenyl vinyl ketone prepared under emulsion conditions was converted to a copolymer of phenyl vinyl ketone and phenyl vinyl ketoxime containing 70.2 mole per cent ketoxime units by oximation of the polyketone under very mild conditions. Infrared analysis was consistent with the proposed copolymer structure with pertinent bands at 3500-3260 $cm.^{-1}$ (-OH); 1665 $cm.^{-1}$ (ArC=O); 1635 $cm.^{-1}$ (C=N); 1600 $cm.^{-1}$, 1580 $cm.^{-1}$ and 1498 $cm.^{-1}$ (aromatic); 914 $cm.^{-1}$.

When this copolymer was subjected to the conditions designed to effect ring closure of the 1,5-dioxime groups to a pyridine moiety, a polymer was obtained which dissolved slowly in dilute hydrochloric acid and was insoluble in sodium hydroxide solution. By contrast the precursor polyketone was completely insoluble in acid. On the basis of the elemental analysis it was possible to estimate that the "pyridine" copolymer consisted of 49.7 mole per cent phenyl vinyl ketone and 50.3 mole per cent 2,6-diphenylpyridine units (VIIb). Infrared analysis indicated the absence of hydroxyl functions (no residual oxime) and showed a new absorption band at 1547-1545 $cm.^{-1}$. This absorption is somewhat lower than would be expected for a 2,6-diphenylpyridine nucleus but is in the general region for C=C, C=N aromatic absorption (cf. 2,6-diphenylpyridine: 1605, 1592, 1568 and 1497 $cm.^{-1}$; phenylpyridine C=C and C=N bands). Additional evidence consistent with the assignment of a 2,6-diphenylpyridine moiety to the copolymer was provided by a comparison of the ultraviolet spectrum of the polymer with the spectrum of 2,6-diphenylpyridine. In dioxane, absorption maxima for the monomeric pyridine occurred at 245 mμ (ϵ 28,200), 285 mμ (shoulder, ϵ 12,280) and 302 mμ (ϵ 11,200). In the same solvent, a similar spectrum was obtained for the copolymer containing 50.3 mole per cent 2,6-diphenylpyridine units. The maxima were found to have undergone a considerable hypsochromic shift with the long wave length bands compressed to a single maximum at 285 mμ (ϵ 11,200) and the main absorption shifted to 236 mμ (ϵ 20,900). Extinction coefficients for the pyridine units of the copolymer were calculated by subtracting the contribution expected from the phenyl vinyl ketone units at the wave lengths of the observed maxima; this contribution was determined from a spectrum of polyphenyl vinyl ketone in dioxane (λ 236, ϵ 7,760; λ 285, ϵ 870).

Thermal stability tests on the pyridine-containing copolymers revealed that neither polymer was appreciably stable. At 225° the copolymer with 2,6-dimethylpyridine units (VIIa) lost 3.2% of its weight in 12 hours and the copolymer with 2,6-diphenylpyridine units (VIIb) lost 2.7% of its weight in the same time. At 300° both polymers exhibited a steady weight loss; after 12 hours polymer VIIa had lost 21.6% of its original weight and VIIb had lost 9.9%.

Chelates of Polymeric Schiff Bases

Earlier work reported from this laboratory[4] has demonstrated that the chelated nickel(II) and cadmium salts of the poly-Schiff base shown in formula VIII have good heat stability but the molecular weight of the polymers thus far obtained are too low for these poly-



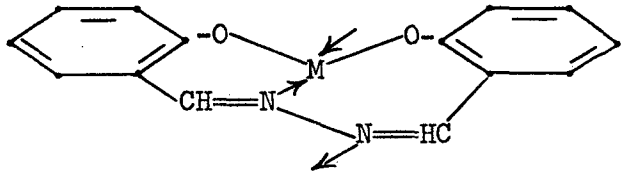
VIII. M = Ni(II) or Cd

mers to have practical usefulness. The polymers which had been prepared previously in tetrahydrofuran or acetic acid solution were assumed to have a molecular weight of 10,000 based on an inherent viscosity of the polymer of 0.05 (1% in dimethylformamide). Numerous attempts had been made to improve the molecular weight of the polymer obtained, i.e., variation in solvent systems, catalysts, use of dehydrating agents, azeotropic removal of water, temperature variations, but none had resulted in any significant improvement in molecular weight of the polymer.

Haley and Maitland[5] have shown that Schiff bases can be formed in yields of 70-90% by mixing in equimolar portions saturated aqueous solutions of the two reactants. Use of solvent modified emulsion systems was therefore investigated in connection with the formation of the poly-Schiff bases from o-phenylenediamine and 5,5'-methylene-bis-salicylaldehyde since this dialdehyde is more readily available than is bis-salicylaldehyde-5,5'-sulfone. The molecular weight of the polymer produced in the ethyl acetate modified emulsion system is improved over that obtained in solvent solutions[4], but the product is still a powdery solid and not tough or plastic.

In the search for heat stable polymeric metal chelates, we next turned to the use of hydrazine to replace o-phenylenediamine in

the reaction with the dialdehyde since hydrazine is a more reactive reagent with aldehydes, and also some earlier work had indicated that a low molecular weight polyazine of terephthalaldehyde[6] did not decompose rapidly at 425°. To check the stability of azines and their chelates, salicylaldehyde azine was prepared by the method of Cajar[7] and the chelates, IX, of nickel(II), copper(II), cadmium, cobalt(II) and zinc were prepared from tetrahydrofuran and water solutions. The chelates were very insoluble and those of cadmium and zinc could not be obtained in a satisfactorily pure condition.



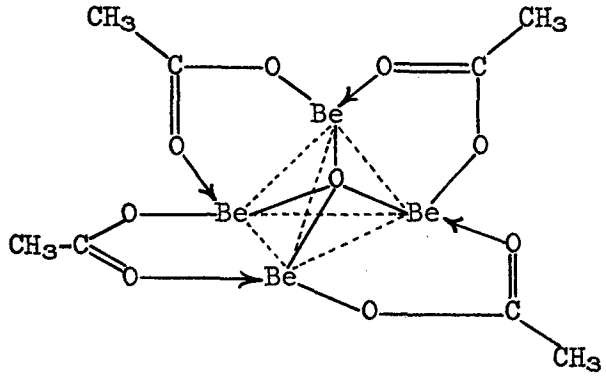
IX. M = Ni, Co, Cu

These chelates were not especially good in their resistance to high temperatures.

Basic Beryllium Carboxylates

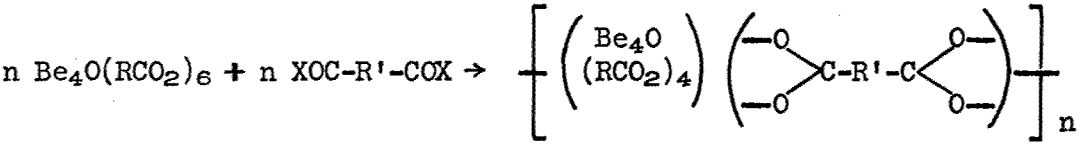
The basic beryllium carboxylates, $Be_4O(RCO_2)_6$, comprise a class of covalent compounds which have intrigued chemists ever since their discovery because of their interesting structure, bonding, and physical properties. They exhibit remarkable thermal stability, being stable to distillation at atmospheric pressure well above 300°C. Thus, as a part of the current research an effort was made to prepare polymers which incorporate the basic beryllium carboxylate structure as a part of the chain and study the thermal and mechanical properties of such materials.

The structure of basic beryllium acetate, X, is that of a

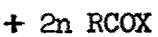


X

tetrahedron with an oxygen atom at the center, a beryllium atom at each vertex, and an acetate group chelated along each of the six edges. Two of the acetate groups are omitted from X to avoid confusing the drawing. To prepare a linear polymer containing the basic carboxylate structure, it is necessary to replace two of the monobasic carboxyl groups by carboxyl groups of a dibasic acid, as illustrated in the following equation:



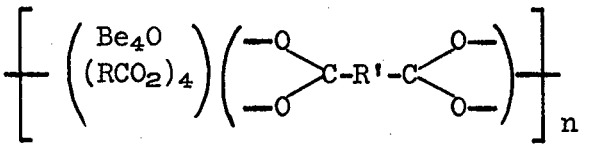
XI



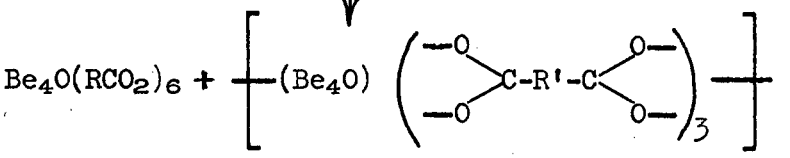
The feasibility of this type of condensation polymerization is indicated by the facile exchange of carboxyl groups observed in this laboratory and by previous workers.[8] Thus it was found that a mixture of the various possible products of carboxyl exchange resulted from the reaction of either basic beryllium propionate or butyrate with excess acetyl chloride. Tanatar and Kurowski[8] and Bragg and Morgan[9] report the isolation of single products from these reactions, but it is believed that their claims rest upon insufficient evidence. The preparation of polymeric basic beryllium carboxylates is not without precedence, since polymeric materials were prepared, though not recognized as such, by Tanatar and Kurowski[8] and Meyer and Mantel[10] who attempted to prepare basic beryllium succinate, $Be_4O(O_2CCH_2CH_2CO_2)_3$. Their product was described as a hard, infusible glass. It seems probable that it was the three dimensional basic succinate polymer rather than the monomeric substance.

Polymers were prepared from basic beryllium acetate, propionate and benzoate and the acid chlorides of adipic, sebacic, beta-ethyladipic, terephthalic, and isophthalic acid by condensation in inert solvents such as benzene, toluene, xylene and chloroform. The polymer precipitated from n-hexane. The polymer solution was coagulated with medium high boiling petroleum ether and the polymer washed with low boiling petroleum ether. Methanol cannot be used as a wash or coagulant because of a degradative reaction in which it participates, leading to crosslinked polymers of unknown composition.

Low molecular weight polymeric materials which showed good stability in organic solvents were obtained. But on standing these rapidly underwent disproportionation to yield basic beryllium acetate and crosslinked insoluble polymers of the dibasic acid.



XI

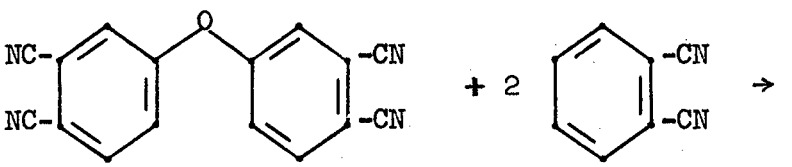


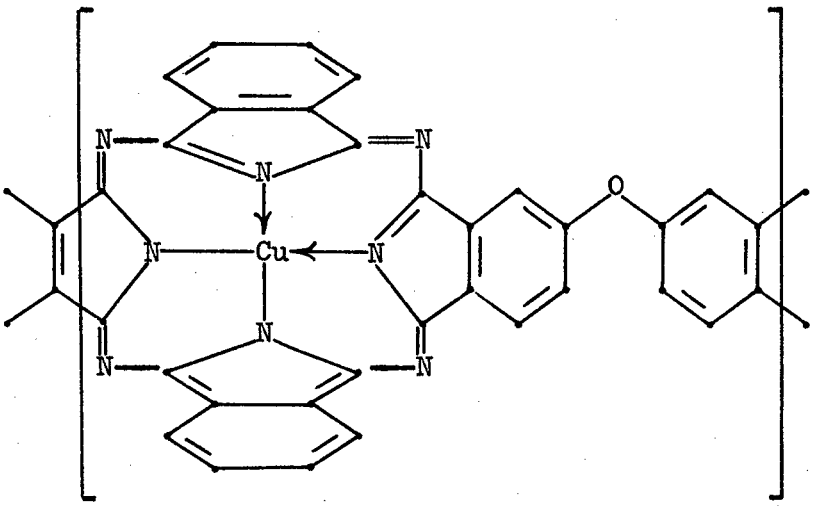
XII

This renders these materials unsuitable for general use as plastics. They do have very remarkable stability toward heat.

Polymeric Phthalocyanines

Finally I might mention attempts to prepare polymeric phthalocyanines from 3,3',4,4'-tetracyanodiphenyl ether and phthalonitrile.





XIII

The fusion of phthalonitrile and 3,3',4,4'-tetracyanodiphenyl ether using a variety of molar ratios with copper-bronze at 275° over three

hours was investigated. The products were purified by washing with boiling acetone and shaking for 20 hours at room temperature with concentrated sulfuric acid. This operation separated the product into an initially sulfuric acid-soluble fraction and an initially sulfuric acid-insoluble fraction. The cold sulfuric acid-insoluble fraction could be dissolved in hot sulfuric acid and did not precipitate on cooling. All of these materials are dark blue, hygroscopic powders with a beautiful metallic purple reflex as isolated from the reaction mixture. After treatment with sulfuric acid, they are dark blue to green-black in color. Their sulfuric acid solutions are brown to red-brown in contrast to the green color of the monomeric copper phthalocyanine in sulfuric acid. They undergo decomposition in air at 350° over 24 hours.

Infrared data leave little doubt that these materials are phthalocyanines. They have bands at 745, 875, 950, 1050, 1090 and 1120 $cm.^{-1}$. Ebert and Gottlieb[11] report that monomeric phthalocyanines have bands at 750, 885, 952, 1060, 1080 and 1123 $cm.^{-1}$.

Three lines of evidence, infrared spectra, viscosities and elemental analyses, indicate that polymerization progressed to a very low degree in the cocondensation reaction. The infrared spectrum of the product, prior to treatment with sulfuric acid, has an absorption band at 2240 $cm.^{-1}$ due to the unreacted cyano groups. After treatment of this product with concentrated sulfuric acid, absorption bands appear at 1715, 1770 and 1840 $cm.^{-1}$, due to five-membered imide and anhydride groups formed by hydrolysis of the ortho-cyano groups. Apparently the higher frequency absorption band of the imide coincides with the lower absorption band of the anhydride, so that only three peaks are observed. Had polymer formation proceeded to a high degree, imide and anhydride absorption would be weak, but these spectra indicate a high concentration of unreacted groups.

It is impossible to designate a definite structure on the basis of analytical results, but it is possible to eliminate many structures. It can be stated definitely that the cocondensation products are not high molecular weight linear polymers, since both copper and nitrogen are much lower than the calculated values. The data for the sulfuric acid-insoluble polymer are consistent with the theoretical values for a completely crosslinked polymer. The nitrogen values for the hot sulfuric acid-insoluble fractions are lower than the corresponding cold sulfuric acid-soluble fractions, due to conversion of imide groups to anhydride groups. By comparing the observed copper values with the possible ones, it can be seen that most of the products give values at the lower end of the acceptable range. This observation indicates a high incorporation of tetranitrile, that is, the presence of numerous imide and anhydride groups, which is consistent with infrared data. The degree of polymerization can at best be only approximated, but the copper values especially are indicative of a low chain length. Many of the observed values are less than 6%,

which is theoretically possible only for monomeric or dimeric compounds. Thus, from infrared, viscosity, and analytical data, it would appear that the product of a cocondensation reaction of phthalonitrile and 3,3',4,4'-tetracyanodiphenyl ether with copper-bronze is a mixture of materials in which polymerization has proceeded no further than the dimer or trimer stage. These low molecular weight polymers did not possess marked heat stability.

Bibliography

1. N. Grassie and I. C. McNeill, J. Polymer Sci., 27, 207 (1958).
2. G. Wittig and U. Schöllkopf, Chem. Ber., 87, 1318 (1954).
3. C. S. Marvel and C. L. Levesque, J. Am. Chem. Soc., 60, 280 (1938).
4. C. S. Marvel and N. Tarköy, J. Am. Chem. Soc., 79, 6000 (1957); ibid., 80, 832 (1958).
5. C. A. Haley and P. Maitland, J. Chem. Soc., 3155 (1957).
6. C. S. Marvel and H. W. Hill, Jr., J. Am. Chem. Soc., 72, 4819 (1950).
7. H. Cajar, Ber., 31, 2807 (1898).
8. S. Tanatar and E. Kurowski, J. Rus. Phys. Chem. Soc., 39, 936 (1907); Chem. Zentr. 79i, 102 (1908).
9. L. W. Bragg and G. Morgan, Proc. Roy. Soc., 104A, 437 (1923).
10. J. Meyer and E. Mantel, Z. anorg. u. allgem. Chem., 123, 43 (1922).
11. A. A. Ebert and H. B. Gottlieb, J. Am. Chem. Soc., 74, 2806 (1952).

Contribution from the Department of Chemistry

Polytechnic Institute of Brooklyn

ANIONIC POLYMERIZATION

Charles G. Overberger

(I) Introduction

Monomers containing different sized alicyclic side chains were synthesized and their polymerization with Ziegler-Natta type catalysts was carried out. Polymeric vinylcycloalkanes of observed crystallinity were obtained and characterized. Enhanced thermal stability in these systems was evident from the magnitude of their decomposition temperatures.

An investigation of a possible termination mechanism in Ziegler-Natta type catalysis by the measurement of molecular weights of poly-alpha-deuterovinylcyclohexane and polyvinylcyclohexane was unsuccessful.

The polymerization of methacrylonitrile by potassium in ammonia was found to differ from lithium catalysis, and mechanisms consistent with the kinetic data and the chemical evidence was proposed.

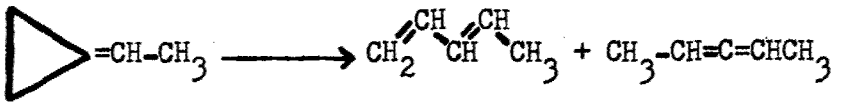
(II) Discussion

(A) Vinylcycloalkanes and Polyvinylcycloalkanes

(1) Vinylcyclopropane (A. E. Borchert)

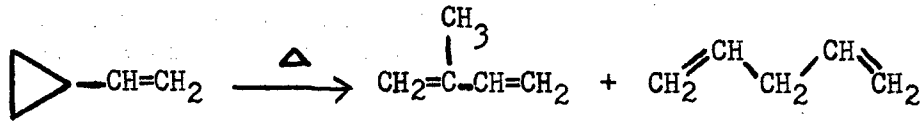
The alleged synthesis of vinylcyclopropane by mineral acid catalyzed dehydration of 1-cyclopropylethanol has previously been reported (1). A lithium aluminum hydride (2) reduction of methyl cyclopropyl ketone yielded 1-cyclopropylethanol (90%) and pentanol-2 (5-8%) in our hands. 1-Cyclopropylethanol was esterified with a mixture of acetic anhydride and sodium acetate (81%), the ester was pyrolyzed (3) over Pyrex glass at 500°, and there was obtained a four component olefin mixture which analyzed for the empirical composition, C_5H_8. Fractional distillation in a 75 theoretical plate concentric tube column yielded the major isomer, tentatively identified as trans 1-methylbutadiene, in greater than 98% purity as evidenced by G.P.C.* Vinylcyclopropane was the isomer in second largest quantity.

The non-stereospecific pyrolysis of acetates (4) has been established. Ethylidenecyclopropane, a statistical product in the pyrolysis of 1-cyclopropylethyl acetate, would be expected to undergo rearrangement under pyrolytic conditions. Possible products produced from this rearrangement include cis-trans 1,3-pentadiene and 2,3-pentadiene.



cis-trans (1)

A similar rearrangement of vinylcyclopropane would produce 1,4-pentadiene, 2-methylbutadiene and cis-trans 1,3-pentadiene.



(2)

A fraction distilling 25-30° (atm.), which is reasonably pure by G.P.C.* (9), has been identified as 1,4-pentadiene from infrared data and from G.P.C.* comparison with a pure sample of 1,4-pentadiene. The major fraction distilled at 43.8-44.0° and was reasonably pure. The physical properties of this material indicate it to be 1,3-pentadiene.

(2) Vinylcyclobutane (A. E. Borchert)

Vinylcyclobutane has been reported but has not been characterized. Cyclobutane carboxylic acid was synthesized (36%) (5) and converted to methyl cyclobutyl ketone by reaction of the acid chloride with ethoxymagnesium ethyl malonate (65%) (6). A lithium aluminum hydride (2) reduction of methyl cyclobutyl ketone yielded 1-cyclobutylethanol (82%) (7) and this alcohol was esterified with acetyl chloride (83%) (8). The pyrolysis of 1-cyclobutylethyl acetate was carried out at 500° (3). Gas phase chromatographic analysis (9) indicated that five components were present in the pyrolysate and fractionation in a 75 theoretical plate concentric tube column yielded the major component in greater than 98% purity.

Isomeric products obtained in the pyrolysis of 1-cyclobutylethyl acetate are viewed to be the result of the non-stereospecific nature of acetate cracking (4). Ethylidenecyclobutane, the statistical isomeric species to vinylcyclobutane, possessing a relatively labile structure, could undergo rearrangement in the acidic, high temperature environment and yield cis-trans 1,4-hexadiene, and cis and trans 3-methyl-1,3-pentadiene.

(3) 2-Methyl-3-isopropenylvinylcyclobutane (A. E. Borchert)

The alkaline, potassium permanganate oxidation of alpha pinene yielded pinonic acid (3,3-dimethyl-4-acetylcyclobutylacetic acid) (20%) (10) which was reduced under Clemmensen conditions (11) to a high distilling three component mixture (63%). A lactone was isolated pure by G.P.C.* the structure of which as deduced from analytical data correspond to 3-hydroxy-4-isopropylcyclobutylacetic acid lactone (I). The gamma lactone was reduced to a diol (II) which was esterified with acetyl chloride (8) to yield an unsaturated acetate (III). The acetate was pyrolyzed at 500° (3) to yield a diene (IV) which was isolated pure by

G.P.C.* (9). The structure of the diene as deduced from analytical data corresponded to 2-methyl-3-isopropenylvinylcyclobutane and this monomer was polymerized to a semi-solid (V) with an aluminum triisobutyl-titanium tetrachloride catalyst at 90-100°. The geometry of 2-methyl-3-isopropenyl-vinylcyclobutane suggested an intramolecular cyclization reaction in the formation of a polymeric product.

A meta migration of a methyl group with simultaneous lactonization (Figure 1) is suggested in formation of I. A multiple migration of hydrogen with simultaneous proton elimination is suggested in formation of III (Figure 1). Cis-trans relationships have not been established for any of the proposed structures; representations have been made in accordance with established mechanisms.

(4) Vinylcyclopentane and Polyvinylcyclopentane
(A. E. Borchert)

The preparation of vinylcyclopentane from the pyrolysis of both 1- and 2-cyclopentylethyl acetate has been reported (12). 1-cyclopentylethanol (51%) and 2-cyclopentylethanol (16%) were synthesized from cyclopentyl bromide employing Grignard reaction conditions, and these alcohols were esterified with acetyl chloride (8). Pyrolysis of 1-cyclopentylethyl acetate yielded ethylidenecyclopentane (26%) in addition to vinylcyclopentane. Pyrolysis of 2-cyclopentylethyl acetate yielded vinylcyclopentane (83%) and no detectable isomers.

Vinylcyclopentane was polymerized with an aluminum triisobutyl-titanium tetrachloride catalyst (13) (2/1 molar ratio) at 80° in a sealed tube. Conversion was 9% and the polymer was fractionated into an ether soluble fraction (30% by weight) and a benzene soluble fraction. Ether soluble polyvinylcyclopentane was amorphous as determined by X-ray analysis, melted at 60-80°, yielded an intrinsic viscosity of 0.08, analyzed incorrectly for carbon and hydrogen and exhibited absorptions for ether linkages in its infrared spectrum (14). A benzene soluble polyvinylcyclopentane was crystalline as determined by X-ray analysis, had a decomposition point greater than 250°, yielded an intrinsic viscosity of 0.56 and analyzed satisfactorily for carbon and hydrogen. Unit cell dimensions have been determined for crystalline polyvinylcyclopentane there being three monomer units in an identity period of 6.6Å for the triclinic system.

The attempted polymerizations of vinylcyclopentane with azo-bis-isobutyronitrile, in bulk, at 60°, with redistilled tin tetrachloride in methylene dichloride, at -78°, and with lithium amide in tetrahydrofuran, at 0° were unsuccessful.

(5) Vinylcyclohexane and Polyvinylcyclohexane
(A. Katchman)

1- Cyclohexylethanol was synthesized from cyclohexene and

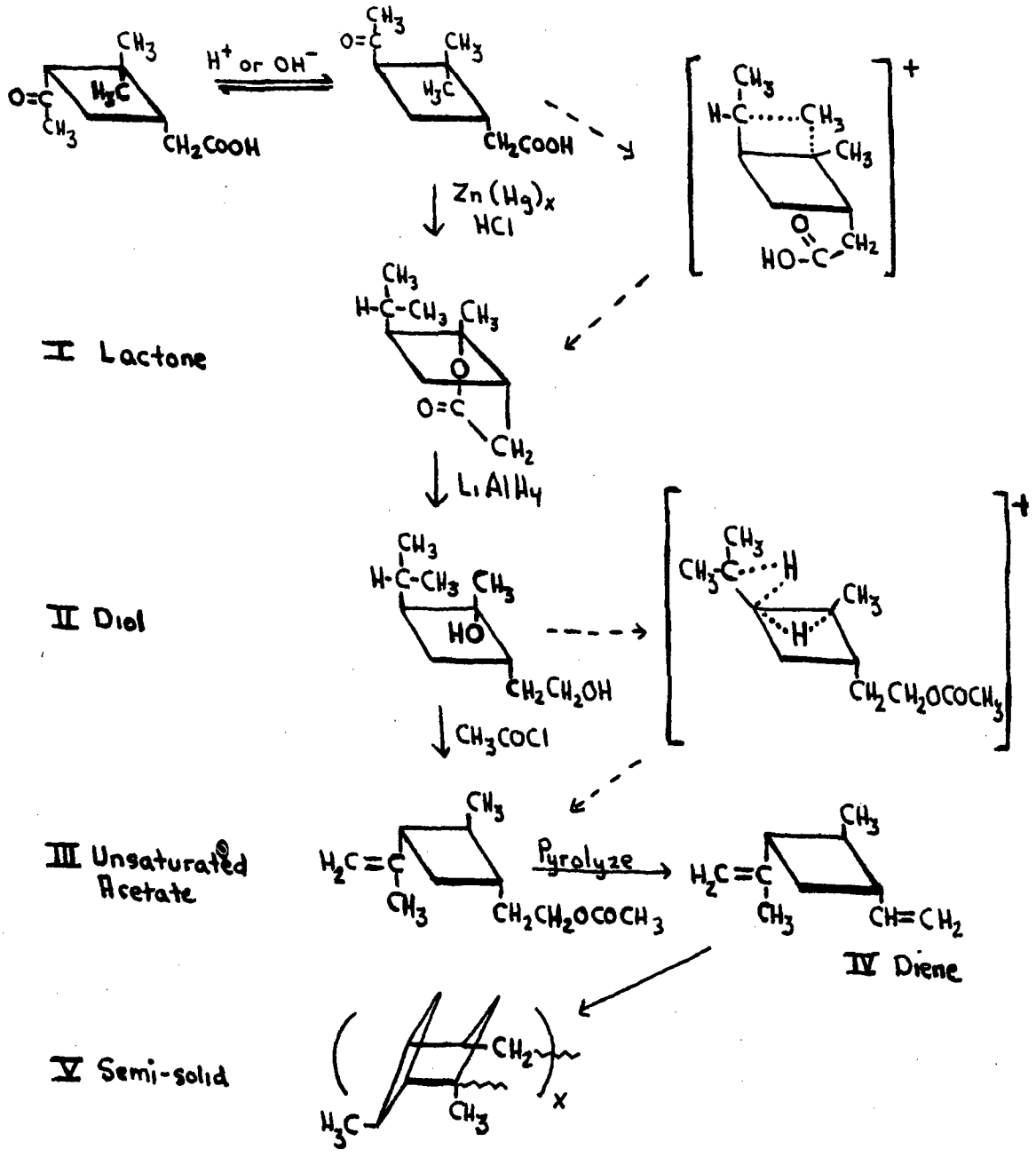


FIGURE 1

A Possible Reduction Product of Pinonic Acid and Possible Lactone Derivatives

acetyl chloride (60%) (15), reduction of the intermediate methyl cyclohexyl ketone was effected with lithium aluminum hydride (84%) (2). 1-Cyclohexylethanol was esterified with acetyl chloride (90%) (8) and 1-cyclohexylethyl acetate was pyrolyzed at 500° (3) to yield a mixture of olefins from which vinylcyclohexane, pure by G.P.C.*, (9) was fractionally distilled.

Vinylcyclohexane was polymerized with an aluminum triisobutyl-titanium tetrachloride catalyst (13) (2/1 molar ratio) to 22% conversion in bulk; higher conversions were realized with n-heptane as a solvent. Methyl ethyl ketone extracted 15-20% of polyvinylcyclohexane and this fraction was amorphous by X-ray analysis but could be oriented by slow evaporation from benzene. The remaining polymer was soluble in benzene and was crystalline as determined by X-ray analysis. An oriented fiber of polyvinylcyclohexane was prepared by extension of the heated sample. Rapid extension produced material exhibiting a 6.6Å identity period along the fiber axis while slow extension yielded a 13.2Å identity period. There are 6 monomer units per unit cell in the latter instance and 3 in the former.

The attempted polymerizations of vinylcyclohexane with benzoyl peroxide in bulk at 75° and with tin tetrachloride in a mixture of nitrobenzene and carbon tetrachloride (50/50) at 0° were unsuccessful. A catalyst of aluminum triisobutyl and titanium trichloride (2/1 molar ratio) in n-heptane at 80° and at 100° polymerized vinylcyclohexane in very poor yield.

(6) 2-Methylvinylcyclohexane and Poly-2-methylvinylcyclohexane. (J. E. Mulvaney)

o-Xylene was monobrominated and converted to o-xylyl cyanide (64%) (16) which in turn was reduced with platinum oxide in the presence of acetic anhydride to give 2-(2-methylcyclohexyl)ethylamine (60%). This amine was dimethylated with a formic acid-formaldehyde solution (59%) (39), and N,N-dimethyl-2-(2-methylcyclohexyl)ethylamine was recrystallized as a picrate salt (52%) which upon regeneration yielded pure cis or trans 2-(2-methylcyclohexyl)ethylamine (47%) as evidenced by vapor phase chromatography(9).

2-Methylvinylcyclohexane was polymerized with a 1.8/1 molar ratio of aluminum triisobutyl to titanium tetrachloride catalyst (13) to 63% conversion in heptane solution. The polymer was almost completely insoluble, the amount soluble in boiling decalin being too small a quantity to characterize. Reaction conditions may have introduced some crosslinking.

(7) 3-Methylvinylcyclohexane and Poly-3-methylvinylcyclohexane. (J. E. Mulvaney)

A Grignard reaction of 3-bromo-1-methylcyclohexane and

acetaldehyde yielded 1-(1-methylcyclohexyl)ethanol (56%) (18) which in turn was esterfied with acetyl chloride (69%) (8). 1-(1-Methylcyclohexyl)ethyl acetate was pyrolyzed (3) over Pyrex glass at 500° to yield a mixture of olefins (51%) from which pure cis or trans 3-methylvinylcyclohexane was isolated by fractional distillation.

Cis or trans 3-methylvinylcyclohexane was polymerized in n-heptane with an aluminum triisobutyl-titanium tetrachloride catalyst (13) (2/1 molar ratio) at 60-85°. Conversion was 42% and the polymer was completely soluble in benzene. An intrinsic viscosity of 0.75, a decomposition range of 276-355° and X-ray evidence of crystallinity were observed. Approximately 65% of the polymer was extracted by ether, the remaining 35% being soluble in heptane and benzene.

(8) 4-Methylvinylcyclohexane and Poly-4-methylvinylcyclohexane. (J. E. Mulvaney)

p-Cresol was hydrogenated over nickel on Kieselguhr to yield 4-methylcyclohexanol (47%) (19) which in turn was converted to 4-methylcyclohexyl bromide (25%) with phosphorous tribromide (20). The Grignard reaction of 4-methylcyclohexyl bromide with acetaldehyde yielded 1-(4-methylcyclohexyl)ethanol (55%) which was esterified with acetyl chloride (75%) (8). Pyrolysis (500° over Pyrex glass) (3) of 1-(4-methylcyclohexyl)ethyl acetate yielded a 4 component olefin mixture (63%) as evidenced by vapor phase chromatographic analysis (9) and pure cis or trans 4-methylvinylcyclohexane was isolated by fractional distillation. The mixture of isomers may include cis and trans 4-methylvinylcyclohexane, vinylidenecyclohexane and an ethylcyclohexene.

4-Methylvinylcyclohexane was polymerized with an aluminum triisobutyl-titanium tetrachloride catalyst (3/1 molar ratio) (13) in n-heptane at 75-100° to 35% conversion. The polymer was completely soluble in ether and benzene and had intrinsic viscosity of 0.45. Poly-4-methylvinylcyclohexane which was oriented by treatment with boiling butanol-1 gave a crystalline X-ray diffraction pattern.

(B). Methylenecycloalkanes

(1) Methylenecyclobutane and Its Attempted Polymerization (H. Gladstone)

The reaction of pentaerythrityl bromide with zinc in aqueous ethanol has been reported (21) to produce a mixture of methylenecyclobutane, spiropentane and 2-methylbutene-1. The preparation of pentaerythrityl bromide, its debromination with zinc in aqueous ethanol and the fractionation of the resulting hydrocarbon mixture have been carried out. Methylenecyclobutane has been isolated pure as evidenced by gas phase chromatographic analysis (9).

A novel synthetic route to methylenecyclobutane has been developed. The reaction of trimethylene dibromide and ethyl malonate yielded 1,1-dicarbethoxycyclobutane (65%) (5) which in turn was reduced with lithium aluminum hydride (83%) (2). 1,1-Dimethylolcyclobutane was converted to the ditosylate (70%) with p-toluenesulfonyl chloride in pyridine which in turn was reacted with sodium iodide in acetone to yield 1,1-bis-(iodomethyl)cyclobutane (70%). 1,1-Bis-(iodomethyl)cyclobutane yielded methylenecyclobutane on treatment with 15% potassium hydroxide in aqueous ethanol (undetermined yield).

Methylenecyclobutane was polymerized in n-heptane with an aluminum triisobutyl-titanium tetrachloride catalyst (3/1 molar ratio) (13) at 25° to 20% conversion. The polymer was soluble in ether and softened in the range 50-100°. Infrared data on polymethylenecyclobutane (potassium bromide technique) revealed that unsaturation was present in the polymer (absorption at 6.08 and 11.27 microns)(14) which may have arisen from the opening of the cyclobutane ring.

(2) Methylenecyclopentane and Its Attempted Polymerization
(A. E. Borchert)

Cyclopentylmethanol was synthesized (34%) via the Grignard reaction of cyclopentyl bromide with formaldehyde (22). This alcohol was esterified with acetyl chloride (59%) (8) and cyclopentylmethyl acetate was pyrolyzed (3) at 510° to yield methylenecyclopentane (35%) (22).

The attempted polymerization of methylenecyclopentane with an aluminum triisobutyl-titanium tetrachloride (4/1 molar ratio) catalyst (13) was unsuccessful. No attempt was made to isolate any high boiling materials which may have been formed during the polymerization runs via poly condensation and/or isomerization reactions.

(3) Methylenecyclohexane and Its Attempted Polymerization
(A. E. Borchert)

Methylenecyclohexane was obtained from the pyrolysis of cyclohexylmethyl acetate (64%) (3). A Grignard reaction of cyclohexyl bromide and formaldehyde yielded cyclohexylmethanol (44%) (22) which in turn was esterified with acetyl chloride (91%) (8) to obtain the necessary acetate. An alternate route to this monomer involved a two step hydrogenation of 1,2,5,6-tetrahydrobenzaldehyde to produce cyclohexylmethanol which was esterified and pyrolyzed (3) at 515° to yield methylenecyclohexane (64%).

Methylenecyclohexane in bulk was reacted with an aluminum triisobutyl-titanium trichloride catalyst (13) (3/1 molar ratio) at 90°. A high distilling oil was obtained (10% of initial monomer weight) which was roughly fractionated but has not been identified.

(C). Olefins Containing the Trifluoromethyl Group

(1) 3,3,3-Trifluoropropene and Its Attempted Polymerization (E. B. Davidson)

1-Trifluoromethylethanol was esterified with acetyl chloride (8) (no yield determined) and 1-trifluoromethylethyl acetate was pyrolyzed (3) at 500° to yield 3,3,3-trifluoropropene. This monomer was purified by conversion to the dibromide under the influence of strong ultraviolet irradiation followed by a zinc debromination (23). An attempted polymerization of 3,3,3-trifluoropropene with an aluminum triisobutyl-titanium tetrachloride catalyst (13) (2/1 molar ratio) in n-heptane was unsuccessful.

(2) 4,4,4-Trifluorobutene-1 (E. B. Davidson)

A reported synthetic route employing the addition of trifluoromethyl iodide to allene under the influence of ultraviolet irradiation and the reduction of the 4,4,4-trifluoro-2-iodobutene-1 adduct with zinc-magnesium in hydrochloric acid (24) was found to be of low yield. 1,1,1,3-Tetrachloropropane was converted to 1,1,1-trifluoro-3-chloropropane with antimony trifluoridedichloride (23) and this in turn was reacted with formaldehyde employing Grignard reaction conditions (54%) (25). 4,4,4-Trifluorobutanol-1 was esterified with acetyl chloride (8) (80%) and 4,4,4-trifluoro-1-butyl acetate was pyrolyzed (3) at 500° to yield 4,4,4-trifluorobutene-1.

(3) 2-Trifluoromethylpropene (E. B. Davidson)

Two moles of methylmagnesium iodide were added to ethyl trifluoroacetate, and the resulting 2-trifluoromethylpropanol-2 was dehydrated over phosphorous pentoxide to yield 2-trifluoromethylpropene (no yield determined). Polymerization attempts with an aluminum triisobutyl-titanium tetrachloride catalyst (2/1 molar ratio) (13), an n-butyllithium catalyst in petroleum ether and a lithium in liquid ammonia catalyst were unsuccessful.

(4) Trifluoromethylacrylonitrile (E. B. Davidson)

The elements of hydrogen cyanide were added to trifluoroacetone to obtain trifluoroacetonecyanohydrin (78%) which was esterified with acetyl chloride (80%) (8). 1-Trifluoromethyl-1-cyanoethyl acetate was pyrolyzed (3) at 500° and trifluoromethylacrylonitrile was obtained (50%). Trifluoromethylacrylonitrile was polymerized to a highly colored polymer of undetermined structure by liquid ammonia. Piperidine and aniline both failed to polymerize this monomer.

(D). Termination in Ziegler Polymerization of Vinylcyclohexane (J. E. Mulvaney)

In a number of examples in which hydrogen is transferred as a proton, the rate of transfer was found to be 4-10 times as great as deuterium (26) (27). Rates for transfer of hydrogen and deuterium atoms are less well known. An attempt was made to utilize the hydrogen-deuterium isotope effect in a study of the polymer chain termination steps in the aluminum triethyl-titanium tetrachloride system. There is reason to believe that the hydrogen atom alpha to the ring is the atom involved in polymer chain termination since Natta (28) has reported that isotactic polypropylene has terminal vinylidene double bonds.

Alpha-deuterovinylcyclohexane was synthesized from methyl cyclohexyl ketone and lithium aluminum deuteride, (92%), the resultant 1-alpha-deuterocyclohexylethanol was esterified with acetyl chloride (95%) (8) and pyrolyzed at 500° (3) to yield a mixture of olefins (68%) from which alpha-deuterovinylcyclohexane was obtained pure by G.P.C.* (9) via fractional distillation in a 75 theoretical plate concentric tube column (34% based on acetate).

The solution polymerization of vinylcyclohexane and alpha-deuterovinylcyclohexane in n-heptane was carried out in sealed pyrex tubes under vacuum. A comparison of results with deuterated and undeuterated monomer is given in Table I.

TABLE I

Comparison of Deuterated and Undeuterated Monomers at 70°

Run No.	(1) Monomer	$AlEt_3$ moles/ℓ.	$TiCl_4$ moles/ℓ.	Al/Ti molar ratio	Time (hrs.)	% Conv.	Intrinsic Viscosity
2	H	0.33	0.15	-	24.00	74	1.00
14	D	0.33	0.18	2.20	24.00	46	1.05
12	H	0.34	0.24	1.38	14.00	70.1	0.69
11	D	0.34	0.23	1.46	14.00	73.5	0.71
8	H	0.31	0.41	0.75	14.00	46.2	0.22
13	D	0.30	0.41	0.73	14.00	52.1	0.24

(1) H, vinylcyclohexane D, alpha-deuterovinylcyclohexane
monomer concentration = 2.10 moles/ℓ.

It may be seen in Table I that no detectable isotope effect in the molecular weight of the polymer is observed from aluminum to titanium ratios of 2.3 to 0.73. Three possibilities present themselves as to why an isotope effect was not observed.

(1) The propagation rate for the two monomers may be different. In the expression $DP=k_p/k_t$ (k_p, propagation rate constant; k_t, termination rate constant) a decrease in the termination rate for the deuterated monomer may have been offset by a decrease in the propagation rate.

(2) If transfer involves the concomitant breaking of two or more bonds, it may be impossible to detect an isotope effect.

(3) In the polymerization of vinylcyclohexane it is not known how large a part terminal double bond formation plays in polymer termination.

The effect of titanium tetrachloride concentration on intrinsic viscosity may be seen in Table II. For aluminum triethyl concentrations between 0.31 and 0.35 mole/ℓ. the decrease of molecular weight with increase in titanium tetrachloride concentration indicates a transfer or termination step with some form of titanium.

TABLE II

Effect of $TiCl_4$ on Intrinsic Viscosity of Polyvinylcyclohexane

Run No.	$AlEt_3$ moles/ℓ.	$TiCl_4$ moles/ℓ.	Al/Ti molar ratio	Time (hrs).	% Conv.	Intrinsic Viscosity
2	0.33	0.15	2.2	24.00	74	1.00
1	0.34	0.15	2.3	24.00	69	0.96
10	0.35	0.20	1.7	14.00	69.3	0.77
12	0.34	0.24	1.4	14.00	70.1	0.69
6	0.32	0.32	1.0	14.00	62.3	0.43
8	0.31	0.41	0.75	14.00	46.2	0.22

monomer concentration 2.10 moles/ℓ.

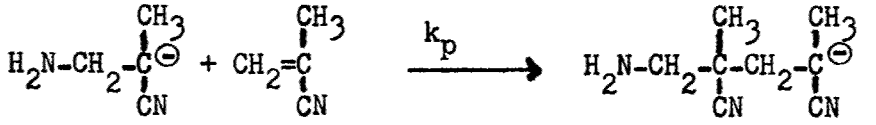
(E). Alkali Metal Polymerizations (H. Yuki)

The polymerization of methacrylonitrile by potassium in liquid ammonia was found to differ from the lithium catalyzed polymerization of this monomer in ammonia. Potassium catalysis yielded polymethacrylonitrile of considerably lower DP; values of 100-300 were observed and these were independent of both initial monomer and catalyst concentrations. Potassium amide initiated the polymerization of methacrylonitrile as rapidly as potassium and yielded polymethacrylonitrile of the same DP magnitude which was found to be independent of the methacrylonitrile and potassium concentrations.

A small amount of isobutyronitrile was detected by gas phase chromatography (9) among the reaction products of methacrylonitrile and potassium in liquid ammonia suggesting the following mechanism:

$$CH_2=\overset{CH_3}{\overset{|}{C}}-CN + 2K^0 + 2NH_3 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}H-CN + 2K^{\oplus} + 2NH_2^{\ominus} \qquad (3)$$

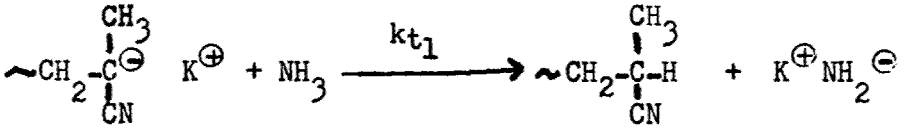
$$NH_2^{\ominus} + CH_2=\overset{CH_3}{\overset{|}{C}}-CN \xrightarrow{k_i} H_2N-CH_2-\overset{CH_3}{\overset{|}{\underset{CN}{\underset{|}{C}}}}{}^{\ominus} \qquad (4)$$



(5)

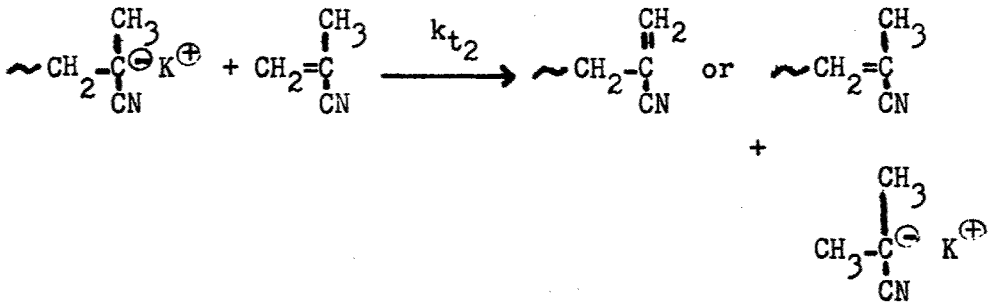
These results are similar to those obtained by Higginson and Wooding for the polymerization of styrene by potassium (29) and by potassium amide (30) in liquid ammonia.

The non-dependency on catalyst concentration of DP in potassium catalysis and the formation of isobutyronitrile could arise from a termination step involving reaction with solvent.



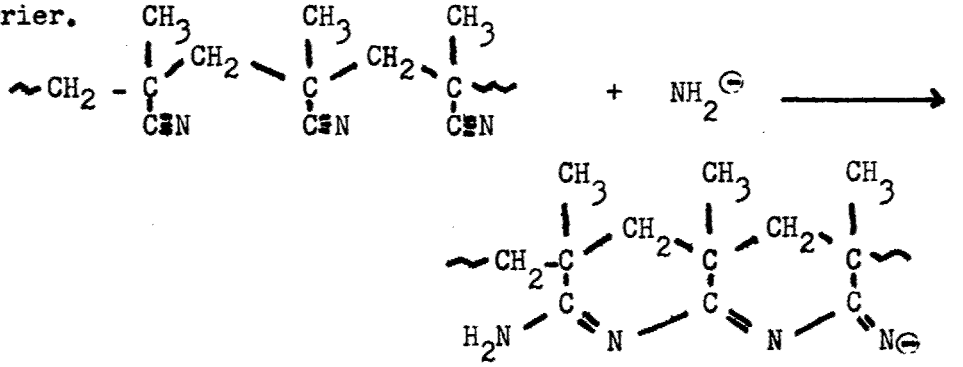
(6)

This termination is more facile than direct reduction (eq. 3) and the amide ion produced is an initiator for a new polymer chain (eq. 4). There is some dependency of the DP on monomer concentration consistent with this mechanism to produce some amide ion. Considerable transfer with monomer is also consistent with the experimental results. Thus, this would involve a chain transfer reaction between the growing chain and a monomer unit as indicated below (eq. 7).



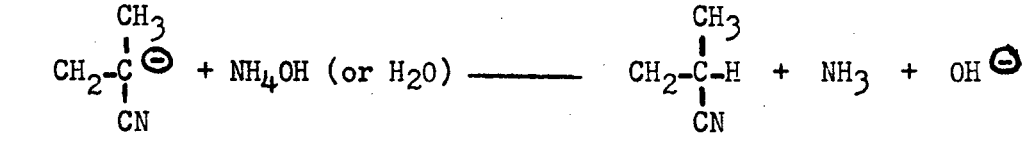
(7)

When the ratio of methacrylonitrile to potassium amide was decreased by lowering the initial monomer concentrations, it was found that some of the resultant polymers were cross-linked and highly colored. Color formation may reside in cyclic structures produced by amide attack at a nitrile group, the propagating carbanion being a potential chain branching carrier.



(8)

The polymerization of methacrylonitrile proceeded rapidly and quantitatively in the presence of a small amount of water in both the potassium- and potassium amide-ammonia systems. The DP was independent of water concentrations smaller than the potassium or potassium amide concentration. When water was added to the monomer in ammonia solution prior to the addition of potassium or potassium amide or when water was added in excess of either of these alkali metal catalyst systems, the DP of polymethacrylonitrile was sharply reduced. In addition, color formation in these polymerizations was diminished with increasing water concentration. Hydroxide ion may initiate the polymerization of methacrylonitrile and either water or ammonium hydroxide may terminate polymethacrylonitrile.



(9)

Potassium hydroxide polymerized methacrylonitrile rapidly in ammonia and the polymethacrylonitrile isolated was colorless. The rate of polymerization was directly proportional to the hydroxide concentration and the DP was essentially independent of hydroxide concentration in the catalyst range investigated. Water had a pronounced but as yet undetermined effect on this system.

(III). SUMMARY

The pyrolysis of 1-cyclopropylethyl acetate and 1-cyclobutylethyl acetate yielded mixtures of olefins. The Clemmensen reduction of pinonic acid yielded a lactone which has tentatively been identified as 3-hydroxy-4-isopropylcyclobutylacetic acid lactone. Vinylcyclopentane has been synthesized and polymerized with a Ziegler-Natta catalyst to give a crystalline polymer. Vinylcyclohexane has also been polymerized with a Ziegler-Natta catalyst to give a crystalline polymer. The isomeric 2,3 and 4-methylvinylcyclohexanes have been synthesized and polymerized with a Ziegler-Natta catalyst. Poly-3- and 4-methylvinylcyclohexanes were crystalline while poly-2-methylvinylcyclohexane apparently was crosslinked. Methylenecyclobutane was prepared and polymerized with a Ziegler-Natta catalyst apparently with ring opening. Methylenecyclopentane and methylenecyclohexane were synthesized, and these monomers failed to yield detectable polymer with a Ziegler-Natta catalyst. 3,3,3-Trifluoropropene and 2-trifluoromethylpropene were prepared, and attempts at their polymerization with a Ziegler-Natta catalyst were unsuccessful. Trifluoromethylacrylonitrile was synthesized and polymerized by ammonia.

An isotope effect on the molecular weight of poly-alpha-deuterovinylcyclohexane polymerized with a Ziegler-Natta catalyst was not observed. Evidence for a possible transfer or termination step with some form of titanium was found.

The polymerization of methacrylonitrile by potassium in ammonia differed from the lithium catalyzed polymerization. Hydroxide ion initiated the polymerization of methacrylonitrile in ammonia and water was

found to significantly effect alkali metal catalysis.

BIBLIOGRAPHY

1. R. V. Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, J. Am. Chem. Soc., 71 , 3595 (1949).
2. R. F. Nystrom and W. G. Brown, J. Am. Chem. Soc., 69,1197(1947).
3. W. J. Bailey and C. King, ibid., 77, 75 (1955).
4. E. E. Royals, J. Org. Chem., 23, 1822 (1958).
5. J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry", Prentice-Hall, New York,1950, p. 304.
6. A. Lebovits, Ph.D. Thesis, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., p. 94.
7. W. H. Perkin Jun. and W. Sinclair, J. Chem. Soc., 50, (1892).
8. W. J. Bailey, F. E. Naylor and J. J. Hewitt, J. Org. Chem., 22, 1076 (1957).
9. Perkin Elmer Model 154-B. A "B" column was employed for olefins and an "A" column for all other materials.
10. V. M. Loeblich, F. C. Magne and R. R. Mod, Ind. Eng. Chem., 47, 855 (1955).
11. O. L. Brady and J. N. E. Day, J. Chem. Soc., 117(1934).
12. J. R. Van der Bij and E. C. Kooyman, Rec. trav. Chim., 71, 837 (1952).
13. G. Natta, J. Pasquon and E. Giachetti, Angew. Chem., 69, 213 (1957).
14. L. J. Bellamy in "The Infrared Spectra of Complex Molecules", John Wiley and Sons, Inc., 1954.
15. R. E. Christ and R. C. Fuson, J. Am. Chem. Soc., 59, 893 (1937).
16. M. S. Newman, J. Am. Chem. Soc., 62, 2295 (1940).
17. H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, J. Am. Chem. Soc., 55, 4571 (1931).
18. S. van Woerden, Rec. trav. chim., 45, 124 (1929).
19. K. von Auwers, R. Hinterseber and W. Trepmann, Ann., 410, 257 (1915).
20. J. Boeseken and B. B. C. Felix, Ber., 62, 1314 (1929).
21. J. M. Derfer, C. E. Boord and K. W. Greenlee, J. Am. Chem. Soc., 71, 175 (1949).
22. R. Ya. Levina and N. N. Mezentsova, Org. Khim., 7, 241 (1950).
23. A. Henne and N. Nager, J. Am. Chem. Soc., 73, 1042 (1951).
24. R. Haszeldine, K. Leedham and B. Steele, J. Chem. Soc., 2 (1954).
25. H. Walbersky, M. Baum and D. Loncrini, J. Am. Chem. Soc., 77, 3637 (1955).
26. W. F. K. Wynne-Jones, J. Chem. Phys., 2, 381 (1934).

27. F. H. Westheimer and N. Nicolaides, J. Am. Chem. Soc., 71, 25 (1949).
28. G. Natta, P. Pino, E.Mantica, F. Danusso, G. Mazzanti and M. Peraldo, Chimeca e industria, 38, 124 (1956).
29. N. S. Wooding and W. C. E. Higginson, J. Chem. Soc., 1178 (1952).
30. W. C. E. Higginson and N. S. Wooding, J. Chem. Soc., 760 (1952).

* G. P. C. Gas Phase Chromatography; H. H. Hausdorff and N. Brenner, The Oil and Gas Journal, June 30, July 14, July 21, and August 4, 1958.

FLUORINE-CONTAINING CONDENSATION POLYMERS AND RESINS

CARL J VERBANIC*

HOOKER CHEMICAL CORPORATION

ABSTRACT

The ultimate goal of the investigations described is the determination of the effect of fluorine and fluorine content on the thermal and oxidative stability of unsaturated polyester laminating resins. An additional function is to aid in the investigations of the perfluorinated amidine polymers currently of interest to Wright Air Development Center.

Polyesters and polyester resin laminates have been prepared using fluorinated glycols as a component of the polyester. The laminates have been aged at elevated temperatures and physical properties measured before and after aging. Comparison of these aging results with polyesters containing hydrocarbon glycol components of the same carbon chain length indicate a noticeable improvement in retention of physical properties of the fluorinated materials over their hydrocarbon analogues. This is true after aging for up to 200 hours at 260°C (500°F) and testing both at room and elevated temperatures (260°C). Room temperature flexural strengths of the fluorinated polyester laminates have decreased only about 35% after 100 hours aging while hydrocarbon glycol polyester have lost 70% of their initial room temperature strength. Initial high temperature strengths (260°C) of the fluorinated polyester laminates have decreased only 10-15% while the corresponding hydrocarbon glycol polyesters have lost 60-70% of their initial high temperature flexural strength.

The report also describes the research performed on the preparation of certain fluorine-containing compounds for use as starting materials for the preparation of polyesters and cross-linking monomers.

A new synthesis of perfluoroglutaronitrile is described and efforts to improve the yields of the dehydration of perfluoroglutaramide are given.

* The author acknowledges the collaboration of Dr David Knutson and the assistance of Mr A M Teller, Mr R N DeLeo and Mr J J Zedick in the performance of the work reported on here under WADC Contract AF 33(616)-5548.

DISCUSSION

A. FLUORINE-CONTAINING UNSATURATED POLYESTER RESINS

As mentioned previously, the ultimate goal of the research being performed by the Hooker Chemical Corporation under contract with the Materials Laboratory, Wright Air Development Center, is to determine the effect of fluorine and fluorine content on the thermal and oxidative stability of unsaturated polyester laminating resins. The basic premises for the program currently under investigation are that esters or polyesters containing no β C-H atoms in the alcohol or glycol segment are not subject to the same pyrolytic degradation at elevated temperatures as are esters containing β C-H groups. Further, the presence of fluorine increases the oxidative stability of compounds and the degree of stability is dependent upon fluorine content and location in the molecule. The latter premise would become important both with regard to the polyester itself and the cross-linking monomer used in the preparation of the resin.

Since there are so many variables contributing to the overall composition of a polyester resin laminate, any attempt to establish the effect of a change in the molecular structure of any of the components must of necessity be done on a comparative basis. Our initial program has been mainly concerned with the substitution of fluorine for hydrogen in the glycol portion of a polyester component and the effect of this substitution on the high temperature aging characteristics of their derived laminates.

The laboratory work to date has been primarily directed toward the preparation of intermediates, establishing esterification conditions for the fluorinated glycols and preparation of polyesters from the corresponding hydrocarbon glycols. Earlier investigations into the polymerization reactions of the fluorinated glycols had indicated that the acid chloride method was the best for preparing these polyesters.[1,2] However, since the higher molecular weight polyesters were not required for the preparation of laminating resins, several attempts were made to prepare the polyesters by direct esterification procedures.

Direct esterification of hexafluoropentane diol (HFPD) and fumaric acid was found to be unsuccessful, primarily because of the insolubility of the fumaric acid in hot HFPD. No appreciable esterification had occurred after heating the mixture for one week at 200°C. Satisfactory polyesters were prepared from HFPD and maleic anhydride catalyzed by either $ZnCl_2$ or p-toluene sulfuric acid. The esterification reaction, however, required a reaction time of 72 hours at elevated temperatures which was not altogether desirable. Surprisingly enough, the incidence of gelation during these esterifications was low although temperatures of 180-200°C were held for long periods of time.

To prepare the fluorinated polyesters with suitable characteristics for compounding with cross-linking monomers, it became necessary to prepare low molecular weight polyesters by reacting an excess quantity

of the fluorinated glycol with fumaryl chloride. The excess of fluorinated glycol to be used to obtain a polyester of the desired molecular weight range was calculated using Flory's equations.[3] Approximations to the molecular weights of these polyesters were also made by comparing the melt viscosities of these polyesters with the melt viscosities of polyesters made from maleic anhydride and the glycols and for which number average molecular weights were determined by end-group titrations.

The initial investigations in preparing the hydrocarbon glycol polyesters were mainly concerned with the reaction with maleic anhydride. This method proved to be unsatisfactory for a number of reasons. It was difficult to esterify the hydrocarbon glycols, 1,4-butane diol, 1,5-pentane diol and 1,6-hexane diol to the low acid number polyesters desired because of the loss of glycols either by volatization or cyclization. Attempts to lower the acid number by heating to elevated temperatures for prolonged periods increased the incidence of gelation. The acid chloride method was subsequently used to prepare these polyesters in the same manner as described for the fluorinated glycols. Due to the exothermic reaction which occurred, it was necessary to run the reaction by slowly adding fumaryl chloride to a calculated excess of the glycol in a benzene solution. After the addition of the fumaryl chloride was completed, the reaction was allowed to warm up and then heated to benzene reflux until HCl evolution ceased. The solvent was removed by means of a vacuum pump.

One further modification with regard to polyester composition which became necessary as the laminate testing program was being developed was the substitution of isophthalate segments for fumarate segments. Due to the high degree of crystallinity of the polyesters, their relatively high melting points and further, the insolubility of the fluorinated polyesters in the cross-linking monomers, it was necessary to prepare acetone solutions of all the resins for the impregnation of glass cloth. During the course of the evaluation of the laminates prepared from these resins, it became apparent that the optimum properties had not been attained, presumably because of one or another of the problems cited above. To reduce the crystallization problem, polyesters were prepared in which 25 mole percent of the fumaryl chloride was replaced by isophthaloyl chloride. The same procedure was followed in the preparation of these polyesters.

As mentioned previously, acetone solutions of the polyester resins were necessary for impregnation of the glass cloth. To prepare the laminates, glass cloth was passed through an acetone solution of the resin until the desired quantity of resin was on the glass. The resin was composed of the polyester, a cross-linking monomer, and the catalysts. The cross-linking monomer was either triallyl cyanurate, diallyl isophthalate or diallyl terephthalate, known for their high temperature properties. The acetone was removed from the glass cloth by placing the impregnated cloth in a vacuum oven-heated to 50-60°C for 30 minutes. After this time, the weight of the impregnated cloth remained fairly constant. This procedure proved to be much more satisfactory than one in which the acetone was removed by heating in an oven at 90°C. Constant

weight could not be obtained using the latter method.

The catalyst system used in the preparation of laminates was particularly satisfactory for the cure cycles eventually employed. Luperco ATC (2%) and tert-butyl perbenzoate (1%) were the mixture of catalysts chosen. The primary cure was accomplished by heating in a press at 80°C for 30 minutes, followed by an oven post cure for four hours employing step-wise elevation of the temperature. The cycle employed was one hour each at 120°C, 170°C, 200°C, and 260°C. The room temperature flexural strengths of the laminates so prepared compared favorably with the strengths of laminates reported in the literature and employing the monomers used in this work.[4]

The laminates were aged in a forced air circulating oven at 260°C (500°F) for extended periods of time. After cooling to room temperature, the aged laminates were weighed to determine weight losses and the flexural strengths were measured. Table I gives all the pertinent information concerning the preparation of the laminates and their high temperature aging.

It was found that the fluorinated polyester resin laminates had a higher retention of room temperature flexural strengths after 100 hours aging at 260°C (500°F) than did the corresponding hydrocarbon glycol polyester laminates. In fact, the fluorinated glycol polyester resin laminates lose only 25-38% of their initial flexural strength after the indicated aging while the corresponding hydrocarbon glycol polyesters lose 66-75% of their initial flexural strengths after aging at the same temperature for the same period of time. These results were obtained with laminates prepared from either triallyl cyanurate, diallyl isophthalate or diallyl terephthalate as the cross-linking monomer. Figure 1 gives room temperature flexural strengths vs. aging time at 260°C for triallyl cyanurate laminates while Figure 2 gives the same type data for diallyl isophthalate cross-linked resins, and Figure 3 presents data for diallyl terephthalate cross-linked resins. Figure 4 presents data for several laminates in which the difference in molecular weights of the glycols was taken into consideration by equalizing the level of unsaturation in the resin. In these data, a fluorinated resin containing 60 pts. triallyl cyanurate (TAC) corresponds to a hydrocarbon polyester resin with 40 pts. TAC and likewise the 50 pts. TAC for the fluorinated resin laminate corresponds to the 33 pts. TAC hydrocarbon glycol polyester resin.

A number of the laminates were aged for 200 hrs. at 500°F., As was the case for the laminates aged 100 hrs. the fluorinated glycol polyester laminates still retain an appreciable amount of strength as compared to the hydrocarbon glycol polyester laminates. For example, laminates 17-A and 18-A have flexural strengths at room temperature of 24,000 and 22,600 psi after 200 hours aging at 500°F while the corresponding hydrocarbon glycol polyester laminates, 19-B and 20-A, have strengths of 10,100 and 8,700 psi after aging for the same length of time at the same temperature. These laminates were prepared with triallyl cyanurate as the monomer. Similar results were obtained for laminates prepared using diallyl

isophthalate as the cross-linking monomer (see laminate 23-B as compared to laminate 22-B). The loss in flexural strength of the fluorinated glycol polyesters is approximately 50% of their initial room temperature flexural strengths, whereas the hydrocarbon glycol polyesters have lost about 80% of their initial room temperature flexural strength after aging 200 hours at 500°F.

An attempt was made to determine the difference, if any, in the high temperature aging characteristics of the laminates based on the difference in the chain lengths of the glycols studied. Figure 5 presents data on the percentage loss of room temperature flexural strength vs. hours of aging at 500°F for triallyl cyanurate cross-linked laminates prepared from the 4, 5 and 6 carbon chain glycol polyesters and their corresponding fluorinated analogues tetrafluorobutane diol, hexafluoropentane diol and octafluorohexane diol. Several of the curves represent average values from more than one laminate. The conclusion may be drawn that no appreciable difference exists between the laminates based on chain length of the glycols in either the hydrocarbon or fluorinated series but a significant difference exists between the fluorinated glycol polyesters which lose 35.5 to 38.5% of their initial strengths after 100 hours at 260°C and the hydrocarbon glycol polyesters which lose 68.5 to 71% of their initial flexural strengths after the same length of time at the same temperature.

The results presented so far would seem to indicate that polyester resins incorporating the fluorinated glycol segment have better high temperature aging characteristics than the corresponding hydrocarbon glycol polyester resin laminates. This is true if only retention of flexural strength were considered. Weight loss data would seem to indicate otherwise, at least when triallyl cyanurate is the cross-linking monomer. In these cases the fluorine containing laminates have undergone a greater weight loss than the corresponding hydrocarbon glycol polyester laminates. For example HFPD polyester have lost 20-22% of their weight (based on laminate; see Table I, laminates 10-A, 10-B, 11-A, 17-A, 18-A, 41-A) while the corresponding pentane diol polyesters have only undergone weight losses of 14-18% (see laminates 13-A, 14-A and 20-A). With diallyl isophthalate or diallyl terephthalate as the cross-linking monomer, the reverse is true; that is, the hydrocarbon glycol polyester laminates undergo a greater loss in weight (see laminates 15-A, 44-A) than the fluorinated glycol polyester laminates (see laminates 16-A, 42-A, 43-A).

The differences in the retention of flexural strengths of the fluorinated glycol polyester laminates and the hydrocarbon glycol polyester laminates when triallyl cyanurate was the cross-linking agent are difficult to interpret when the weight loss data are examined. It would have been expected that the results would have paralleled each other as is the case when diallyl isophthalate or diallyl terephthalate is the cross-linking monomer. For these reasons, and because of the limited amount of data actually available, no attempt has yet been made to interpret these data. Furthermore, it is not at all certain as to the importance of the weight loss in view of the flexural strength retention observed for the fluorinated glycol laminates.

TABLE I

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex. Str. x 10-3 R.T.	Flex. Str. After Aging at 260°C (Weight Losses Based on Laminates) 8 Hrs	25 Hrs	50 Hrs	100 Hrs	200 Hrs
9-D	BD - FC, IPC 75:25	TAC	53.1	47.1 (6.2)	32.1 (9.9)	28.5 (12.0)	20.8 (14.7)	
14-A	PD - FC, IPC 75:25	TAC	35.6	29.2 (8.1)	19.2 (12.2)	13.3 (15.0)	10.1 (17.6)	
13-A	PD - FC, IPC 75:25	TAC	35.6	33.9 (8.2)	17.4 (12.5)	12.3 (15.5)	10.6 (18.6)	
10-A	HFPD-FC, IPC 75:25	TAC	40.1	39.6 (6.1)	35.1 (12.6)	31.8 (18.1)	27.6 (21.5)	
10-B	HFPD-FC, IPC 75:25	TAC	39.6	38.2 (6.4)	31.3 (13.5)	29.7 (17.3)	26.9 (21.8)	
11-A	HFPD-FC, IPC 75:25	TAC:DAN 50:50	40.9	37.3 (8.6)	32.7 (15.3)	30.8 (18.6)	27.3 (22.2)	
15-A	PD-FC, IPC 75:25	DAIP	44.2	34.3 (10.9)	24.0 (19.3)	17.6 (22.2)	10.5 (23.6)	
16-A	HFPD-FC, IPC 75:25	DAIP	47.1	46.1 (3.1)	37.3 (11.0)	36.5 (16.2)	34.4 (20.1)	
12-A	HFPD-MA, 2FHET	TAC	59.6	50.4 (6.1)	40.5 (13.3)		28.2 (18.4)	

TABLE I (continued)

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex. Str. x 10^{-3} R.T.	Flex. Str. After Aging at 260°C (Weight Losses Based on Laminate) 8 Hrs	25 Hrs	50 Hrs	100 Hrs	200 Hrs
17-A	HFPD-FC,IPC 75:25	TAC 50:50	46.1	47.3 (5.7)	36.9 (12.3)	34.7 (15.3)	32.1 (20.6)	24.0 (30.0)
18-A	HFPD-FC,IPC 75:25	TAC 60:50	49.7	44.6 (4.8)	37.3 (10.9)	33.2 (16.3)	31.9 (20.0)	22.6 (23.2)
19-B	PD - FC,IPC 75:25	TAC 50:33	44.9	37.4 (6.2)	29.5 (11.3)	18.1 (14.2)	12.8 (16.5)	10.1 (19.8)
20-A	PD - FC,IPC 75:25	TAC 50:40	44.1	33.1 (6.6)	21.6 (10.3)	17.6 (13.3)	16.1 (13.6)	8.7
22-B	PD - FC,IPC 75:25	DAIP	46.9	45.9 (6.5)	32.8 (17.3)	22.3 (21.5)	13.4 (22.2)	8.0 (25.6)
23-B	HFPD-FC,IPC 75:25	DAIP	50.2	41.0 (3.1)	39.5 (9.7)	35.1 (15.9)	29.5 (19.6)	24.9 (23.8)
24-B	PD - FC,IPC 75:25	DAN:DAIP 50:50	47.2	41.7 (7.6)	23.4 (14.5)	12.7 (17.4)	9.9 (18.9)	6.0 (20.8)
25-A	BD - FC,IPC 75:25	TAC	35.2	31.0 (5.6)	24.6 (11.2)	13.8 (14.3)	11.0 (16.0)	9.1 (18.5)
27-A	BD - FC,IPC	DAIP	35.5	34.4 (6.6)	24.4 (18.0)	16.8 (23.2)	12.8 (26.0)	7.2 (28.0)

TABLE I (continued)

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex. Str. x 10^{-3} R.T.	Flex. Str. After Aging at 260°C (Weight Losses Based on Laminates) 8 Hrs	25 Hrs	50 Hrs	100 Hrs	200 Hrs
26-A	HD - FC, IPC 75:25	TAC	40.9	37.7 (6.3)	22.2 (11.4)	16.4 (14.1)	12.8 (16.6)	7.7 (19.5)
28-A	HD - FC, IPC 75:25	DAIP	50.0	43.7 (8.0)	25.5 (18.1)	18.7 (20.5)	11.9 (21.8)	
23-A	HFPD-FC, IPC 75:25	DAIP	40.5	38.6	-	31.6	26.6	
24-A	PD-FC, IPC 75:25	DAN-TAC 50-50	44.5	32.0	-	14.7	9.4	
31-A	TFBD-FC, IPC 75:25	TAC	30.0	-	26.2 (11.1)	24.6 (18.1)	19.2 (20.8)	
29-A	OFHD-FC, IPC 75:25	TAC	31.9	-	24.9 (15.3)	20.7 (20.3)	17.5 (24.3)	
22-A	PD - FC, IPC 75:25	DAIP	49.4	39.6	-	14.9	9.2	
21-A	BD - FC, IPC 75:25	DAIP	50.6	39.7	-	17.8	11.6	
29-B	OFHD-FC, IPC 75:25	TAC	36.5	30.2 (6.3)	26.6 (12.3)	25.0 (17.1)	23.5 (21.3)	
31-B	TFBD-FC, IPC	TAC	33.7	26.6 (4.7)	28.0 (9.7)	23.6 (14.4)	20.0 (18.7)	

TABLE I (continued)

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex. Str. x 10^{-3} R.T.	Flex. Str. After Aging at 260°C (Weight Losses Based on Laminates) 8 Hrs	25 Hrs	50 Hrs	100 Hrs	200 Hrs
43-A	HFPD-FC,IPC 75:25	DATP	37.4	36.4 (3.0)	29.1 (11.6)	27.1 (15.8)	25.5 (20.0)	
44-A	PD - FC,IPC 75:25	DATP	35.9	36.9 (7.2)	23.6 (19.6)	16.1 (23.1)	9.5 (25.6)	
41-A	HFPD-FC,IPC 66:34	TAC	41.7	-	38.1 (12.4)	33.6 (16.6)	28.0 (20.3)	
42-A	HFPD-FC,IPC 66:34	DAIP	50.9	44.2 (2.9)	34.5 (10.5)	38.0 (14.3)	32.0 (18.5)	

- - - - -

Catalyst
2% Luperco ATC
1% tert-Butyl perbenzoate

Cure Schedule
30' at 80°C (press)
60' at 120°C (oven)
60' at 175°C (oven)
60' at 200°C (oven)
60' at 260°C (oven)

BD - Butane diol
PD - Pentane diol
HD - Hexane diol
HFPD - Hexafluoropentane diol
OFHD - Octafluorohexane diol
TFBD - Tetrafluorobutane diol
DAN - Diallyl Nadate

TAC - Triallyl cyanurate
DAIP - Diallyl isophthalate
DATP - Diallyl terephthalate
FC - Fumaryl chloride
IPC - Isophthaloyl chloride
MA - Maleic anhydride
2FHET - Difluoro HET Anhydride

Note: All panels made with 6 plies 181 Volan A fabric. Flexure tests conducted on specimens 1/2" x 3 1/2" x thickness with 1 1/4 " span.

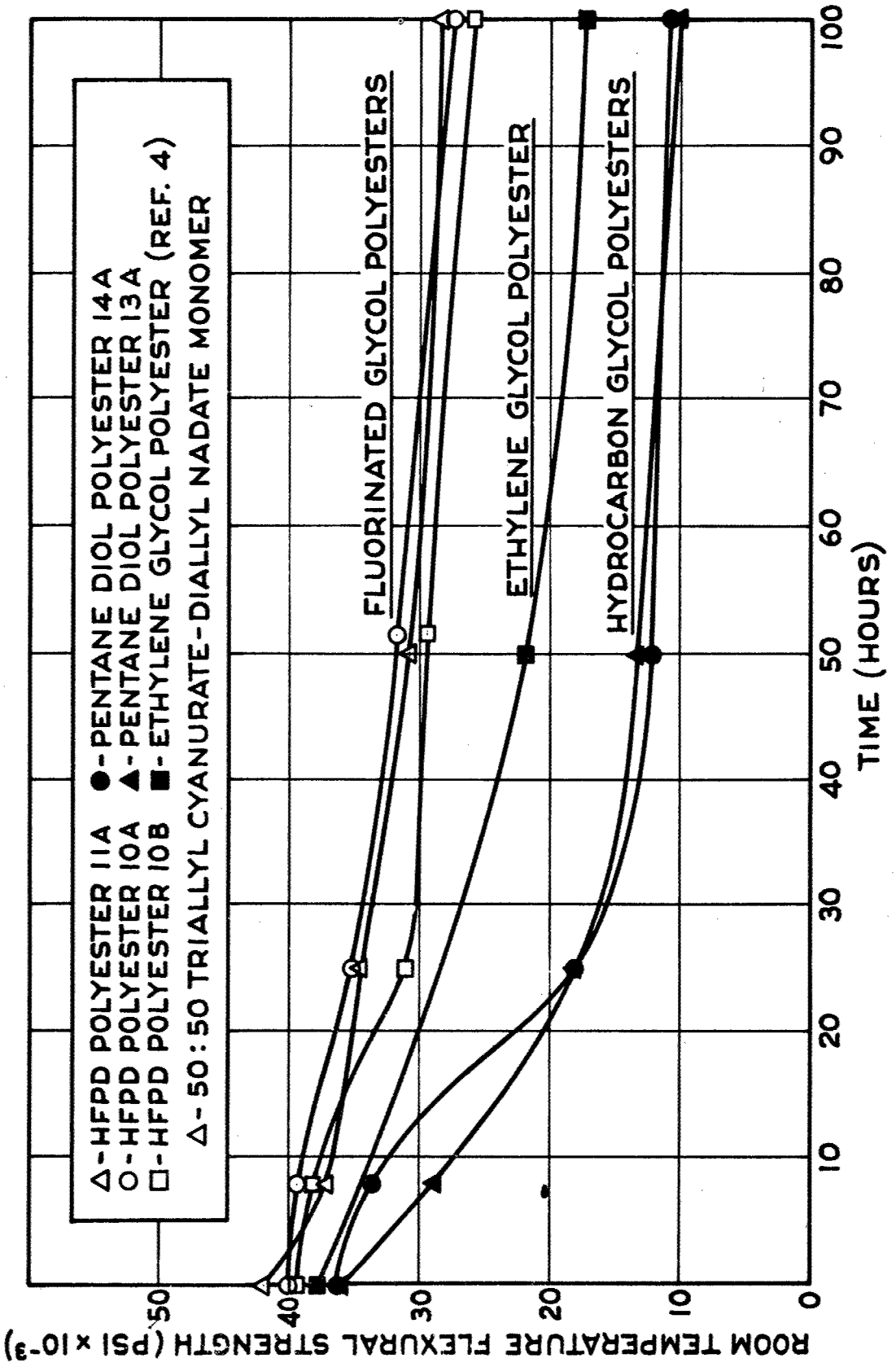


FIG. 1

ROOM TEMPERATURE FLEXURAL STRENGTH VS.
HOURS OF AGING AT 260°C.-TRIALLYL CYANURATE MONOMER

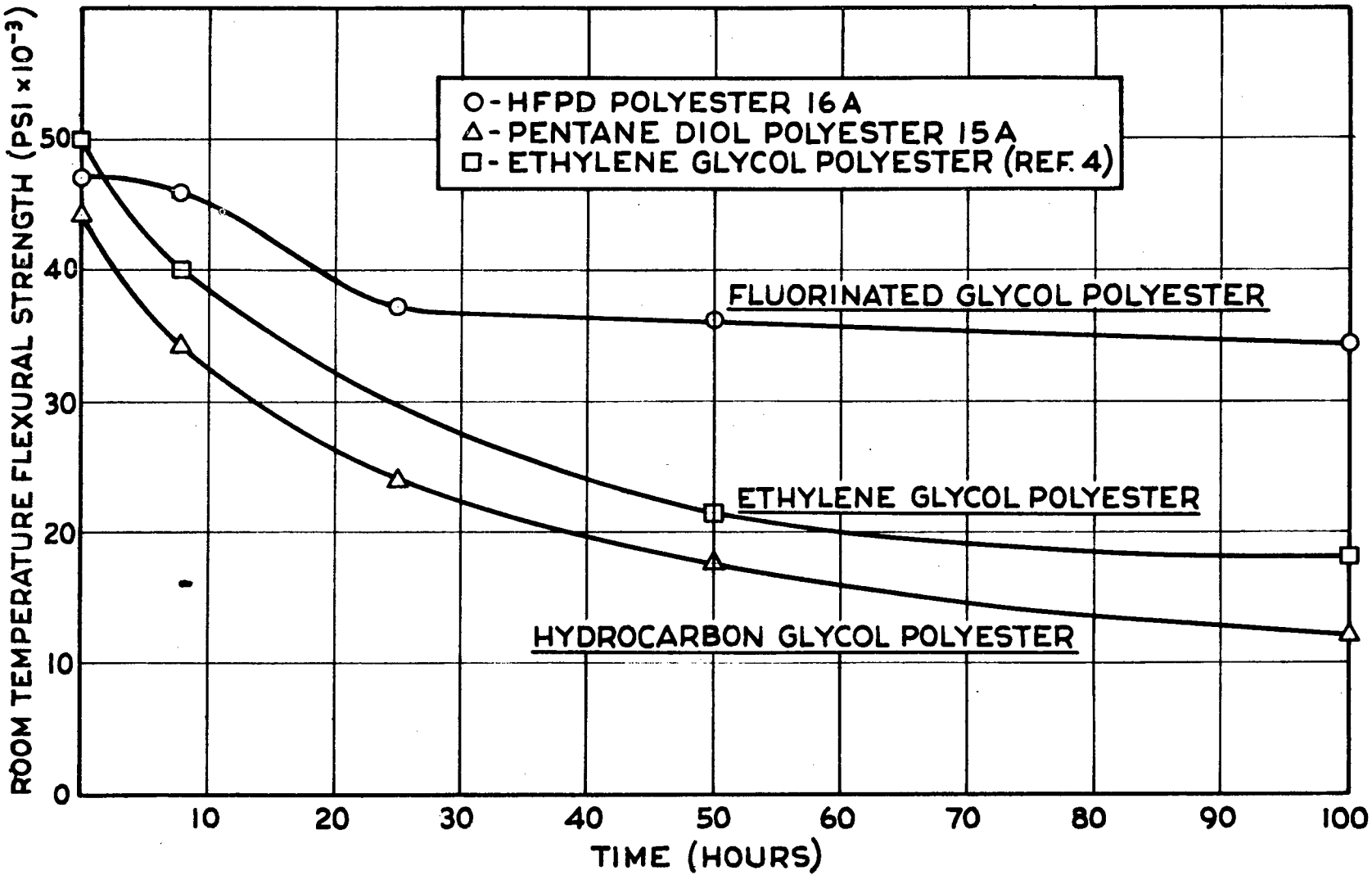


FIG. 2
ROOM TEMPERATURE FLEXURAL STRENGTH VS.
HOURS OF AGING AT 260°C.-DIALLYL ISOPHTHALATE MONOMER

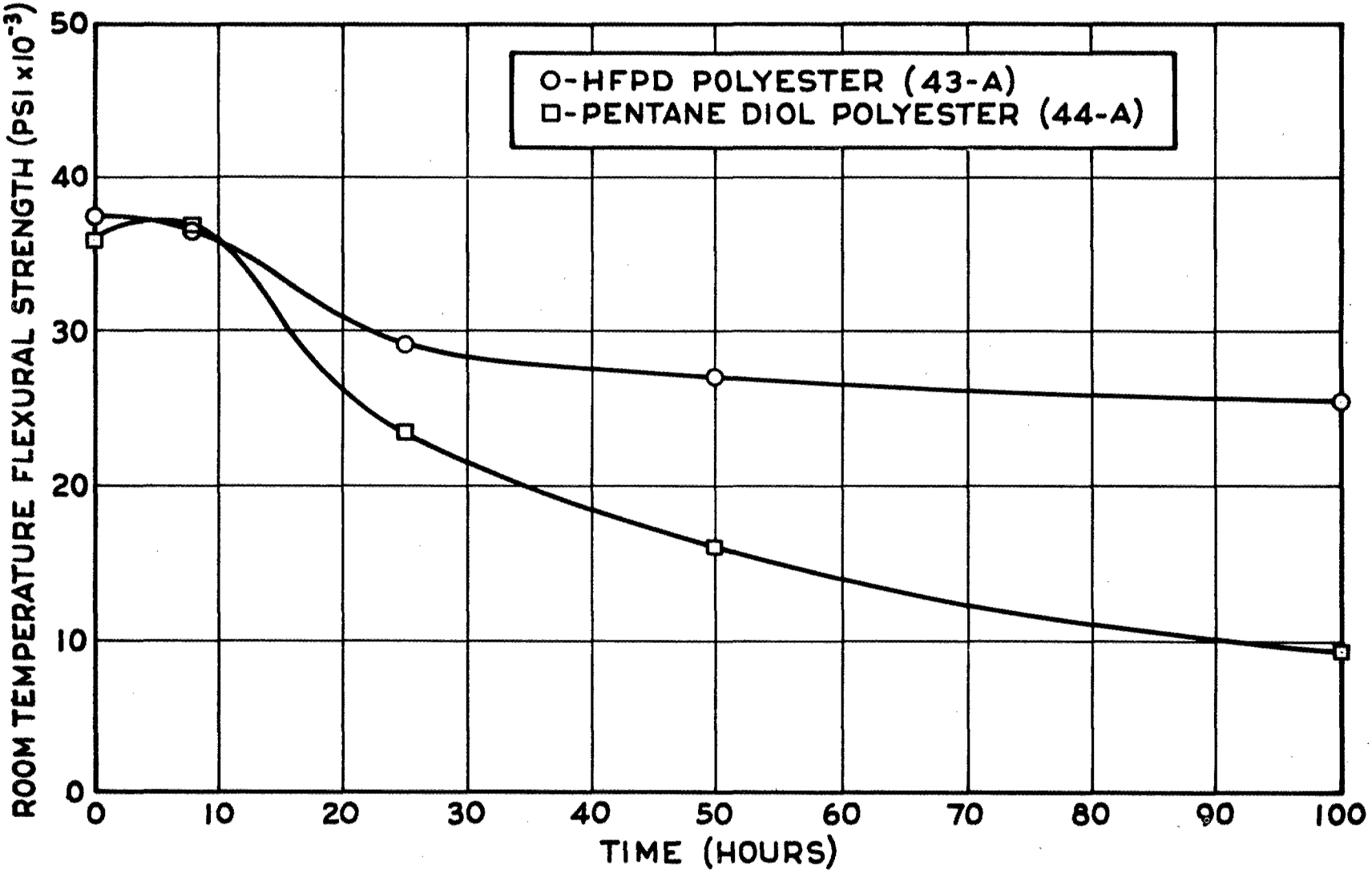


FIG. 3

ROOM TEMPERATURE FLEXURAL STRENGTH VS. HOURS OF AGING AT 260° C. DIALLYL TEREPHTHALATE MONOMER

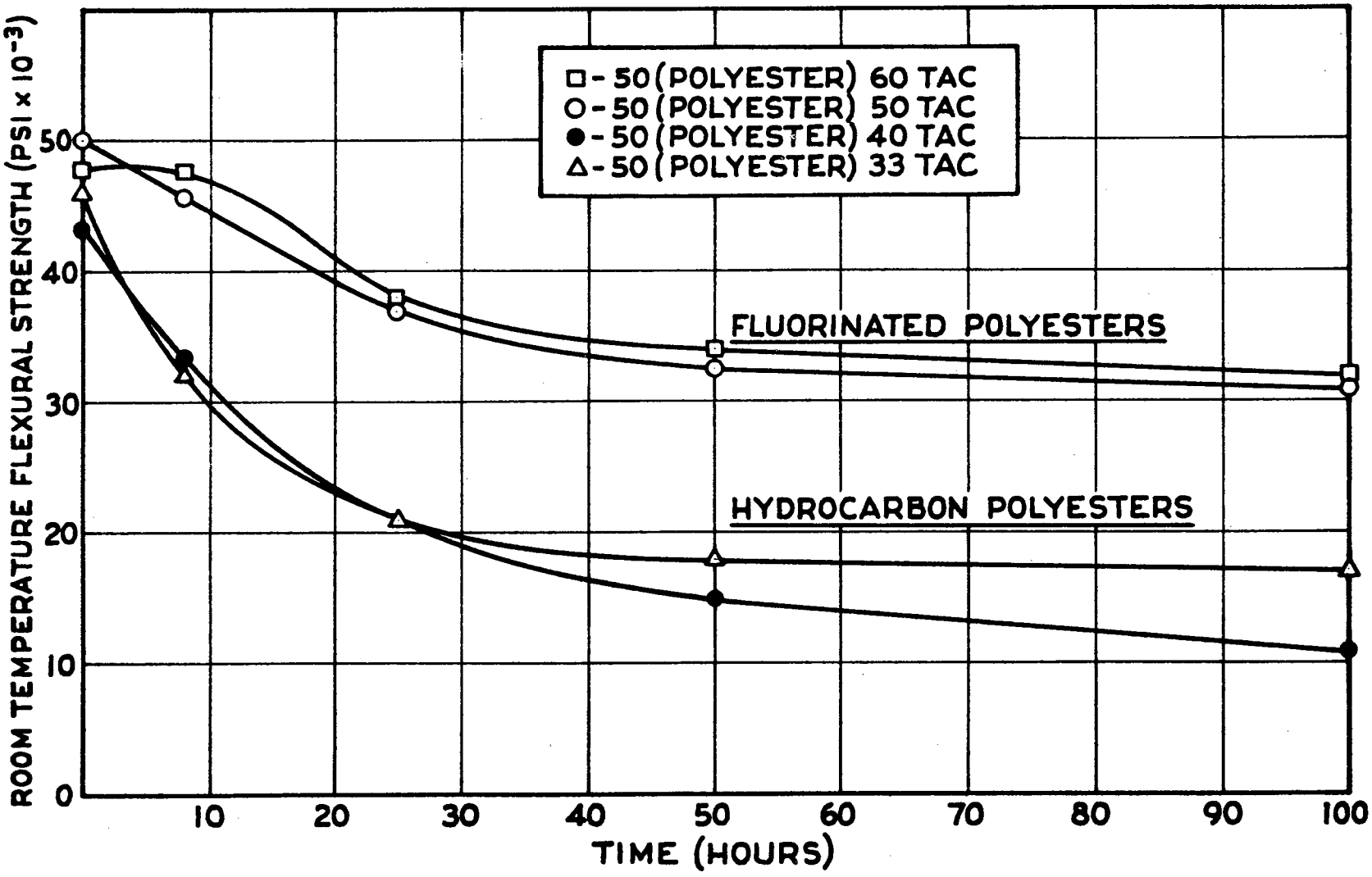


FIG. 4
ROOM TEMPERATURE FLEXURAL STRENGTH VS.
HOURS OF AGING AT 260°C.- TRIALLYL CYANURATE MONOMER

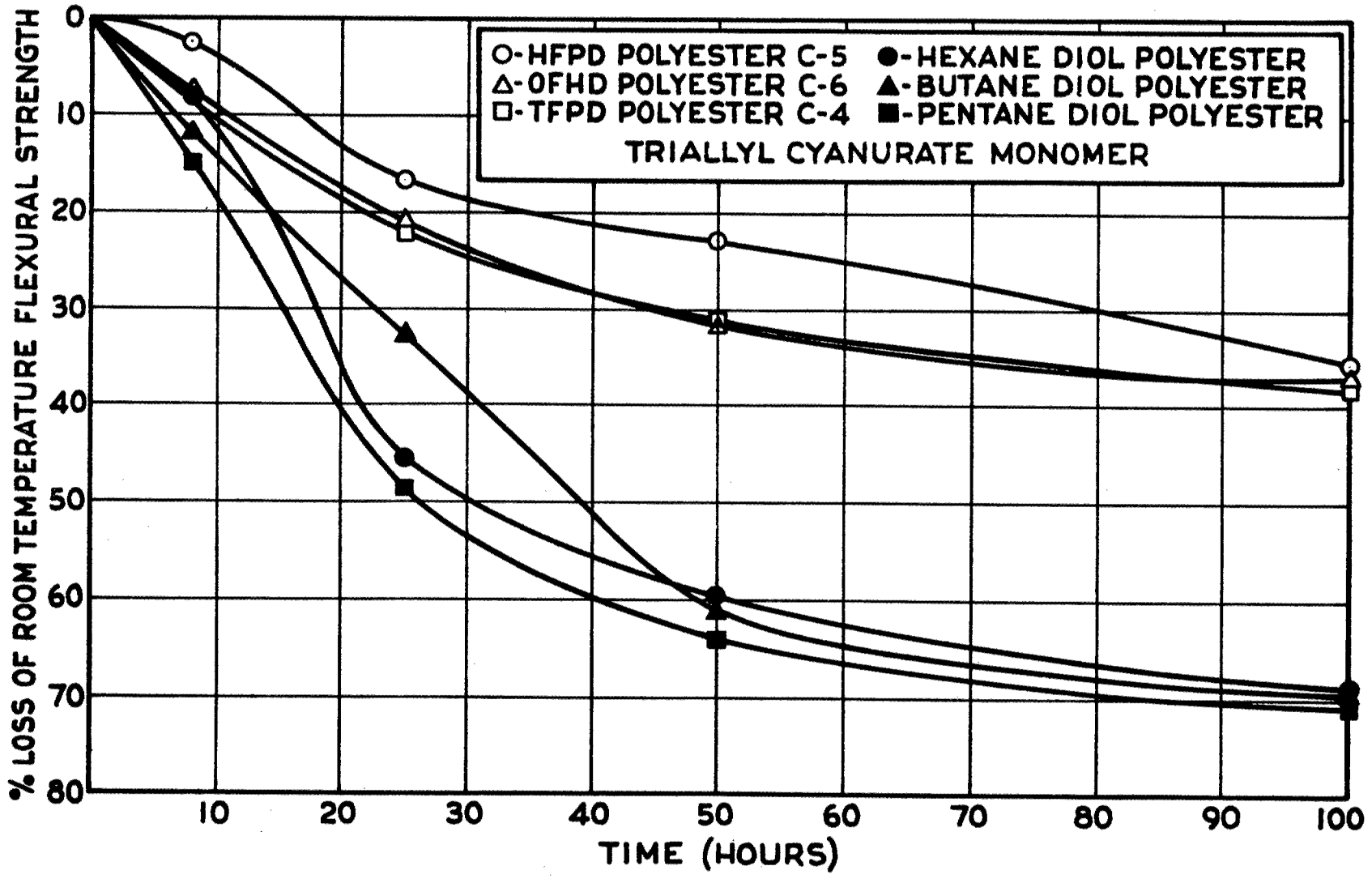


FIG. 5

PER CENT LOSS OF ROOM TEMPERATURE FLEXURAL STRENGTH VS. HOURS OF AGING AT 260°C.

A program of high temperature testing of the polyester resin laminates has been begun, but only a limited amount of data is presently available. The results of these elevated temperature testing of the laminates along with other pertinent information are tabulated in Table II. The results further confirm the improved high temperature aging characteristics of the fluorine-containing polyester resin laminates as compared to their corresponding hydrocarbon glycol polyester laminates. This may be seen (Figure 6) by comparing the high temperature (260°C) flexural strengths after aging of a triallyl cyanurate cross-linked polyester resin prepared from HFPD (laminate 35-A) with its corresponding pentane diol polyester resin laminate (33-A). After 100 hours at 260°C, the fluorinated polyester laminate still retains 90% of its initial high temperature strength whereas the hydrocarbon glycol polyester retains only 29% of its initial high temperature strength. A similar result was obtained when diallyl isophthalate was the cross-linking monomer. The fluorinated polyester laminate (36-A) retains 85% of its initial elevated temperature strength after aging 100 hours at 260°C whereas the hydrocarbon glycol polyester laminate retains only 40% of its initial strength.

Examination of the data of Table II permits one to draw certain other conclusions regarding the polyester resin both with regard to the cross-linking monomer and to the polyester itself especially to the possible effect of fluorine on the thermal stability of the polyester resin laminates. In all cases, diallyl isophthalate cross-linked polyester resin laminates (34-A, 36-A, 39-A, 40-A) are weaker at 260°C than the triallyl cyanurate cross-linked polyester resin laminates (33-A, 35-A, 37-A, 40-A). This result has been demonstrated previously.[4] In our work, the diallyl isophthalate cross-linked polyester resin laminates of the hydrocarbon glycol polyesters (34-A, 39-A, 40-A) are undergoing further cross-linking during at least the first 25 hours of the aging process at 260°C. The only instance in which this did not occur was when diallyl isophthalate was used to cross-link a fluorinated glycol polyester (36-A). No improvement in elevated temperature flexural strength occurred during the aging process indicating no further cross-linking.

TABLE II

PREPARATION, HEAT AGING AND HIGH TEMPERATURE TESTING OF POLYESTER LAMINATES*

Laminate Code	Polyester	Monomer	Flex. Str. x 10^{-3} R.T.	Flex. Str. at 260°C After Aging (Weight Losses Based on Laminate)					
				0 Hrs	8 Hrs	25 Hrs	50 Hrs	66 Hrs	100Hrs
33-A	PD - FC,IPC 75:25	TAC	27.2	26.6 -		19.8 (10.4)		9.7 (14.8)	7.7 (15.9)
34-A	PD - FC,IPC 75:25	DAIP	37.4	17.6		21.7 (18.9)	14.4 (23.2)	11.3 (23.0)	7.2 (24.2)
35-A	HFPD-FC,IPC 75:25	TAC	41.8	27.4		27.4 (12.6)		27.8 (18.9)	24.5 (21.3)
36-A	HFPD-FC,IPC 75:25	DAIP	48.8	16.8		15.2 (10.2)	14.3 (17.4)		14.1 (20.3)
37-A	BD - FC,IPC 75:25	TAC	43.8	24.3		23.2 (11.2)	16.2 (14.9)		14.4 (16.3)
38-A	HD - FC,IPC 75:25	TAC	48.1	29.4		26.4 (11.3)	13.8 (13.7)		12.1 (16.6)
39-A	BD - FC,IPC 75:25	DAIP	47.2	13.9	13.5 (7.1)	27.1 (19.2)	22.7 (22.4)		10.8 (25.4)
40-A	HD - FC,IPC 75:25	DAIP	47.6	13.3	13.9 (8.5)	23.6 (19.3)	20.3 (21.3)		10.6 (23.1)

- - - - -

*Key for Table II same as Table I.

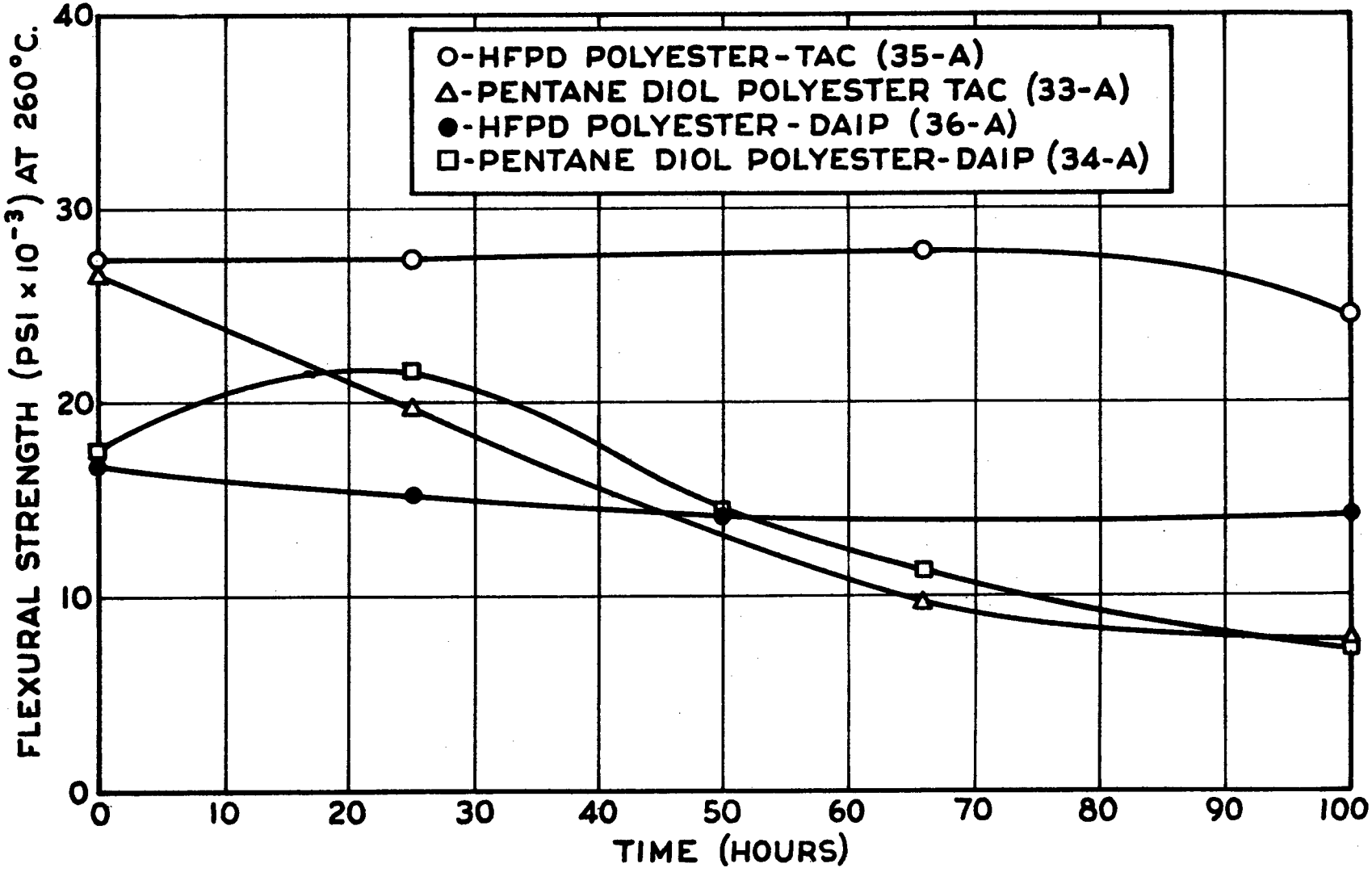


FIG. 6
ELEVATED TEMPERATURE (260°C.) FLEXURAL STRENGTHS VS. HOURS OF AGING AT 260°C.

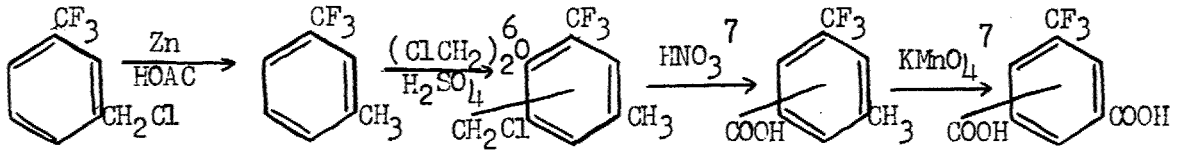
B. FLUORINE-CONTAINING INTERMEDIATES FOR POLYESTER RESINS

A portion of the research program was devoted to the synthesis of new fluorine-containing acid, alcohols and esters for use in the preparation of polyesters or unsaturated monomers. The following discussion covers some of the synthetic work undertaken during the past year.

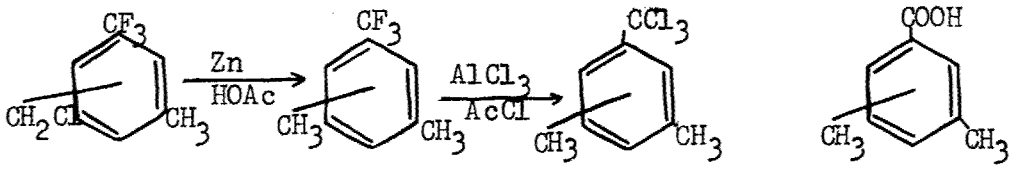
Hexafluoropentamethylene diacrylate and hexafluoropentamethylene dimethacrylate were prepared by the reaction of HFPD and acrylyl and methacrylyl chloride respectively. The diacrylate polymerized readily with either benzoyl peroxide (0.5%) or MEK peroxide (0.5%) at 50°C to give a hard, clear, infusible polymer. Further work with these monomers is planned either in homopolymerization or as polyester resin monomers.

Difluoro HET Anhydride (1,4,5,6-tetrachloro-7,7-difluorobicyclo [2.2.1] -hept-5-ene-2,3-dicarboxylic acid anhydride) was prepared from maleic anhydride and 1,2,3,4-tetrachloro-5,5-difluorocyclopentadiene.[5] Polyesters will be prepared with this anhydride, maleic anhydride, hexafluoropentane diol or the corresponding hydrocarbon glycol 1,5-pentane diol.

We also attempted to prepare a number of derivatives of benzotrifluoride and xylene hexafluoride for use in the polyester program. The following sequence of reactions indicates attempts to prepare some trifluoromethyl phthalic acids:

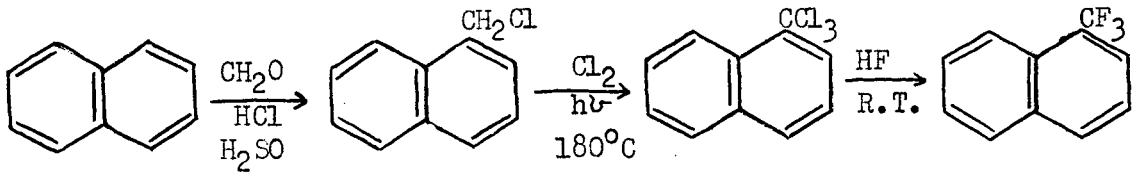


The chloromethylation[6] reaction on 3-trifluoromethyl toluene gives a 65/35 mixture of isomers in which the chloromethyl group is 65% para and 35% ortho to the methyl group. Separation of the isomers has so far been difficult. Partial separation by distillation of the chloromethylation product gave materials which could be transformed to known compounds and, with the derivatives of which, the original isomers were conclusively established.



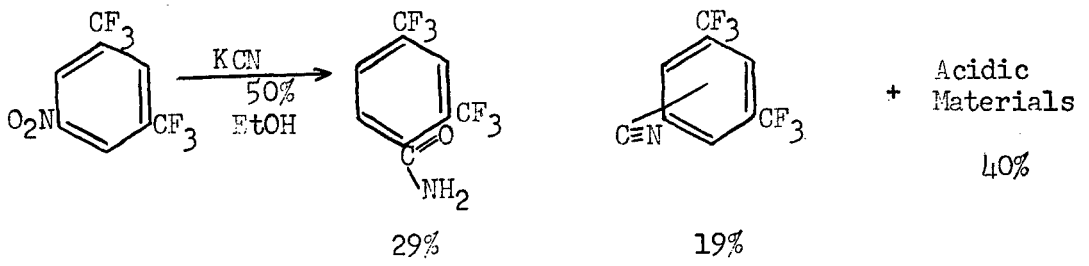
The dimethyl benzoic acids were identified by their melting points and by their amide, anilide and nitrile derivatives as 3,4-dimethyl benzoic and 2,5-dimethyl benzoic acid.

Another route to a trifluoromethyl phthalic acid was attempted. This is illustrated by the following sequence of reactions.



All attempts to oxidize the trifluoromethylnaphthalene to a trifluoromethyl phthalic acid were unsuccessful. These included, potassium permanganate in basic and acidic media, sodium dichromate in sulfuric acid and chromic oxide in acetic acid. Several other approaches to the preparation of a trifluoromethyl phthalic acid were also unsuccessful.

Another reaction which was attempted proved to be somewhat interesting. When the Von-Richter reaction was attempted on 3,5-bis-(trifluoromethyl)nitrobenzene we were able to isolate both an amide and a nitrile compound in the neutral portion of the reaction products.



The isolation of an amide and a nitrile, which could be converted to the same amide, in this reaction is the first known case of these materials being found as the products of a Von-Richter reaction.[8]

C. PERFLUORINATED NITRILE AND AMIDINES

As mentioned previously, the copolymers of perfluorinated diamidines and monoamidines give thermally stable fluids and elastomeric materials. Because of the great interest by the military in such thermally stable materials, it is desirable that a thorough investigation be undertaken of these polymers and whatever modifications are possible to verify the preliminary evaluations. One problem encountered in the preparation of the amidines themselves, especially the amidine percursor, the perfluorinated dinitrile, is that the most readily-available acid amide, perfluoroglutaramide cyclizes on dehydration[9] to give greater yields of the cyclic imide, perfluoroglutarimide, than of the desired perfluoroglutaronitrile.

With regard to the first problem, the supply of the perfluorinated dibasic acid, sufficient quantities of this acid and its amide derivative are now available or could be made available for a rapid expansion of effort in investigations of the perfluorinated polyamidines. The second problem, dehydration of the amides to the nitriles in high yields, notably the preparation of perfluoroglutaronitrile, therefore becomes an important area of investigation.

The research program initiated by the Hooker Chemical Corporation has as its objectives, therefore, to investigate the preparation of perfluoroglutaronitrile by all the known means of nitrile formation so that an easy, convenient method for its preparation may be developed. It is further an objective to prepare perfluoroglutaronitrile in sufficient quantities to allow other WADC contractors designated by that agency to continue investigations in the realm of perfluorinated diamidine polymers and elastomers. The investigations will be extended to other fluorinated nitriles such as perfluorosuccinonitrile and perfluoroadiponitrile. At a later stage in the program our intention is to prepare the corresponding diamidines and to study their polymerization to give resins which under suitable conditions may be molded to give materials which might have unusual thermal stability.

Initial investigations on the dehydration of perfluoroglutaramide have been mainly performed using phosphorus pentoxide as the dehydrating agent. Perfluoroglutaronitrile was first prepared by McBee and Wiseman,[9] via the phosphorus pentoxide dehydration of the amide. They reported yields of 16% for the nitrile and 19% for the cyclic imide. Under somewhat more vigorous conditions we were able to obtain somewhat better results. In a pair of duplicate experiments, yields of 25.8 and 24.8% for the nitrile and 38 and 40% for the imide were obtained while the amide and P_2O_5 were dispersed in sand. We also have found that the dehydration may be performed with the amide and P_2O_5 dispersed in an inert solvent such as dichlorobenzene or trichlorobenzene. Yields in these solvents parallel to those obtained with or without sand, that is, nitrile yields of 25-30% are obtained with imide yields ranging between 30-40%. The mole ratio of phosphorus pentoxide to amide was examined and found to have no effect upon either the nitrile or imide yield. When nitrobenzene was used as the solvent, somewhat higher yields (35 and 42%) of the nitrile could be obtained on distillation.

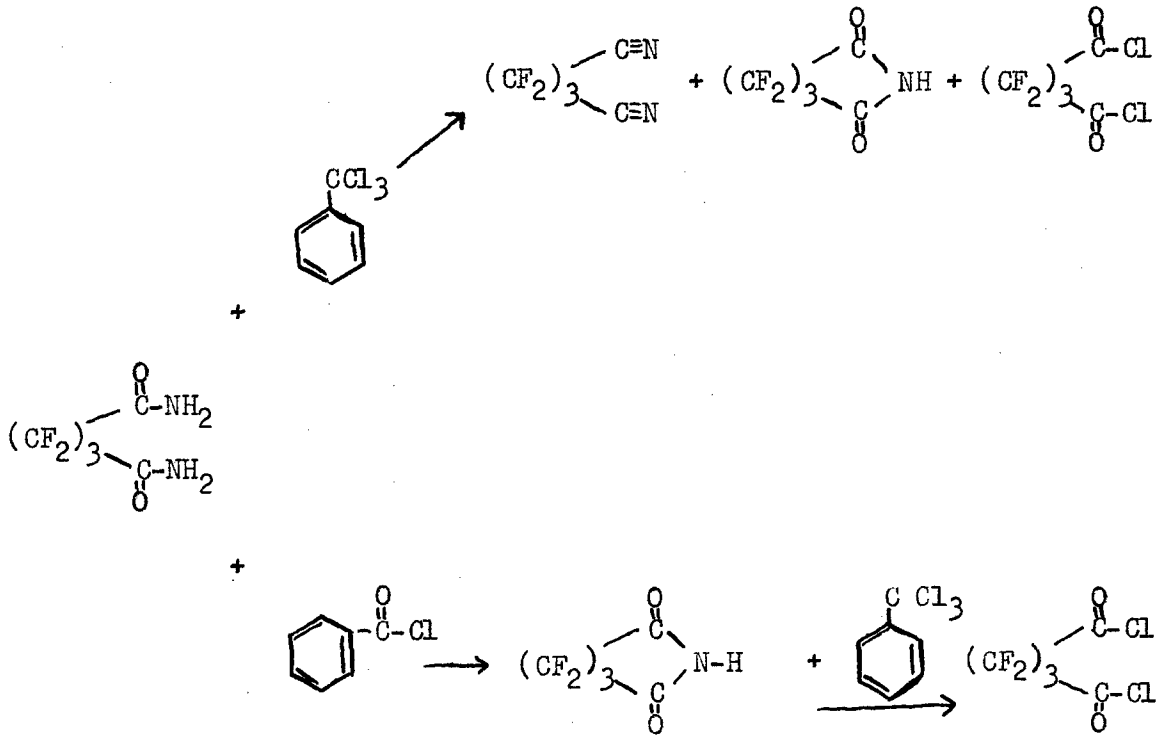
One problem encountered during all these P_2O_5 dehydrations was the tendency for the solids to form a hard, porous cake. It was thought that much of the amide became bound up in this cake or else the products became physically trapped. With the addition of barium oxide, the cake formation was eliminated and a fine slurry was obtained. However, the yields of nitrile or imide were not changed. When a more basic acid acceptor such as dimethyl aniline was used with P_2O_5 in dichlorobenzene, only nitrile was obtained and no imide could be recovered. A similar result was obtained using P_2O_5 and barium oxide in nitrobenzene.

More recently we have found that perfluoroglutaramide could be dehydrated by means of benzotrichloride[10] at elevated temperatures. The

yields of nitrile are much higher than those obtained with P_2O_5 and at present approach 55-60%. As is the case with P_2O_5, by-product may be varied by the amount of benzotrichloride used in the dehydration.

When a mole ratio of amide to benzotrichloride of 1:1 was used, a 47% yield of nitrile was obtained with perfluoroglutarimide as the only by-product. When the mole ratio was 1:2 a 45% yield of nitrile was obtained as well as some perfluoroglutarimide and some perfluoroglutaryl chloride.[11] With a mole ratio of amide to benzotrichloride of 1:3 a 42% yield of perfluoroglutaryl chloride and no imide. A mole ratio of 1:10 gives nitrile yields of 55-60% with small yields ($\approx$5%) of perfluoroglutaryl chloride.

The reason for the variation in the type of by-product with different mole ratios of reactants is not completely understood. Theoretically, 1 mole of perfluoroglutaramide should react with 2 moles of benzotrichloride to give 1 mole of perfluoroglutaronitrile and 2 moles of benzoyl chloride and hydrogen chloride, respectively. It was demonstrated that benzoyl chloride when heated with perfluoroglutaramide gave perfluoroglutarimide and no perfluoroglutaronitrile or perfluoroglutaryl chloride. Likewise, perfluoroglutarimide and benzotrichloride react to give perfluoroglutaryl chloride. Efforts are being continued to further understand the reaction of the amide with benzotrichloride in an attempt to improve the yields of perfluoroglutaronitrile still further. The following series of equations illustrate the present extent of our knowledge concerning this reaction:



A number of other reagents have been used in an attempt to prepare perfluoroglutaronitrile. However, none have been as successful as P_2O_5 or benzotrichloride. Among those tried has been, thionyl chloride, phosphorus oxychloride, phosphorus pentachloride, and acetic anhydride. Tables III and IV contain a list of all the attempts to prepare perfluoroglutaronitrile and the reagents used as well as the nitrile, imide and acid chloride yields.

TABLE III

PREPARATION OF PERFLUOROGLUTARONITRILE PHOSPHORUS PENTOXIDE DEHYDRATIONS

Medium	Mole Ratio P_2O_5/Amide	% Nitrile Yield	% Imide Yield	% Total
Sand-Flame	3:1	25.0	38	63.8
Sand-Mantle	3:1	24.8	40	64.8
Dichlorobenzene	3:1	30.6	37	67.6
Dichlorobenzene Dimethyl Aniline	3:1	23.8	0	23.8
Nitrobenzene	3:1	35	-	35.0
Dichlorobenzene Barium Oxide	3:1	29.3	31	60.3
Dichlorobenzene Barium Oxide	6:1	27.2	31	59.2
Dichlorobenzene Barium Oxide	12:1	26	38	64

TABLE IV

PREPARATION OF PERFLUOROGLUTARONITRILE BENZOTRICHLORIDE DEHYDRATIONS

Reagent	Mole Ratio Amide/BTC	Nitrile Yield %	Imide Yield %	Perfluoro-Glutaryl Chloride Yield %	Total Yield %
BTC	1:1	47.1	16.0	5.2	68.3
BTC	1:2	45.0	5	5.0	55.0
BTC	1:3	43.4		29.6	73.0
BTC	1:4	33.8		33.7	67.5
BTC	1:10	58.0		3.0	61.0
XHC	1:5	60.6		3.5	64.1
BC	1:3		60.0		60.0
BTC	1:3*			50.0	50.0

BTC - Benzotrichloride

XHC - Xylene hexachloride

BC - Benzoyl chloride

*Perfluoroglutarimide

BIBLIOGRAPHY

1. Verbanic, C. J., Knutson, D. K., Wier, J. E., Gouinlock, E. V., Bean, C. T. - WADC TR-55-221 Pt V.

2. Schweiker, G. C., Verbanic, C. J., Marks, B. S., Gouinlock, E. V., Lucas, B. L. - WADC TR 55-221 Pt IV.

3. Flory, P. J., J. Amer. Chem. Soc., 62, 1057 (1940).

4. Cohen, M., Cypher, G. A., Ind. & Eng. Chem., 50, 1541 (1958).

5. Smith, D. K., Thesis, Purdue University, 1954.

6. Berezovskii, V. M., Kurdyukova, V. A., Preobrazhenskii, N. A., Zhur. Obshchei Khim., 21, 1163 (1951) C.A. 46, 5006 (1952).

7. Organic Synthesis, Coll. Vol. III, J. Wiley and Sons, Inc., New York, New York, p. 791.

8. Bunnett, J. F., Rauhut, M. M., J. Org. Chem., 21, 934, 939, 944 (1956) and references cited therein.

9. McBee, E. T., Wiseman, P.; U. S. P. 2,515,246 (1950).

10. Hopff, H.; German Patents 517,760 (1928); 524,715 (1929).

11. Ref. 2, p. 68.

SOME ASPECTS OF ORGANOTIN HYDRIDE CHEMISTRY WITH A VIEW TO THE POSSIBILITY OF PREPARING ORGANOTIN POLYMERS

Dr.J.G.Noltes

Institute for Organic Chemistry T.N.O., Utrecht, Holland

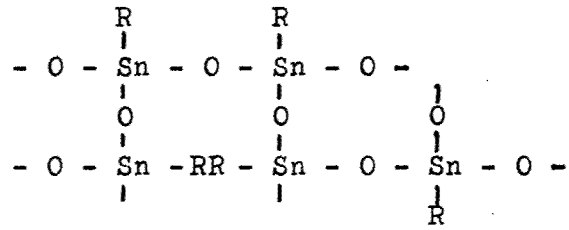
Very recently a program aiming at the synthesis of organotin polymers containing exclusively tin-carbon bonds has been started at this Institute. The poly-addition of organotin dihydrides to suitable dienic compounds may lead to the formation of such polymers. In the present paper some results of previous investigations in the field of organotin hydride chemistry which have a bearing on the existing research program will be given.

Although in recent times a considerable number of organometallic polymeric materials has been reported, of the organometallic compounds derived from the IVth Group elements only the organosilicon polymers are of wide significance. As is well known, the ability of appropriately substituted organosilanes to be hydrolyzed to cyclic or linear polymeric compounds containing Si-O-Si chains, has allowed the synthesis of a great variety of products with diverse physical properties.

From the position of tin in the fourth main group of the periodic system it might be expected that the properties of organotin compounds could be deduced from the corresponding compounds of silicon. However, just like corresponding compounds of carbon and silicon show as many differences as similarities, very striking differences in physical and chemical properties have been observed between corresponding organic derivatives of silicon and tin. The organotin halides R_2SnX_2 on the analogy of the organodihalosilanes might be expected to be a favourable starting material for the preparation of organotin polymers. In only two known cases upon hydrolysis with dilute alkali are the corresponding dihydroxides $R_2Sn(OH)_2$ formed (di-tert.butyl- and di-tert.amyltin dihydroxide). In all other cases the formation of dialkyl- or diaryltin oxides having the empirical formula R_2SnO is observed. These are white, amorphous, insoluble and infusible powders which exist in the polymeric form $[-R_2SnO-]_n$. Their physical properties resemble those of the metallic oxides and

thus are quite different from those of the silicones which have a similar chemical composition.

Another group of compounds containing Sn-O bonds, the alkyl and arylstannonic acids, have recently received some interest at our Institute. Alkylstannonic acids are amorphous and infusible substances of polymeric structure $[RSnOOH]_n$ which are insoluble in most solvents but readily soluble in the lower aliphatic alcohols. It is not knowns whether alkylstannonic orthoesters $RSn(OR')_3$ or polymeric products of the type $[RSnOOR']_n$ are formed. Recently the organotitanic esters of the type $Ti(OR)_4$ have been converted to three-dimensional titanium-oxygen polymers by controlled hydrolysis and heat treatment. Similarly, evaporation of the solvent from the alkylstannonic ester and subsequent heat treatment yields a transparent polymeric material for which the following structure is probable:



Since in this case the polymer still contains an organic group R, the "organic" character of the tin-oxygen polymer may be varied by the variation of the organic group.

The dialkyltin oxides $[-R_2SnO-]_n$ have weakly basic properties and with mineral acids normal salts are formed. Recently Montermoso et al.[1] have described reactions of dibutyltin oxide with a number of dicarboxylic acids or anhydrides leading to the formation of polymeric dibutyltin dicarboxylates of structure $[-(C_4H_9)_2SnOCORCOO-]_n$. Whereas short chain aliphatic acids such as succinic and adipic acid yielded soluble cyclic derivatives of low molecular weight, terephthalic acid and the long chain sebacic acid gave linear polymers of considerable molecular weight. The latter products are the first reported well-defined organotin polymers. However, the resistance towards hydrolytic cleavage of the tin-oxygen bond in organotin esters is rather poor and ready depolymerisation under hydrolytic conditions must be envisaged. With a view to the much greater chemical stability of the tin-carbon bond, the preparation of polymeric organotin compounds containing tin atoms exclusively bound to carbon would be of interest. A program aiming at the synthesis of such polymers has recently been started at our Institute.

Many methods for the synthesis of tin-carbon bonds are available at present. Most of these require the use of other organometallic compounds as intermediates, e.g. organomagnesium or lithium compounds. Quite a number of other methods are known which suffer, however, of lack of general applicability and give good results in incidental cases only. A discussion of their merits falls outside the

scope of this paper.

In recent years at our Institute much attention has been paid to a new method for the synthesis of tin-carbon bonds, viz. the reaction of organotin hydrides R_nSnH_{4-n} with compounds containing a double or triple carbon-carbon bond [2]). It appears that organotin hydrides display a surprisingly great reactivity towards carbon-carbon unsaturated bonds, resulting in an addition reaction with formation of a new tin-carbon bond:

$$R_3SnH + CH_2=CH-R' \longrightarrow R_3SnCH_2CH_2R' \qquad (1)$$

The first reaction studied was the cyanoethylation of triphenyltin hydride which proceeds in almost quantitative yield:

$$(C_6H_5)_3SnH + CH_2=CH-CN \longrightarrow (C_6H_5)_3SnCH_2CH_2CN \qquad (2)$$

It soon became clear that this reaction is of a very general nature. A great variety of unsaturated compounds can be made to react with both triphenyltin hydride and trialkyltin hydrides. Moreover, the presence of a functional substituent in the unsaturated reactant in general does not interfere. Although examples have been found of interaction of the Sn-H group with the functional substituent, reaction with the olefinic bond is more general. Consequently, a direct and widely applicable method for the introduction of functional substituents into organotin compounds -a hitherto mainly unsolved problem- became available. By reaction of triphenyltin hydride and the appropriately substituted terminal olefins compounds of the type $(C_6H_5)_3SnCH_2CH_2R'$ have been prepared in which R' stands a.o. for -CN, $-CH_2CN$, $-COOCH_3$, $-CH_2COOC_2H_5$, $-CH(OC_2H_5)_2$, $-CH_2CH_2CH_2COCH_3$, $-OC_6H_5$, $-CH_2OH$, $-OCOCH_3$, $-CH_2OCOCH_3$, $-CH_2NHCOCH_3$ and $-C_5H_4N$.

An interesting polymeric product is obtained from the reaction of triphenyltin hydride and acrylic acid. The primarily formed addition compound is not stable, one molecule of benzene being spontaneously split off:

$$(C_6H_5)_3SnH + CH_2=CH-COOH \longrightarrow [(C_6H_5)_3SnCH_2CH_2COOH]$$

$$\xrightarrow{-C_6H_6} [-(C_6H_5)_2SnCH_2CH_2COO-]_n \qquad (3)$$

As this product is an unmeltable and infusible powder the monomeric structure of an organotin lactone: $(C_6H_5)_2Sn(-CH-CH_2)(O-C=O)$ may be excluded.

Similarly, but less readily, tributyl-2-carboxyethyltin splits off a molecule of butane with formation of a polymeric product:

$$(C_4H_9)_3SnCH_2CH_2COOH \xrightarrow{-C_4H_{10}} [-(C_4H_9)_2SnCH_2CH_2COO-]_n \qquad (4)$$

Similarly, addition products are formed from compounds containing carbon-carbon triple bonds. The reaction of an organotin monohydride with a substituted acetylenic hydrocarbon constitutes a general method for the preparation of organotin compounds containing a substituted vinyl group. For example triphenyltin hydride and phenylacetylene quantitatively yield triphenyl-β-styryltin in an exothermal reaction:

$$(C_6H_5)_3SnH + CH{\equiv}C\text{-}C_6H_5 \longrightarrow (C_6H_5)_3SnCH{=}CH\text{-}C_6H_5 \qquad (5)$$

With excess organotin hydride di-addition products may be obtained. E.g.:

$$2\ (C_6H_5)_3SnH + HC{\equiv}C\text{-}C_6H_5 \longrightarrow (C_6H_5)_3SnCH_2CH(C_6H_5)Sn(C_6H_5)_3 \qquad (6)$$

In contradistinction to corresponding reactions of triphenylsilane and triphenylgermane addition reactions of triphenyltin hydride proceed without a catalyst. They are best carried out in the absence of solvent. Examples of exothermal additions are known but usually heating at 80-100°C. for a period dependent on the reactivity of the olefin is required.

The available evidence points to an ionic mechanism for the tin hydride addition reaction. Upon prolonged heating triphenyltin hydride and n.octene-1 react in the absence of any catalyst to give triphenyl-n-octyltin. It is noteworthy that elsewhere attempts to realize this reaction using hydrocarbon solvents and peroxide catalyst or ultraviolet irradiation remained unsuccessful. This makes a free radical mechanism unlikely. Additional evidence for this view is obtained from the observation that the addition of triphenyltin hydride to styrene is not perceivably influenced by the presence of appreciable quantities of hydroquinone.

The reactivity towards olefinic double bonds of the aliphatic tin hydrides as compared with triphenyltin hydride is decidedly lower. Whereas tripropyltin hydride reacts in the absence of a catalyst with a variety of olefinic compounds containing activating substituents, no reaction occurs between several trialkyltin hydrides and simple olefins like e.g. n-octene-1. Also attempts to add tripropyltin hydride to allyl alcohol failed whereas triphenyltin hydride reacts quantitatively with this compound under very mild conditions. From the fact that tripropyltin hydride readily adds to simple n-alkynes and propargylic alcohol according to:

$$(C_3H_7)_3SnH + HC{\equiv}C\text{-}C_4H_9 \longrightarrow (C_3H_7)_3SnCH{=}CH\text{-}C_4H_9 \qquad (7)$$

$$(C_3H_7)_3SnH + HC{\equiv}C\text{-}CH_2OH \longrightarrow (C_3H_7)_3SnCH{=}CH\text{-}CH_2OH \qquad (8)$$

it appears that the reactivity of aliphatic organotin hydrides towards carbon-carbon triple bonds is decidedly greater than towards olefinic double bonds.

Thus, in certain cases at least, finding a catalyst for the organotin hydride addition reaction would be required. As the Sn-H

bond is very susceptible to attack by chemical reagents, one is very much restricted in the choice of such a catalyst. For this reason peroxide catalysts which are extensively used in corresponding reactions of organosilanes and organogermanes cannot be used. The usefulness of platinum catalysts which have been found very active in catalyzing addition reactions of various organosilanes has been investigated. Neither platinized carbon nor hexachloroplatinic acid caused tripropyltin hydride and n-octene-1 or allylalcohol to react. A suitable catalyst so far has not been found.

In all cases which have been investigated it appeared that upon reaction of an organotin hydride with a terminal olefin the organotin moiety becomes attached to the terminal carbon atom.

Direct evidence for the linear structure of the cyanoethylation product of triphenyltin hydride was obtained after unambiguous synthesis of one of the possible isomers, viz. triphenyl-1-cyanoethyltin according to:

$$(C_6H_5)_3SnOCOCH(CH_3)CN \longrightarrow (C_6H_5)_3SnCH(CH_3)CN + CO_2 \qquad (9)$$

Comparison of the melting point and the infrared spectrum of this product and the actual addition product revealed the linearity of the latter compound.

The compounds obtained on reaction of triphenyltin hydride with n-octene-1 and styrene, respectively, were obtained by unambiguous synthesis using the Grignard procedure:

$$\left.\begin{array}{l}(C_6H_5)_3SnH + CH_2{=}CH\text{-}(CH_2)_5\text{-}CH_3 \\ (C_6H_5)_3SnCl + BrMg(CH_2)_7CH_3\end{array}\right\} \longrightarrow (C_6H_5)_3Sn(CH_2)_7CH_3 \qquad (10)$$

$$\left.\begin{array}{l}(C_6H_5)_3SnH + CH_2{=}CH\text{-}C_6H_5 \\ (C_6H_5)_3SnCl + BrMgCH_2CH_2\text{-}C_6H_5\end{array}\right\} \longrightarrow (C_6H_5)_3SnCH_2CH_2C_6H_5 \qquad (11)$$

Identical infrared spectra and mixed melting points proved their identity.

Other reactions with non-terminal olefins afforded evidence that steric factors have an important influence on the course of these reactions. One example may be cited. Whereas upon reaction of tripropyltin hydride with acrylonitrile the organotin moiety becomes attached to the terminal carbon atom, it could be proven that upon reaction with cinnamonitrile the tripropyltin group has become attached to the ethenoid carbon adjacent to the cyano group, i.e. again to the carbon atom bearing the smaller substituent:

$$(C_3H_7)_3SnH + CH_2{=}CH\text{-}CN \longrightarrow (C_3H_7)_3SnCH_2CH_2CN \qquad (12)$$

$$(C_3H_7)_3SnH + C_6H_5\text{-}CH{=}CH\text{-}CN \longrightarrow (C_3H_7)_3SnCH(CN)CH_2C_6H_5 \qquad (13)$$

This, in combination with the direct evidence obtained in reactions with terminal olefins leads to the conclusion that the formation of

unbranched addition products is the general rule.

The reaction of a diolefinic hydrocarbon with two molecules of an organotin monohydride leads to the formation of organotin compounds having a bridge of carbon atoms between tin atoms:

$$2\ R_3SnH + CH_2{=}CH\text{-}R'\text{-}CH{=}CH_2 \longrightarrow R_3SnCH_2CH_2R'CH_2CH_2SnR_3 \qquad (14)$$

Some addition products obtained on reaction of various dienic compounds with excess triphenyltin hydride have been listed in Table I.

Table I

Dienic compound	Adduct
$CH_2{=}CH\text{-}C_6H_4\text{-}CH{=}CH_2$ p-divinylbenzene	$(C_6H_5)_3SnCH_2CH_2\text{-}C_6H_4\text{-}CH_2CH_2Sn(C_6H_5)_3$
$CH_2{=}C(CH_3)CH_2CH_2C(CH_3){=}CH_2$ 2,5-dimethylhexadiene-1,5	$[(C_6H_5)_3SnCH_2CH(CH_3)CH_2\text{-}]_2$
$CH_2{=}CHC(=O)\text{-}O\text{-}C(=O)CH_2{=}CH_2$ acrylic anhydride	$[(C_6H_5)_3SnCH_2CH_2C(=O)\text{-}]_2O$
$CH_2{=}CHC(=O)OCH_2CH_2OC(=O)CH{=}CH_2$ glycol diacrylate	$[(C_6H_5)_3SnCH_2CH_2COCH_2\text{-}]_2$
$CH_2{=}CHCH_2OCH_2CH{=}CH_2$ allyl ether	$[(C_6H_5)_3SnCH_2CH_2CH_2\text{-}]_2O$

By the reaction of organotin dihydrides with suitable olefinic compounds two new tin-carbon bonds could be established. As the thermal stability of organotin hydrides decreases with increasing number of tin-hydrogen bonds in the molecule, the application of this reaction is limited to such addition reactions which involve reactive olefins and thus, do not require prolonged heating. E.g. dipropyl-bis(2-phenylethyl)tin and diphenyl-bis-(2-carbomethoxyethyl)tin were readily obtained by this method:

$$(C_3H_7)_2SnH_2 + 2\ CH_2{=}CH\text{-}C_6H_5 \longrightarrow (C_3H_7)_2Sn(CH_2CH_2C_6H_5)_2 \qquad (15)$$

$$(C_6H_5)_2SnH_2 + 2\ CH_2{=}CH\text{-}COOCH_3 \longrightarrow (C_6H_5)_2Sn(CH_2CH_2COOCH_3)_2 \qquad (16)$$

As already stated, formation of tin-carbon bonds by means of addition of an organotin hydride to an olefinic double bond may proceed in almost quantitative yield when suitable reactants and reaction conditions are employed. An other important advantage of this method is that the reaction is very clean, i.e. the reaction product is not contaminated with undesirable by-products as is often the case with other methods of synthesis of the tin-carbon bond.

The fact that both dienic compounds and organotin dihydrides can be used in this type of reactions makes it in principle possible to prepare by a direct reaction polymeric organotin compounds containing exclusively tin-carbon bonds, namely by the reaction of organotin dihydrides with an equimolecular amount of a suitable dienic compound:

$$R_2SnH_2 + CH_2=CH\text{-}R'\text{-}CH=CH_2 \longrightarrow [-R_2SnCH_2CH_2R'CH_2CH_2-]_n \quad (17)$$

So far only few preliminary experiments have been carried out.

Since, as has been stated before, the aliphatic organotin hydrides only react readily with activated olefinic double bonds and a suitable catalyst so far has not been found, simple dienes such as butadiene or hexadiene cannot be used in reactions with dialkyltin dihydrides. It could be expected that dienic compounds having very reactive double bonds like acrylic anhydride or glycol diacrylate would be more suitable reactants. In fact from the reaction of dipropyltin dihydride with glycol diacrylate (5 hrs. at 80° under N_2) a rubber-like poly-addition product resulted:

$$(C_3H_7)_2SnH_2 + CH_2=CHCOOCH_2CH_2OCOCH=CH_2 \longrightarrow$$

$$[-(C_3H_7)_2SnCH_2CH_2COOCH_2CH_2OCOCH_2CH_2-]_n \quad (18)$$

So far no physical measurements have been made and it cannot be said whether the polymer has a straight-chain or a cyclic structure.

Since tripropyltin hydride had been found to be very reactive towards styrene, the reaction of equimolecular amounts of dipropyltin dihydride and p.divinylbenzene was studied. When heating these reactants under N_2 at 100°, the viscosity of the reaction mixture considerably increased. After 6 hrs. the temperature was raised to 130°C. and after 3 hrs. a colourless, completely transparent rubbery solid resulted:

$$(C_3H_7)_2SnH_2 + CH_2=CH\text{-}C_6H_4\text{-}CH=CH_2 \longrightarrow$$

$$[-(C_3H_7)_2SnCH_2CH_2\text{-}C_6H_4\text{-}CH_2CH_2-]_n \quad (19)$$

With the p.vinyl groups being in a relatively fixed position, cyclization seems not likely and a linear structure may be expected for this polymer. Also here, so far no physical measurements have

been made.

Recently at our Institute reactions of phenyltin hydrides with various vinyl derivatives of the IVth main Group elements Si, Ge, Sn and Pb have been studied[3]). These were carried out in order to study the possibility of preparing polymeric substances containing alternatively tin and silicon or tin and germanium atoms separated by carbon atoms.

Triphenyltin hydride readily adds to triphenylvinyl silane and triphenylvinyl germane with formation of 1-triphenylsilyl-2-triphenylstannylethane and 1-triphenylgermyl-2-triphenylstannylethane, respectively:

$$(C_6H_5)_3SnH + CH_2{=}CHMe(C_6H_5)_3 \longrightarrow (C_6H_5)_3SnCH_2CH_2Me(C_6H_5)_3 \qquad (20)$$

(Me = Si or Ge)

The reaction of triphenyltin hydride with diphenyldivinylsilane and diphenyldivinylgermane in the molar ratio 2:1 afforded the expected addition products containing three metal atoms:

$$2\ (C_6H_5)_3SnH + (CH_2{=}CH)_2Me(C_6H_5)_2 \longrightarrow$$

$$(C_6H_5)_3SnCH_2CH_2Me(C_6H_5)_2CH_2CH_2Sn(C_6H_5)_3 \qquad (21)$$

(Me = Si or Ge)

On the basis of these results reaction of diphenyltin dihydride with these divinylmetal derivatives might be expected to yield organometallic polymers of the type $[-Sn(C_6H_5)_2CH_2CH_2Me(C_6H_5)_2CH_2CH_2-]_n$. Reaction of diphenyldivinylsilane with diphenyltin dihydride afforded, however, a crystalline product (m.p. 134-135°C.) with molecular weight pointing to the monomeric structure n = 1. With the aid of infrared spectroscopy the product was identified as a 1-stanna-4-silacyclohexane derivative:

$$(C_6H_5)_2SnH_2 + (CH_2{=}CH)_2Si(C_6H_5)_2 \longrightarrow$$

$$\longrightarrow [H\text{-}Sn(C_6H_5)_2CH_2CH_2Si(C_6H_5)_2CH{=}CH_2] \longrightarrow$$

$$\longrightarrow \begin{array}{l} C_6H_5 \\ C_6H_5 \end{array}\!\!>\!Sn\!<\!\begin{array}{l} CH_2\text{-}CH_2 \\ CH_2\text{-}CH_2 \end{array}\!\!>\!Si\!<\!\begin{array}{l} C_6H_5 \\ C_6H_5 \end{array} \qquad (22)$$

Similarly, reaction of diphenyltin dihydride with diphenyldivinylgermane afforded the first example of 1-stanna-4-germanacyclohexane derivative:

$$(C_6H_5)_2SnH_2 + (CH_2{=}CH)_2Ge(C_6H_5)_2 \longrightarrow$$

$$\longrightarrow \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!Sn\!<\!\begin{matrix} CH_2\text{-}CH_2 \\ CH_2\text{-}CH_2 \end{matrix}\!\!>\!Ge\!<\!\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \qquad (23)$$

Apparently, ring closure of the intermediately formed unsaturated tin hydride is the favored reaction.

Another possible route leading to organotin polymers is given by the reaction of organotin dihydrides with acetylenic hydrocarbons. Such a reaction would give rise to the formation of an organotin compound containing hydrogen and an unsaturated group bound to the same tin atom which upon further reaction by a poly-addition might give organotin polymers:

$$R_2SnH_2 + HC{\equiv}C\text{-}R' \longrightarrow [H\text{-}Sn(R)_2\text{-}CH{=}CH\text{-}R'] \longrightarrow$$

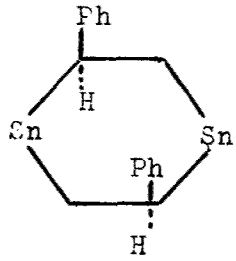
$$\longrightarrow [\text{-}Sn(R)_2CH_2CHR\text{-}]_n \qquad (24)$$

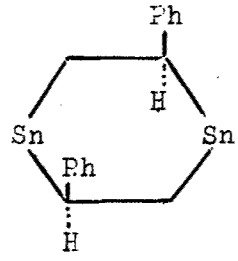
As a representative example the reaction of diphenyl-and dipropyltin dihydride with phenylacetylene has been studied[3]). As has been stated before, triphenyltin hydride adds to phenylacetylene in a 1:1 and 2:1 ratio. Upon reaction of equimolecular amounts of diphenyltin dihydride and phenylacetylene (6 hrs. at 100° under N_2), a solid which we supposed to have a polymeric structure was obtained:

$$(C_6H_5)_2SnH_2 + HC{\equiv}C\text{-}C_6H_5 \longrightarrow [H\text{-}Sn(C_6H_5)_2\text{-}CH{=}CH\text{-}C_6H_5] \longrightarrow$$

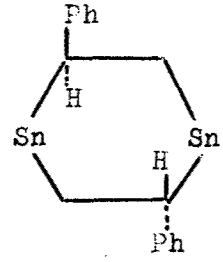
$$\longrightarrow [\text{-}Sn(C_6H_5)_2CH_2CH(C_6H_5)\text{-}]_n \qquad (25)$$

The product was, however, soluble in hot n.butanol. Fractional crystallization from this solvent afforded two fractions with m.p. 70-72°C. and 144-145°C., respectively. These proved to be identical in various aspects. Analytical determinations revealed the composition $[\text{-}Sn(C_6H_5)_2CH_2CH(C_6H_5)\text{-}]_n$. Molecular weight determinations pointed to a dimeric structure (n = 2) for both compounds. As there was no evidence for the presence of Sn-H or $Sn\text{-}CH{=}CH\text{-}C_6H_5$ in their infrared spectra, both reaction products were identified as 1,4-distannacyclohexane derivatives. Apparently, two molecules of the intermediately formed diphenyl-β-styryltin hydride react to form the cyclic adduct 1,1',2,4,4',5-hexaphenyl-1,4-distannacyclohexane. As the presence of two phenyl groups in the 2- and 5-position of the 1,4-distannacyclohexane ring gives rise to the occurrence of optical and geometric isomerism, isolation of two isomeric forms is not surprising. A planar model has two cis-trans isomers. The cis-form will be resolvable in optical antipodes, the trans-form has a centre of symmetry and for that reason cannot be resolved:





Cis-form (d and l)



Trans-form

Equivalent amounts of dipropyltin dihydride and phenylacetylene reacted exothermally to give a mobile liquid. Upon prolonged heating in vacuo (140°C. and 0.001 mm.Hg) a very viscous oil was obtained. It is assumed that also here a two-step reaction has occurred with formation of a polymeric product. So far no physical measurements have been made but the high viscosity seems to exclude a dimeric structure as has been found with the phenyl compounds.

Acknowledgement. The author is indebted to Prof.G.J.M.van der Kerk, Director of this Institute, for many stimulating discussions and to Dr.E.S.Hedges, Director of the International Tin Research Council, for his supporting interest. Part of this work was carried out in co-operation with Dr.M.C.Henry (U.S.Army Quartermaster R. and E. Center, Natick, Mass.).

References

1. T.M.Andrews, F.A.Bower, B.R.La Liberte and J.C.Montermoso, J.Am.Chem.Soc., 80, 4102 (1958)
2. J.G.Noltes and G.J.M.van der Kerk, "Functionally Substituted Organotin Compounds", Tin Research Institute, Greenford, England, 1958, 125 pp.
3. M.C.Henry and J.G.Noltes, submitted for publication to J.Am.Chem. Soc.

Novel Epoxy Resins

P. E. Ritt
Melpar, Inc.

INTRODUCTION

In the last few years, epoxy resins have enjoyed one of the fastest growth rates of the many plastic materials now used in commercial applications. Even more impressive than this rapid growth rate is the variety of applications to which epoxy resins have been put in the short time since they reached commercial importance. Due to their outstanding strength, adhesion, and chemical resistance, these resins have played an important role in broadening the total utility of plastics in industry.

Recently, increasing requirements for thermal stability of polymers of this type was recognized by Wright Air Development Center and Melpar, Inc. was authorized to conduct a research program on modification of epoxy resins for this purpose.

There is considerable evidence to show that certain semi-organic polymers have unusual thermal stability. In particular, certain organo-phosphorus compounds have received considerable attention stemming from their possible use in high-temperature polymers. In view of this and because of the high thermal stability of the -C-P- bond, it seemed that a program directed toward modification of epoxide resins by incorporation of phosphorus as an integral part of the epoxide molecule would be a fruitful area to explore.

At the offset of the program, characteristic thermal properties of commercially available epoxy resins were determined. With this information, it was possible to compare any resins that were developed in the program with these commercial resins. For this investigation, Heat Distortion Temperature, Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) were used.

Experimental efforts in the synthesis phase were concentrated in the following general areas:

1) Reactions of tetrakis (hydroxymethyl) phosphonium chloride (THPC).
2) Reactions of tris (hydroxymethyl) phosphine oxide (THPO).
3) Miscellaneous preparations of organo-phosphorus compounds.

Testing of Commercial Epoxy Resins

Table I lists commercial epoxy resins obtained with their respective mixing ratios and curing schedules. When specified by the vendor, laminate samples were prepared only for heat of distortion measurements; castings of the laminating resin were made for thermo-gravimetric and

differential thermal analysis.

The heat distortion temperature test closely followed ASTM Designation D 648-45T. Figure 1 shows a picture of the apparatus. The test consisted primarily of supporting the sample, applying a load and measuring the deformation.

The sample to be tested was submerged in a sesame oil bath (in instances where high heat distortion resins were tested, Dow Corning 710 fluid was used). Results of these tests are shown in Table 2.

To study reactions which involve changes in the enthalpy of a material, Differential Thermal Analysis was used. DTA is a means of determining magnitude and duration of an endothermic or exothermic reaction as a function of sample temperature. Figure 2 shows the arrangement of the equipment at a rate of 5°C per minute by a programed increase of power input to the furnace windings. In order to insure that sample particle dispersion would be as constant as possible, resin samples were mechanically crushed and passed through a 200 mesh seive. Aluminum oxide was then added as a diluting agent. (90% Al_2O_3 and 10% sample). For these DTA curves, the first prominent peak was taken as the "end point". Table 3 shows the thermal stability of the polymers in decreasing order as interpreted from DTA curves.

Thermal Gravimetric Analysis is a useful tool in determining composition changes which occur during the heating of a sample. A continuous weighing of the sample at elevated temperatures is necessary. A schematic diagram is shown in Figure 3. In operation, the furnace is heated at roughly 5°C per minute by a controlled variac setting. Temperature is indicated to within 1.5°C by a potentiometer. If the sample loses weight, the slug will rise inside the transformer and produce an increased output. If the sample increases in weight, the slug lowers toward the center of the transformer producing at first, a lower output until the "null" is reached, and then a greater output. Table 4 lists the results of TGA.

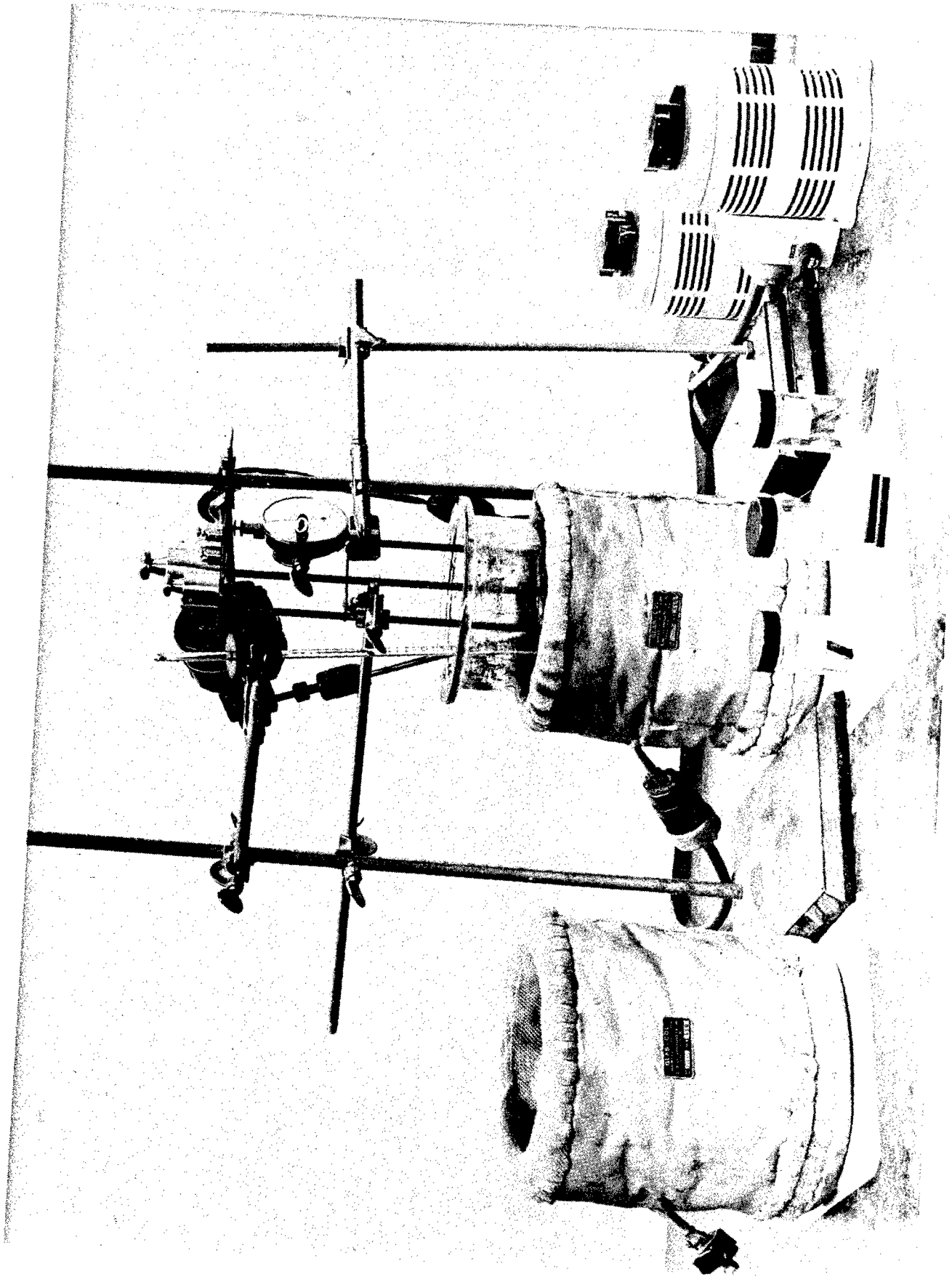


TABLE I

COMMERCIAL EPOXY RESINS, MIXING RATIO & CURING SCHEDULE

RESIN (TRADE NAME)	MANUFACTURER	MIXING RATIO	CURING RATE
Epoxy Novolac X 2638.3	Dow Chem. Co., Plastics Dpt., Midland, Mich.	X 2638.3 - 100 gm, Nadic Anhydride - 101 gm Pyridine - 0.1 cc	2 Hr. @ 200°F 15 Hr. @ 450°F
Eccomold L266 (Laminate with Garan	Emerson & Cumings, Inc. 869 Washington Street Canton, Massachusetts	Eccomold L266 - 100 gm Catalyst 17 - 45 gm	Press Cure Laminate 1 Hr. @ 150°C@25psi Post-Cure 3 Hr. @ 300°F 16 Hr. @ 400°F
Stycast 2662		Stycast 2662 - 90 gm Catalyst 14 - 22.5 gm	48 Hr. @ 25°C 3 Hr. @ 100°C 2 Hr. @ 150°C
Epoxylite #813	The Epoxylite Corp. 10829 E. Lentral Ave. El Monte, California	Epoxylite #813 - 100 gm Catalyst 9 - 39 gm	Gel-0.5 Hr. @ 250°F Cure - 1Hr. @ 250°F 4Hr. @ 350°F
Maraset #617	Marblette Corp. 37-21 30th Street Long Island City 1, N. Y.	Maraset #617 - 100 gm Hardener #886 - 18 gm	2 Hr. @ 200°F 5 Hr. @ 400°F

TABLE I (Continued)

Sealcast 506	Minneapolis Honeywell Regulator Co., 2755 4th Avenue, S. Minneapolis 8, Minn.	Sealcast 506 - 95.8 gm Sealcast 705 - 4.2 gm	3 Hr. @ 250°F 4 Hr. @ 300°F
Epon X1310 (Laminate with Garan 181 Glass Cloth)	Shell Development Co. Emeryville, Calif.	Epon X1310 - 60 gm Acetone - 40 gm Curing Agent - 0.6 gm BF 3400 (Shell)	Press Cure Laminate 1 Hr. @ 150°C @25psi Post-cure 3 Hr. @ 205°C
Epon 828		Epon 828 - 100 gm; Pyromellitic di-anhydride - 17 gm; Maleic Anhydride - 23 gm; Pyridine - 0.1 cc	1 Hr. @ 100°C 1 Hr. @ 130°C 1 Hr. @ 150°C 1 Hr. @ 170°C 1 Hr. @ 190°C 24 Hr. @ 230°C
Epon X1310 Epon 828		Sample # 1 Epon X1310 - 60 gm Epon 828 - 40 gm Diaminodiphenylsulfone - 30 gm	2 Hr. @ 100°C 2 Hr. @ 130°C 2 Hr. @ 160°C 1 Hr. @ 200°C
	Sample # 2 Epon X1310 - 70 gm Epon 828 - 30 gm Diaminodiphenylsulfone - 30 gm	Sample # 3 Epon X1310 - 80 gm Epon 828 - 20 gm Diaminodiphenylsulfone - 30 gm	Same as for Sample #1

TABLE I (Continued)

Permacel ST 3994	Permacel-LePage's, Inc. New Brunswick, New Jersey	Permacel ST 2994 - 100 gm Part B - 30 gm	Add part B when ST 3994 has been heated to 130°C. Cure: 2 Hr. @121°C 4 Hr. @150°C 2 Hr. @180°C
Epon 828 Triethanol-amine Titanote (TAT-21)	Shell Chemical Co. E. I. DuPont de Nemours	Sample I 100 gm 828, 8.3 gm TAT Sample II 100 gm 828, 12.5 gm TAT Sample III 100 gm 828, 16.6 gm TAT	80°C - 3 Hr. 100°C - 3 Hr. 125°C - 2 Hr. 150°C - 2 Hr. Sample I gelled in 44 Hr. Hardened in 68 Hr. Sample II gelled in 24 Hr. Hardened in 44 Hr. Sample III gelled in 20 Hr. Hardened in 40 Hr.

TABLE 2

COMMERCIAL EPOXIES, HEAT OF DISTORTION (264 psi)

	Sample	Distortion Temperature °C
1.	Dow Epoxy Novalac X2638.3	254°C
2.	Eccomold L 266	350°C
3.	Stycast 2662	No suitable sample
4.	Epoxylite No. 813	290°C
5.	Maraset No. 617	Sample broke at 325°C
6.	Sealcast 506	325°C
7.	Epon X1310 Laminate	350°C
8.	Epon 828/PMDA-MA	No suitable sample
9.	Epon 828 - Epon X1310	
	Sample I	295°C
	Sample II	298°C
	Sample III	303°C
10.	Epon 828 - Triethanol Amine Titanate	
	Sample I	73°C
	Sample II	88°C
	Sample III	82°C
11.	Permacel ST 3994	199°C

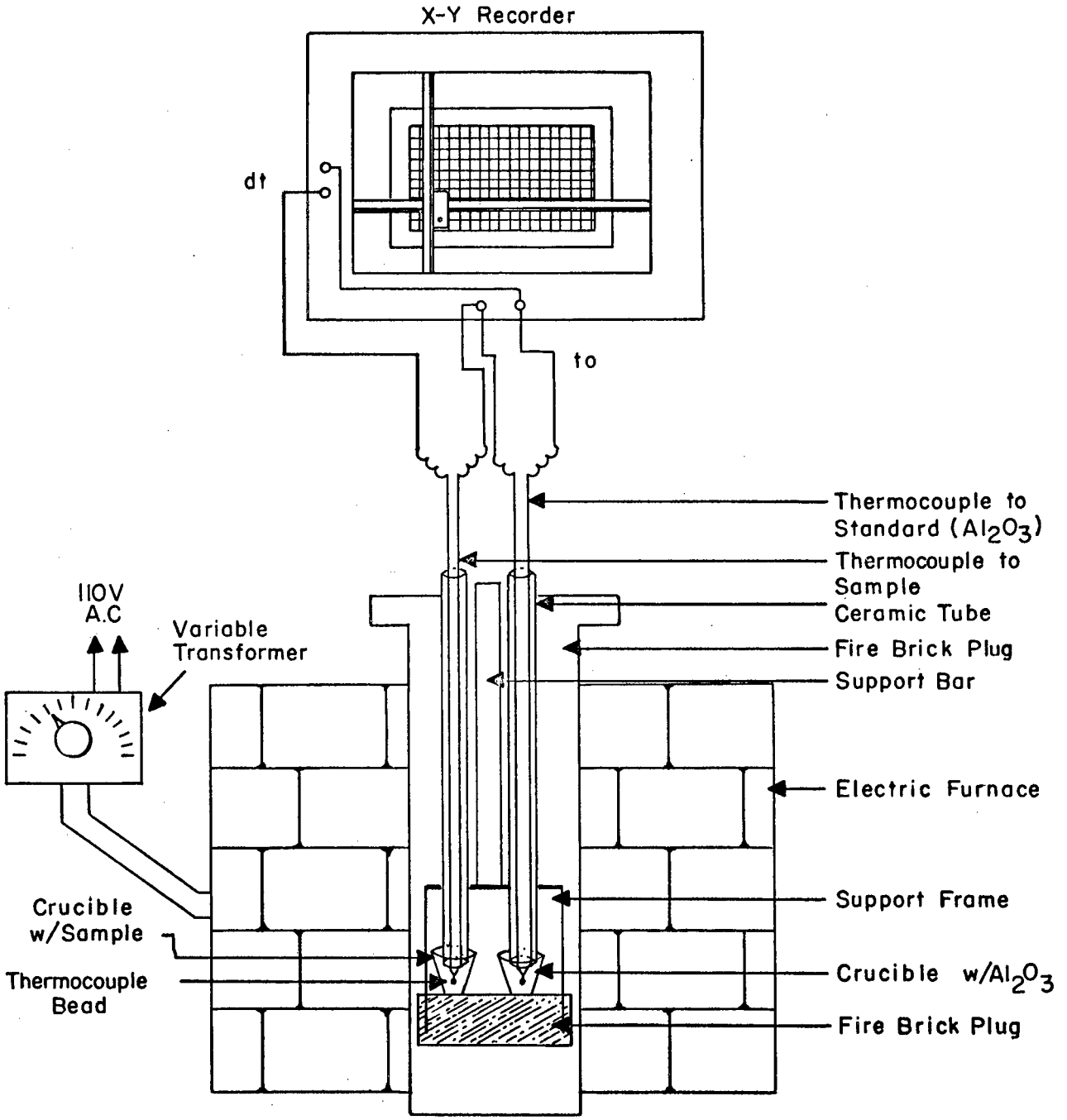


Figure 2. Arrangement of D. T. A. Apparatus

TABLE 3

DTA DEGRADATION TEMPERATURE

Sample	Degradation Temp. (°C)
Stycast 2662	355
Eccomold L266	340
Dow X2638.3	340
Epoxylite 813	330
Maraset 617	325
Epon X1310	320
Sealcast 506	320
Epon 828/PMDA-MA	313
Epon 828 and X 1310/DDS II	296
Epon 828 and X 1310/DDS I	296
Permacel ST-3994	293
Epon 828 and X 1310/DDS III	269

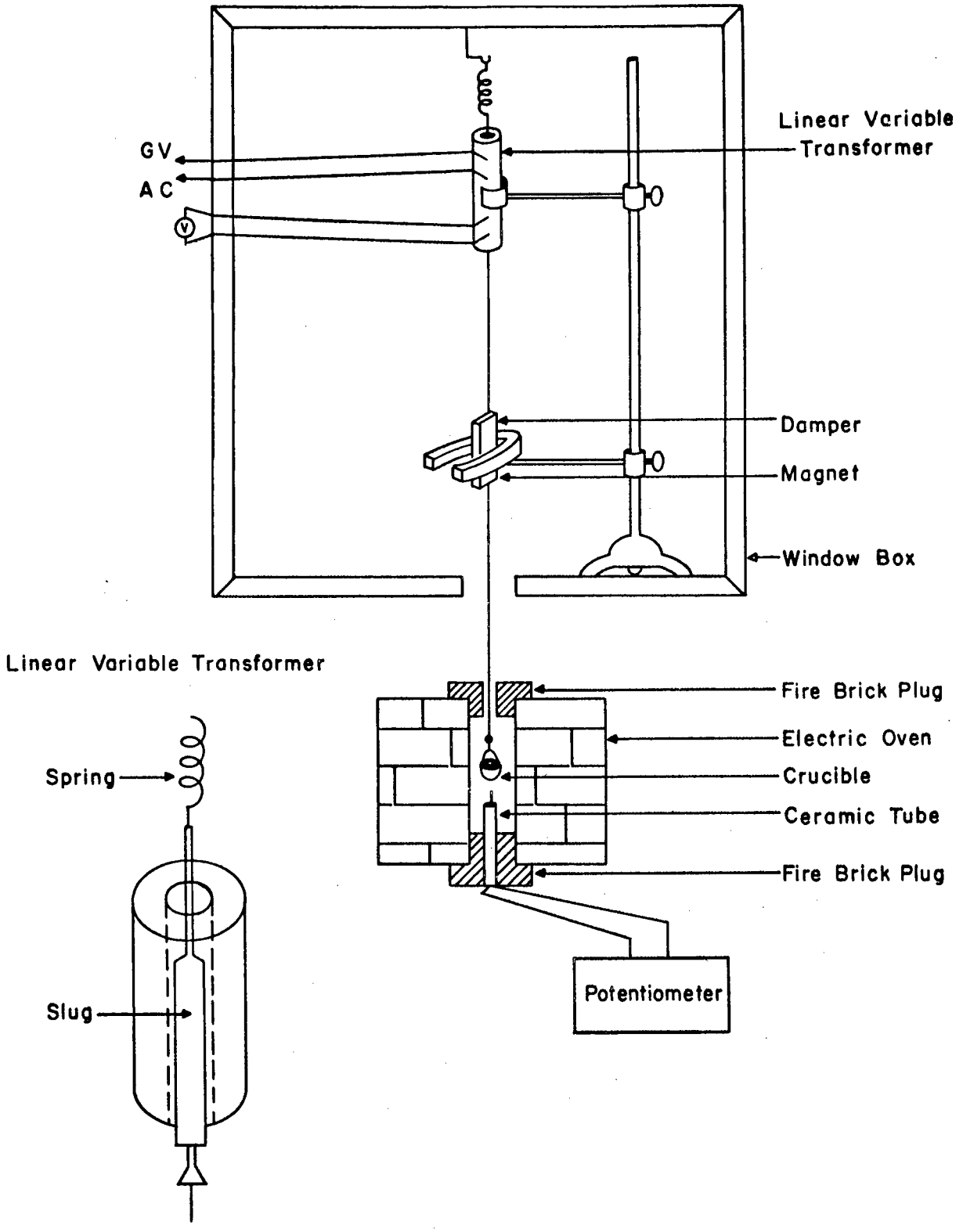


Figure 3. Arrangement of T. G. A. Apparatus

TABLE 4

TGA DEGRADATION TEMPERATURE

Sample	Degradation Temp. (°C)
Eccomold L266	375
Epon 828 and X1310/DDS II	365
Stycast 2662	350
Maraset 617	350
Epon 828 and X1310/DDS (I)	350
Epon 828 and X1310/DDS III	350
Dow X2638.3	330
Epoxylite 813	325
Sealcast 506	312-325
Epon 828/PMDA-MA	317
Epon X1310	-
Permacel ST-3994	-

Base Catalyzed Reactions of THPC and Epichlorohydrin

Tetrakis (hydroxymethyl) phosphonium chloride (THPC) is the salt of a weak base and a strong acid, and has a pH in an aqueous solution of approximately 2. In the presence of alkali, THPC liberates formaldehyde and hydrogen to form tris (hydroxymethyl) phosphine oxide (THPO).

$$[P(CH_2OH)_4]Cl \xrightarrow{NaOH} O=P(CH_2OH)_3 + CH_2O + NaCl + H_2$$

Reeves and Guthrie[1] have reported that THPC is converted to THPO during reaction in alkaline, neutral or mildly acidic solutions, or when heated. Under these conditions the compound acts as a trifunctional monomer.

Initially the reactions of epichlorohydrin and THPC were carried out in the presence of an excess of base as is employed in the commercial epichlorohydrin/bisphenol reaction. The postulated structure of the THPC-epichlorohydrin condensation is shown in Figure 4. Through the use of this trifunctional monomer formation of three dimensional polymers was anticipated. In these reactions it was postulated that the hydroxyl units of the THPC would behave similar to the phenolic hydroxyl in the typical epichlorohydrin-bisphenol A reaction. The base would act as a catalyst and as a neutralizer for the hydrochloric acid which is formed.

Various mole ratios of epichlorohydrin and THPC were reacted varing the time and temperature of reaction and amount of sodium hydroxide solution. The most promising polymer products resulting from these experiments were obtained from ratios of 3 moles of epichlorohydrin and 1 mole of THPC (stoichiometric amount). The amount of 30% NaOH required for these reactions ranged from 44 to 51% by weight. The products from each of these reactions were water soluble.

The Infra-red spectra of these products showed very intense hydroxyl absorption bands with some slight indication of the presence of epoxy groups. In addition, a new band at 6.25μ appeared which was thought to be due to water of hydration. During the curing of these products the complete disappearance of this 6.25μ band was observed.

The curing of these polymers was obtained through the use of both amine and anhydride curing agents. Curing with amine type curing agents such as BF 3-400, a boron trifluoride amine complex, gave water soluble foam products whereas anhydride type curing agents such as Pyromellitic Anhydride and Maleic Anhydride gave hard, water insoluble foams.

[1] W. A. Reeves and John D. Guthrie, "Intermediates for Flame Resistant Polymers," Ind. and Eng. Chem., 48, No. 1: 64-7 (1956).

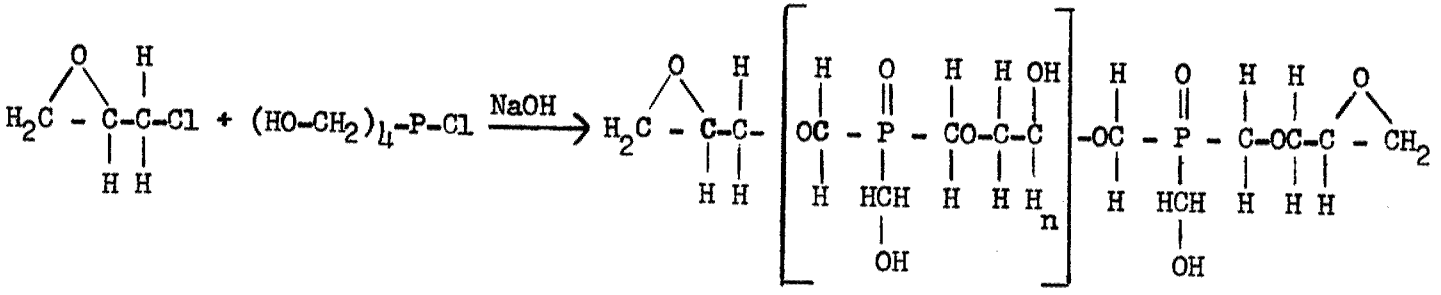


FIGURE 4

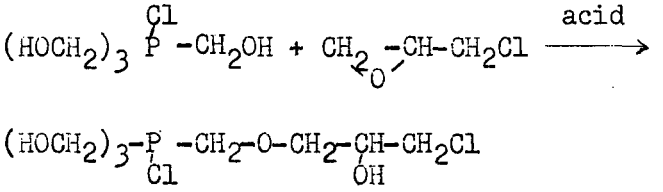
Formation of Phosphorous Bearing Epoxy Polymers with THPC and Epichlorohydrin

Various attempts to circumvent the water soluble products obtained from the epichlorohydrin-THPC reaction were made. To determine the effect of the reaction medium on the final solubility of the reaction product, THPC was reacted with epichlorohydrin in ethyl alcohol using potassium ethoxide as the base. Although the subsequent product was water soluble, curing with Pyromellitic-Maleic Anhydride gave a water insoluble foam.

Attempts at reacting THPC and epichlorohydrin in a pyridine medium did not prove successful.

In previous runs in which aqueous sodium hydroxide was used to condense THPC and epichlorohydrin, there was evidence of considerable hydrolysis and little epoxide formation. It was thought, therefore, that the THPC hydroxyls might react more directly as alcoholic hydroxyls. Although the use of aqueous sodium hydroxide can be employed successfully to produce glycidyl ethers by the condensation of phenolic hydroxyls with epichlorohydrin, the condensation of alcoholic hydroxyls and epichlorohydrin to give glycidyl ethers is usually carried out in two steps. The first step was an acid catalyzed condensation under anhydrous conditions to give the chlorohydrin. The second step was a dehydrohalogenation with base to give the epoxide.

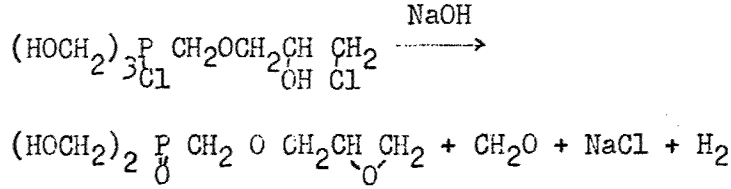
It can be assumed that the hydroxyl groups of THPC behave as alcoholic hydroxyls, an acid catalyzed reaction with epichlorohydrin might, therefore, be expected to proceed as follows:



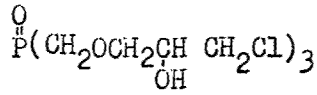
The reaction is not limited to the condensation of one mole of epichlorohydrin with a mole of THPC as shown above. Theoretically, each of the hydroxyl groups of the THPC is capable of reacting with a mole of epichlorohydrin. The subsequent treatment of the chlorohydrin with strong NaOH should effect ring closure to give the epoxide. Since it is known[1] that THPC in aqueous base is converted to THPO, it was postulated that the second step of the reaction would proceed as follows:

---

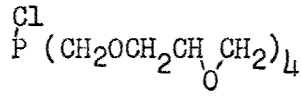
[1] W. A. Reeves and John D. Guthrie, Ind. and Eng. Chem., 48, No. 1, P. 64-7, 1958.



The instability of THPC raises certain questions concerning the probable course of the reaction. Decomposition to THPO may occur during the initial acid catalyzed reaction, in which case only three hydroxyl groups would react and the final product after reaction with three moles of epichlorohydrin would be:



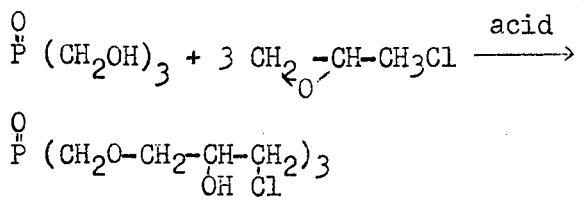
On the other hand, it was quite possible that under mild anhydrous conditions, all four hydroxyls would react. In this case, decomposition to the tertiary phosphine oxide would not occur even during the ring closing step with base, and the final product would have the structure:



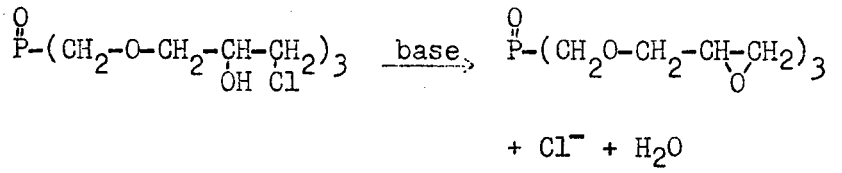
In conducting this reaction it was found that both steps were highly exothermic and difficult to control. A method was developed for controlling the reaction in the first step, but in the second step there was either a violent exothermic reaction resulting in a mixture of crosslinked-insoluble polymeric materials or a product which contained no detectable epoxide groups and failed to cure with the usual epoxide curing agents.

It has been pointed out that THPC is converted to THPO during reaction under alkaline, neutral, or mildly acid conditions or when heated. During the course of our work, purified THPO became available from the Hooker Chemical Corporation. By using this compound as a starting material, it was reasoned that some of the complications caused by the instability of THPC could be eliminated and a clearer picture of the expected reactions could be realized. The reactions proposed for the two step preparation of the epoxide from THPO and epichlorohydrin are essentially the same as the reactions proposed for THPC and epichlorohydrin mentioned previously. However, the reaction in which THPC decomposes to THPO is eliminated since THPO is the starting material.

The first step of the reaction is represented by the acid catalyzed condensation of THPO and epichlorohydrin under anhydrous conditions:



Subsequent treatment of the chlorohydrin with base should effect ring closure to give the epoxide:



Investigation of these reactions is not yet complete, but a considerable amount of progress has been made. It appears that the acid catalyzed condensation proposed for the first step does occur. This is based on the fact that a completely homogeneous liquid is obtained which contains practically no oxirane oxygen. Because of the difficulty in obtaining a pure sample of the reaction products, positive identification and structure proof have remained a problem.

We have attempted ring closing experiments with a number of the most promising condensation products. The most promising experiments indicated that some ring closure took place since the percentage of chlorine decreased significantly. However, the actual amount of chlorine present after ring closure indicated that the reaction was far from complete. This was confirmed by the fact that the amount of oxirane oxygen was less than the amount calculated for the proposed reaction.

In polymer chemistry, it is often found that useful products can be obtained from reactions which are not as well characterized or complete as desired. Therefore, some of the samples obtained from the THPO-epichlorohydrin, were cured with various epoxy curing agents. The results of the most promising samples are summarized in Table 5.

Preparations of Organo-Phosphorous Intermediates

In addition to THPC and THPO, other organo-phosphorous compounds were considered in the synthesis program for developing heat stable epoxy resins. The preparation of other phosphorous compounds containing one or more epoxide groups was investigated briefly. It was proposed that these compounds be self-polymerized or used as reactive modifiers with commercial epoxide resins.

Diethyl 2,3 Epoxy Propane Phosphonate was prepared as a phosphorous containing epoxide compound. It was thought that this compound might prove useful as a reactive resin modifier. The compound was

TABLE 5

Sample	Curing Agent	Curing Conditions	Description of Cured Product
1	Phthalic Anhydride 30 PHR*	24 hrs. at 120°C 2 hrs. at 200°C	Thermoplastic. Solid at room temp. Softens at about 80-100°C.
2	Pyromellitic Anhydride 55 PHR	20 hrs. at 220°C	Rigid non-uniform foam
3	Curing agent Z** 20 PHR	2 hrs. at 80°C 2 hrs. at 150°C	Rigid non-uniform foam.

*Parts per hundred resin
**Shell Chemical Co.

initially made by reacting triethyl phosphite with epichlorohydrin. It was found that the reaction was very slow and only a trace of product was isolated, however, when triethyl phosphite was reacted with epibromohydrin a 50% yield of essentially pure product was obtained boiling at 101°/35 mm. The reaction is represented as follows:

$$P\text{-}(O\ C_2H_5)_3 + CH_2\underset{O}{\diagdown\diagup}CH\ CH_2\ Br \longrightarrow CH_2\ CH\ CH_2\ \overset{O}{\overset{\|}{P}}\text{-}(O\ C_2H_5)_2Br + C_2H_5Br$$

The Diethyl 2,3 Epoxy phosphonate was reacted with Epon 828 and Diethylene Triamine to yield a product exhibiting a heat of distortion at 155°C. (Epon 828 cured with Diethlene Triamine gave a heat of distortion at 255°C.) This result was not altogether disappointing since the epoxy phosphonate, having only one reaction site acted as a diluent for the Epon 828.

In the reaction of Bis-(chloropropyl)chloropropane phosphonate with Glycidol, it was proposed that a defunctional epoxide intermediate be obtained. The reaction was expected to proceed in the following manner:

$$Cl\text{-}C_3H_6O\diagdown \overset{O}{\overset{\|}{P}}\text{-}C_3H_6Cl + 3CH_2\underset{}{\overset{O}{\diagup\diagdown}}CH\ CH_2\ OH \xrightarrow{NaOH}$$
$$Cl\text{-}C_3H_6O\diagup$$

$$(CH_2CH\ CH_2\ O\ C_3H_6O)_2\ P\text{-}C_3H_6O\ CH_2\underset{}{\overset{O}{\diagup\diagdown}}CH\ CH_2 + NaCl$$

The solid NaOH was added and the entire mixture refluxed. A heavy brown viscous material exhibiting water solubility was obtained. The infra red data obtained for this material indicated that the water soluble material resulted from the self-polymerization of glycidol.

In addition to the work on THPO and epichlorohydrin and the organo phosphorous intermediates, we have undertaken the preparation of other organo-phosphorous epoxides, which will be cured and tested as described earlier. These include: (1) organo-phosphorous compounds containing multiple phenolic groups which will be reacted with epichlorohydrin, (2) unsaturated organo-phosphorous compound which will be epoxidized by means of per-acids.

Some work is also planned for investigating various organo-phosphorous amines and acids as epoxide curing agents.

THERMAL DEGRADATION OF POLYMERS AT TEMPERATURES UP TO 850°C[1/]

S. L. MADORSKY, NATIONAL BUREAU OF STANDARDS

INTRODUCTION

In view of the growing interest of industry and government in the use of polymers at temperatures above 500° C, the National Bureau of Standards has undertaken, at the request of the Wright-Air Development Center, to investigate the behavior of polymers at these high temperatures. The investigation described here was carried out by pyrolyzing polymer samples, mostly in a vacuum but in some cases in helium at atmospheric pressure, at temperatures up to 850° C.

A considerable amount of work has been carried out during the last twenty-five years on thermal degradation of polymers at temperatures up to about 500° C. This work has shown, among other things, that the stability and the mechanism of thermal degradation, as well as the chemical nature and relative amounts of the volatile and nonvolatile products of degradation, depend primarily on the molecular structure of the polymer. Thus, for example, tertiary carbon atoms in the chain weaken the adjacent C-C bonds in the chain. Quaternary carbon atoms are even more effective in this respect than tertiary carbons. Abundance of hydrogen on the chain leads to the formation, through random scissions, of volatile products which vary in size from those containing one carbon atom to those containing as many carbons as will permit the fragments to vaporize at the temperature employed in the pyrolysis. On the other hand, scarcity of hydrogen on the main chain will cause the formation of monomers by an unzipping process at the original chain ends as well as at the new ends formed by random scissions.

With regard to the nature of thermal degradation, several types of polymers should be differentiated:

(1) Polymers in which scissions occur primarily in the backbone of the chain. These polymers tend to vaporize completely at sufficiently high temperatures.

(2) Polymers in which the scissions occur primarily between carbons of the backbone and side group. Such scissions results in formation of double bonds in the chain and, perhaps, also crosslinkages between the chains [1].[2/] Such polymers on prolonges heating become more or less stabilized in the form of a partially carbonized residue.

1/ Manuscript released by the authors April 1, 1959, as a WADC Technical Report.

2/ Figures in brackets indicate the literature references at the end of this report.

(3) Polymers that are highly crosslinked. These polymers are converted on heating into honeycombed structures of carbonized residue.

The thermal behavior of some representative members of the first two types of polymers is illustrated in figure 1. In this figure each point represents an experiment consisting of pyrolyzing in a vacuum a polymer sample of about 50 mg or less during a 5-minute preheating period, followed by 30 minutes of heating at the indicated temperature. Curves for polymers of type (1) are shown extending to about 100% volatilization, while curves for polymers of type (2) show stabilization at 60-70% volatilization. Additional details of the behavior of these polymers are given in table 1.

As seen from figure 1 and table 1, poly(α-methylstyrene) [2] and poly(methyl methacrylate) [2], both having quaternary carbons, and a scarcity of hydrogen atoms on the chain backbone, are the least stable of the group and yield only monomers. Polyisobutylene [3], which also has quaternary carbon atoms and a scarcity of hydrogen on the main chain, come next in stability, and its yield of monomeric fragments is only 31.5%. Polystyrene [2,4] has tertiary carbon atoms, but the chain is stabilized by resonance from the phenyl groups. It occupies the next position in thermal stability, and its monomeric yield is 42%. Polybutadiene [3], with every 4th bond being double, which imparts strength to the chain, comes next. Abundance of hydrogen on the chain results in a low yield of monomeric fragments. Polymethylene [5], with only secondary carbons in the chain and with an abundance of hydrogen attached to it, comes next. It breaks up at random into fragments of various sizes. Teflon [6], with only secondary carbon atoms in the chain and fluorine replacing hydrogen is the most thermally stable of the group, and yields over 97% monomer.

Of the representative polymers of type (2), shown in figure 1 and table 1, poly(vinyl chloride) [7] yields a V_{25} fraction containing 98 mole percent HCl and 2 mole percent benzene, polyacrylonitrile [8] yields a V_{25} fraction containing 50 mole percent HCN, and poly(vinylidene fluoride) [6] yields 50 percent HF.

As to polymers of type (3), poly(trivinylbenzene) serves as an example. This polymer, as well as its copolymers with styrene, have been studied by Winslow and coworkers [9,10]. Poly(trivinylbenzene) during pyrolysis at about 500° C for 30 minutes yields a carbonized residue of about 40% or less of the original sample, depending on temperature of pyrolysis and rate of heating to this temperature.

MATERIALS

Polystyrene is the only polymer of group (1) used in this investigation. This polymer was the same pure material as was used in previous pyrolysis studies by the present author and his coworkers [4]. It was prepared thermally and had a molecular weight of 230,000 as determined by the osmotic-pressure method.

The polymers of group (2) used in this investigation were poly(vinylidene fluoride), a white rubbery material, and polyacrylonitrile in the form of a white powder. These materials were the same as those used previously in the work on pyrolysis [6,8]. The poly(vinylidene fluoride) was polymerized by γ-radiation and had a high molecular weight. The polyacrylonitrile had a number-average molecular weight of 40,000.

Polymers of group (3) that were used were poly(trivinylbenzene) and four thermoset plastics. The poly(trivinylbenzene), in the form of a light amber rod, was obtained from F. H. Winslow of Bell Telephone Company, and had been prepared thermally at 80° C in a nitrogen atmosphere and without reagents. The thermoset plastics were as follows:

a) Polyester (Vibrin) - This material was prepared from Vibrin 136-A, which consists of equal parts by weight of maleic anhydride and triallyl cyanurate. Tertiary butyl perbenzoate was used as the curing agent. The cured material was a transparent glass of light amber color.

b) Epoxy - This material was prepared from Epon 1310, which is a condensation product of epichlorhydrin with a polyphenol, containing from 3 to 4 phenolic groups per molecule and having a molecular weight of 200 per epoxide group. Boron trifluoride in acetone solution was used as the curing agent. The plastic was a transparent glass of a darker amber color than the Vibrin.

c) Phenolic - This plastic material was obtained by curing a high-temperature phenol-formaldehyde resin. The cured material was a very dark brown glass.

d) Silicone - This resin contained methyl and phenyl groups attached to silicon atoms in a silicon-oxygen chain. It was a transparent glass of light amber color with a pinkish tint..

APPARATUS AND PROCEDURE

Most of the experiments at temperatures below 500° C were carried out in an apparatus that has been described previously in connection with a study of pyrolysis in a vacuum of cellulose and related materials [11] and also of tetrafluoroethylene and hydrofluoroethylene polymers [6]. The samples were placed in a small quartz tube that fitted into a larger quartz tube projecting horizontally from the vacuum apparatus. The furnace was heated to the required temperature and was then moved quickly into position to heat the sample. It usually took about 5 minutes for the temperature of the sample in the small quartz tube to reach equilibrium temperature. The sample was then heated for 30 additional minutes at this temperature. For convenience, this apparatus will be referred to as apparatus I.

Apparatus II, which was used in pyrolysis experiments at 500 to 850° C, is shown diagramatically in figure 2. It is similar in many respects to apparatus I, except that it could be heated to a higher temperature, and the furnace could be moved more quickly horizontally by means of ball-bearings. The sample holder was a cylindrical platinum crucible. A heavy stainless-steel cylindrical cup fitting tightly into the furnace served as an efficient distributor of heat to the quartz tube containing the platinum sample holder. Due to this efficient heat distribution the time required for the thermocouple E (figure 2) to reach equilibrium after the furnace was moved into position for pyrolysis was only about one minute for temperatures up to about 800 to 850° C. In some experiments apparatus II was used at temperatures below 500° C, as will be described later.

In all the pyrolysis experiments described here, unless stated otherwise, a vacuum of better than 10^{-4} mm of Hg was used. The temperature control was about ±0.5° C. Samples weighed about 10-50 mg.

PYROLYSIS EXPERIMENTS

Polystyrene

The thermal behavior of polystyrene at moderately high temperatures is well known. When heated in a vacuum [4] or in a neutral atmosphere [12] it was found to vaporize completely at temperatures below 400° C. In the present investigation it was of interest to determine degradation when a sample of this polymer, in a vacuum or in a neutral atmosphere, is suddenly thrust into a hot zone at a temperature far above 400° C. Experiments were carried out at 362° C and at 850° C

in apparatus II, in a vacuum and in helium at atmospheric pressure. The results are shown in table 2. As seen from this table, either a higher temperature or a higher pressure, or a combination of the two, produce a greater yield of small molecular fragments (V_{25}) at the expense of the larger fragments (V_{pyr}).

Fraction V_{-190} has not been analyzed. According to previous work [4] at temperatures below 500° C it amounts to less than 0.1% by weight of the sample. Mass spectrometer analysis of fraction V_{25} for all four experiments is given in table 3. Here again, as in the case of table 2, a higher temperature and a higher pressure favor a greater fragmentation of the volatile products.

Fractions V_{pyr} from experiments 2, 3, and 4 were tested for their average molecular weight by a microcryoscopic method in benzene solution, with the following results:

Expt. No.	Average Molecular Weight
2	310
3	310
4	321

Fraction V_{pyr} from polystyrene obtained in vacuum pyrolysis in the temperature range 325° to 375° C was found in previous work to have an average molecular weight of about 264. This fraction, according to information found in the literature and also in our earlier work, consists of a mixture of dimers, trimers, tetramers, and smaller amounts of longer chain fragments. The high molecular weight of fractions V_{pyr} from experiments 2, 3, and 4 could indicate that they contain larger proportions of the heavier fragments than fraction V_{pyr} from experiment 1.

Poly(vinylidene fluoride) and Polyacrylonitrile

As was pointed out above, poly(vinylidene fluoride) and polyacrylonitrile at higher temperatures yield a carbonaceous residue. The results of pyrolysis are shown in table 4. Experiments 1 to 8 for poly(vinylidene fluoride) and 1 and 2 for polyacrylonitrile were carried out in apparatus I, and the other experiments in apparatus II. A comparison between slow heating and rapid heating to the same temperature is shown in experiments 9, 10, and 11 for poly(vinylidene fluoride).

Mass-spectrometer analysis of fractions V_{25} and V_{-190} for those experiments in table 4 that were taken from references [6, 7, and 8] have been described in those references. In the case of poly(vinylidene fluoride), V_{25} consisted mainly of HF. Fraction V_{-190} amounted to less than 0.1% of the total volatilized part and consisted mainly of H_2 and CO. Fraction V_{25} from polyacrylonitrile consisted mainly of hydrogen cyanide, acrylonitrile, and vinylacetonitrile. The V_{-190} fraction was very small and consisted of H_2. Analysis of fractions V_{25} and V_{-190} from pyrolysis of both polymers at 500° C and higher temperatures is now in progress. The average molecular weight of fraction V_{pyr} from polyacrylonitrile was found previously [8] to be 330. No suitable solvent could be found to make a microcryoscopic determination of the average molecular weight of fraction V_{pyr} from poly(vinylidene fluoride). However, an attempt is being made to determine this value by vaporizing this fraction directly into the mass spectrometer.

The residues from poly(vinylidene fluoride) were black and pulverized easily when pressure was applied. The residues from polyacrylonitrile were black powders.

Studies on rates of thermal degradation in a vacuum were made on poly(vinylidene fluoride) at 400°, 410°, and 420° C using a tungsten-spring balance [13], and also at 371.3° and 390° C using an electronic balance [14]. Pertinent data on these studies are shown in table 5. The activation energy as calculated from the maxima of these rates is 48 kcal/mole. Rate studies on polyacrylonitrile with the tungsten-spring balance have been described previously [8]. Due to a very rapid rate at the higher temperatures, the activation energy could not be accurately determined, although pronounced rate maxima were obtained for 250° and 260° C. Three more rate determinations have now been made, one at 240° C in the spring balance, and two at 218° and 228° C, respectively, in the electronic balance. Pertinent data on the previous and present work are shown in table 5. The activation energy as calculated from the maxima is 31 kcal/mole.

Poly(trivinylbenzene)

Results of pyrolysis of this polymer are shown in table 4. The curve begins to level off at about 500° C, and the additional loss by volatilization from 500° to 800° C is only about 10%. These results are in fairly good agreement with those obtained by Winslow and coworkers [9,10], whose method consisted in heating the samples slowly, at the rate of 100° C

per hour. In Winslow's work volatilization at corresponding temperatures is generally lower than that in this work. On comparing experiment 6, where the sample was heated slowly to 800° C during 135 minutes and then kept at this temperature for 5 minutes, with experiments 7 and 8, where the samples were thrust into the furnace at 800° C and kept there for 5 minutes, we find that the slower rate of heating resulted in smaller losses by volatilization.

Mass-spectrometer analysis of fraction V_{25} from experiments 4 and 8 are shown in table 6, and those for V_{-190} in table 7. Here too, as in the case of polystyrene, a higher temperature of pyrolysis resulted in a greater fragmentation of the volatile products, as evidenced by the fact that the hydrogen yield in weight percent, was 0.35% at 500° and 3.1% at 800° C. The average molecular weight of fraction V_{pyr} from poly(trivinylbenzene) was determined by a microcryoscopic method in benzene solution. Three determinations showed an average molecular weight of 338. The carbonized residue from pyrolysis, even at 800° C, retained its original shape, but shrank in size and was hard and firm.

Rates of thermal degradation in a vacuum were studied at 420°, 430°, and 440° C, in the tungsten-spring balance, and also at 394° in the electronic balance. The activation energy, calculated from the initial rates, is 73 kcal/mole.

Thermoset Plastics

Results of pyrolysis in a vacuum of four thermoset plastics are shown in table 8. Fractions V_{25} and V_{-190} were analyzed in the mass spectrometer separately but the results are combined in table 9. In terms of increasing thermal stability these thermoset plastics can be arranged in the following order: Vibrin, epoxy, phenolic, and silicone. The more volatile products of pyrolysis consisted mainly of benzene in the case of silicone, and of carbon dioxide in the case of the other three plastics. Methyl chloride and ethyl chloride in the pyrolysis products of the epoxy resins at 360° C are due to the epichlorhydrin used in the preparation of Epon 1310. It is rather surprising that no chlorides showed up in the products from pyrolysis at 500° and 800° C.

CONCLUSIONS

When heated at temperatures of about 500° C or higher, highly crosslinked polymers, or those which form complex crosslinkages during the heating, stabilize to yield a

carbonaceous residue. In figure 3 a summary of such carbonization in the temperature range 350° to 800° C is shown for seven polymers which were investigated. Curves for polymethylene and Teflon are shown for comparison. Taking the percentage of residue as a measure of thermal stability, the three most stable polymers can be arranged in the following order of stability:

Silicone resin phenolic resin poly(trivinylbenzene)

The other four less-stable polymers, Vibrin, polyacrylonitrile, epoxy, and poly(vinylidene fluoride), have about the same stability.

Higher temperatures and higher pressures in the pyrolysis of polymers result in greater fragmentation of the volatile products. However, it is not clear from this work whether this greater fragmentation takes place during the primary reaction when the fragment breaks off from the polymer, or in a secondary reaction, after the fragment has already been formed. In the case of a higher temperature, a fragment already formed might break up further while passing through the hot zone in the furnace. In the case of a higher pressure a further breakup of a fragment could take place while its escape from the hot zone is retarded through collisions with other molecules.

The overall activation energy of the bond scissions in kcal/mole was 73 for poly(trivinylbenzene) 48 for poly(vinylidene fluoride), and 31 for polyacrylonitrile. The values for the thermoset plastics have not as yet been determined. The activation energy of poly(trivinylbenzene) is about the same as that of polymethylene [5]. It is much higher than that of any of the other polymers shown in figure 1, except Teflon [6]. This high thermal stability of poly(trivinylbenzene) is undoubtedly due to its highly crosslinked structure.

FUTURE PLANS

It is planned to continue work on the pyrolysis of polymers along the same lines as described here and to extend the temperature range of pyrolysis up to about 1300° C.

Table 1. Thermal Degradation of Some Representative Polymers at Temperatures Below 500° C

(In Weight Percent of Volatilized Part)

Polymer	Fraction V_{25} [1] yield %		Fraction V_{pyr} [1] Yield %	Molecular size
		TYPE 1		
Poly(α-methylstyrene)	100		0	------
Poly(methyl methacrylate)	100		0	------
Polystyrene	42.0		58	Dimer, trimer, tetramer
Polyisobutylene	31.5		68.5	543 molecular weight
Polybutadiene	2.2		97.8	739 " "
Polymethylene	3.2		96.8	692 " "
Teflon	97.0		3.0	Mostly C_3F_6
		TYPE 2		
Poly(vinylchloride)	100	(HCl)	0	------
Polyacrylonitrile	12	(50 mole % HCN) [2]	88	330 molecular weight
Poly(vinylidene fluoride)	50	(HF)	50	500-600 [3] molecular weight

1/ The fractions are defined as follows: V_{pyr} - volatile at the temperature of pyrolysis, but not at room temperature. V_{25} - volatile at room temperature, but not at -190° C; this fraction usually consists of monomer or monomer-size molecules. V_{-190} - volatile at the temperature of liquid nitrogen.

2/ On standing, HCN tended to polymerize with the other fragments and it was difficult to determine its original yield.

3/ Estimated.

Table 2. Pyrolysis of Polystyrene in a Vacuum and in Helium at Atmospheric Pressure

Expt. No.	Temp. °C	Duration[1]	Volatilization %	Fractions, based on volatilization V_{25} %	V_{-190} %	V_{pyr} %
			IN VACUUM			
1	362	1 hr	83	43	Trace	57
2	850	35 sec	100	68	"	32
			IN HELIUM			
3	362	1 hr	83	55	Trace[2]	45
4	850	35 sec	98	72	"[2]	28

1/ Time at operating temperature.

2/ Estimated.

Table 3. Mass Spectrometer Analysis of Fraction V_{25} from Polystyrene

Component	Expt. 1	Expt. 2	Expt. 3	Expt. 4
	mole %	mole %	mole %	mole %
Styrene	94.4	34.0	50.5	12.9
Toluene	5.6	5.5	5.6	14.1
Benzene	0	58.2	43.9	18.5
Propadiene	0	1.9	0	1.1
Ethylene	0	0	0	49.2
Ethane	0	0	0	4.2
TOTAL	100.0	100.0	100.0	100.0

Table 4. Pyrolysis of High-temperature Polymers

Expt. No.	Duration	Temp.	Volatilization	Fractions, based on volatilization V_{25}	V_{-190}	V_{pyr}
	min	°C	%	%	%	%
			POLY(VINYLIDENE FLUORIDE)[1]			
1	30	380	4	---	---	---
2	30	433	15	41	Trace	59
3	30	444	48	52	"	48
4	30	450	67	69	"	31
5	30	456	66	---	---	31
6	30	484	68	---	---	---
7	30	500	76	68	Trace	32
8	30	530	71	48	"	52
9	140	800	68	73	"	27
10	5	800	82	61	"	39
11	5	800	87	59	"	41
			POLYACRYLONITRILE[2]			
1	30	350	58	12	Trace	88
2	30	455	73	12	"	88
3	5	800	94	14	"	86
			POLY(TRIVINYLBENZENE)[3]			
1	30	360	0	---	---	---
2	30	430	26	43	---	---
3	30	470	53	24	---	---
4	30	500	55	13	5	82
5	30	500	59	8	---	---
6	140	800	63	5	---	---
7	5	800	68	3	---	---
8	5	800	68	5	11	84

1/ Expt. Nos. 1, 2, 3, 5, 6, 8 taken from reference [6]. In Expt. No. 9., the sample was heated from room temperature to 800° during 135 minutes and then kept at this temperature for 5 minutes.

2/ Expt. Nos. 1 and 2 taken from reference [8].

3/ In Expt. No. 6 the sample was heated from room temperature to 800° C during 135 minutes and kept at this temperature for 5 minutes.

Table 5. Rates of Thermal Degradation of Poly(vinylidene fluoride), polyacrylonitrile, and poly(trivinylbenzene)

Temperature	Heating duration	Loss of weight	Rate	
		%	%/min	
	POLY(VINYLIDENE FLUORIDE)			
371.3	9 hr	47.6	0.14	(max)
390	3 hr 10 min	49.9	0.36	"
400	2 hr 20 min	55.5	0.66	"
410	1 hr 40 min	58.0	1.15 1/	"
420	1 hr 30 min	62.5	2.05 1/	"
	POLYACRYLONITRILE			
218	22 hr	6.0	0.01	(max)
228	16 hr 50 min	9.7	0.05	"
240	1 hr 40 min	11.8	0.36	"
250	1 hr 40 min	14.0	0.63	"
260	1 hr 40 min	16.5	1.14	"
	POLY(TRIVINYLBENZENE)			
394	44 hr	39.2	0.03	(initial)
420	3 hr 30 min	45.2	0.28	"
430	2 hr 20 min	46.0	0.59	"
440	1 hr 20 min	47.8	1.22	"

1/ Estimated.

Table 6. Mass Spectrometer Analysis of Fraction V_{25} from Pyrolysis of Poly(trivinylbenzene)

(In Mole Percent of Fraction)

Component	Temperature of pyrolysis 500° C	800° C
$C_{11}H_{16}$	1.9	0.9
$C_{10}H_{14}$	6.4	3.6
C_9H_{12}	9.1	8.8
C_9H_{10}	3.0	2.0
C_8H_{10}	5.0	7.7
C_8H_8	0.4	0.4
C_7H_8	1.1	4.9
C_6H_6	0.3	2.1
C_6H_{10}	0.4	---
C_5H_{10}	0.6	0.4
C_4H_8	6.7	4.6
C_3H_8	7.9	6.5
C_3H_6	9.9	8.0
C_3H_4	1.1	0.6
C_2H_6	21.1	19.9
C_2H_4	25.1	25.0
CH_4	----	4.6
TOTAL	100.0	100.0

Table 7. Mass Spectrometer Analysis of Fraction V_{-190} from Pyrolysis of Poly(trivinylbenzene)

(In Mole Percent of Fraction)

Component	Temperature of pyrolysis 500° C	800° C
C_3H_6 and higher H-C	1.7	1.9
C_2H_6	2.0	0.7
C_2H_4	3.4	1.0
CH_4	55.1	21.5
H_2	37.8	74.9
TOTAL	100.0	100.0

Table 8. Pyrolysis of Thermoset Plastics

Plastic	Temp.	Duration at operating temperature	Volatilization	Fractions, based on volatilization		Appearance[1] of residue
				$V_{25} + V_{-190}$	V_{pyr}	
	°C	min	%	%	%	
Vibrin	360	60	28	66.5	33.5	A,B,D
	500	30	83	47.4	52.6	A,C,F
	800	5	89	55.7	44.3	A,F,K
Epoxy	360	60	38	36.4	63.6	A,B,D
	500	30	75	18.0	82.0	A,C,F
	800	5	86	26.9	73.1	A,F,K
Phenolic	360	60	11	25.0	75.0	G
	500	30	28	50.1	49.9	A,B,D,F
	800	5	47	40.1	59.9	A,B,F
Silicone	360	60	2	----	----	G
	500	30	6	91.3	8.7	B,D,E,H
	800	5	13	86.7	13.3	A,B,D

1/ Meaning of letters:

A - turned black
B - retained shape
C - retained shape, but became slightly buckled
D - retained gloss
E - retained some transparency
F - became opaque
G - no apparent change
H - smoky in color
K - shrunk

Table 9 - Part 1. Analysis of Volatile Products from Pyrolysis of Thermoset Plastics

(In Weight Percent of Total Volatilized Part)

Component	Vibrin			Epoxy		
	360°	500°	800°	360°	500°	800°
$V_{-190} + V_{25}$	%	%	%	%	%	%
Hydrogen	---	---	0.7	---	---	0.8
Carbon monoxide	3.3	2.9	9.2	4.7	3.1	11.2
Carbon dioxide	62.4	41.4	29.3	16.2	6.0	3.7
Methane	---	0.7	1.8	1.0	0.8	1.6
Methanol	---	---	---	---	0.2	---
Ethane	---	0.6	---	---	---	---
Ethylene	---	0.6	6.5	---	---	3.0
Acetaldehyde	---	---	---	0.3	---	---
Acetone	---	---	---	0.9	2.2	---
Propane	---	---	---	---	1.1	---
Propylene	0.8	---	2.5	6.5	2.3	2.2
Propanol	---	---	---	---	0.3	---
Butane	---	---	---	---	---	1.6
Butene	---	---	1.5	---	0.2	---
Butadiene	---	---	0.3	---	---	---
Pentane	---	0.7	---	---	0.5	---
Pentene	---	0.5	---	---	---	---
Pentadiene	---	---	2.6	---	---	---
Benzene	---	---	1.3	---	1.3	2.8
Methyl chloride	---	---	---	5.1	---	---
Ethyl chloride	---	---	---	1.7	---	---
V_{pyr}	33.5	52.6	44.3	63.6	82.0	73.1
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0

Table 9 - Part 2. Analysis of Volatile Products from Pyrolysis of Thermoset Plastics

(In Weight Percent of Total Volatilized Part)

Component	Phenolic			Silicone	
	360°	500°	800°	500°	800°
	%	%	%	%	%
$V_{-190} + V_{25}$					
Hydrogen	---	---	5.2	---	18.4
Carbon monoxide	---	3.5	9.4	---	---
Carbon dioxide	0.5	5.5	2.4	0.6	0.6
Methane	---	4.3	11.8	6.3	14.7
Ethylene	---	---	1.8	---	1.6
Acetone	6.7	17.6	---	2.3	---
Propylene	4.0	---	0.8	6.1	---
Propanol	10.9	11.1	---	---	---
Butane	---	---	6.8	---	---
Butene	---	---	---	1.2	---
Butanol	2.9	---	---	---	---
Butadiene	---	---	---	1.2	---
Hexadiene	---	---	---	1.2	---
Benzene	---	2.5	0.7	72.4	51.4
Toluene	---	4.7	1.2	---	---
Dimethyl benzene	---	0.9	---	---	---
V_{pyr}	75.0	49.9	59.9	8.7	13.3
TOTAL	100.0	100.0	100.0	100.0	100.0

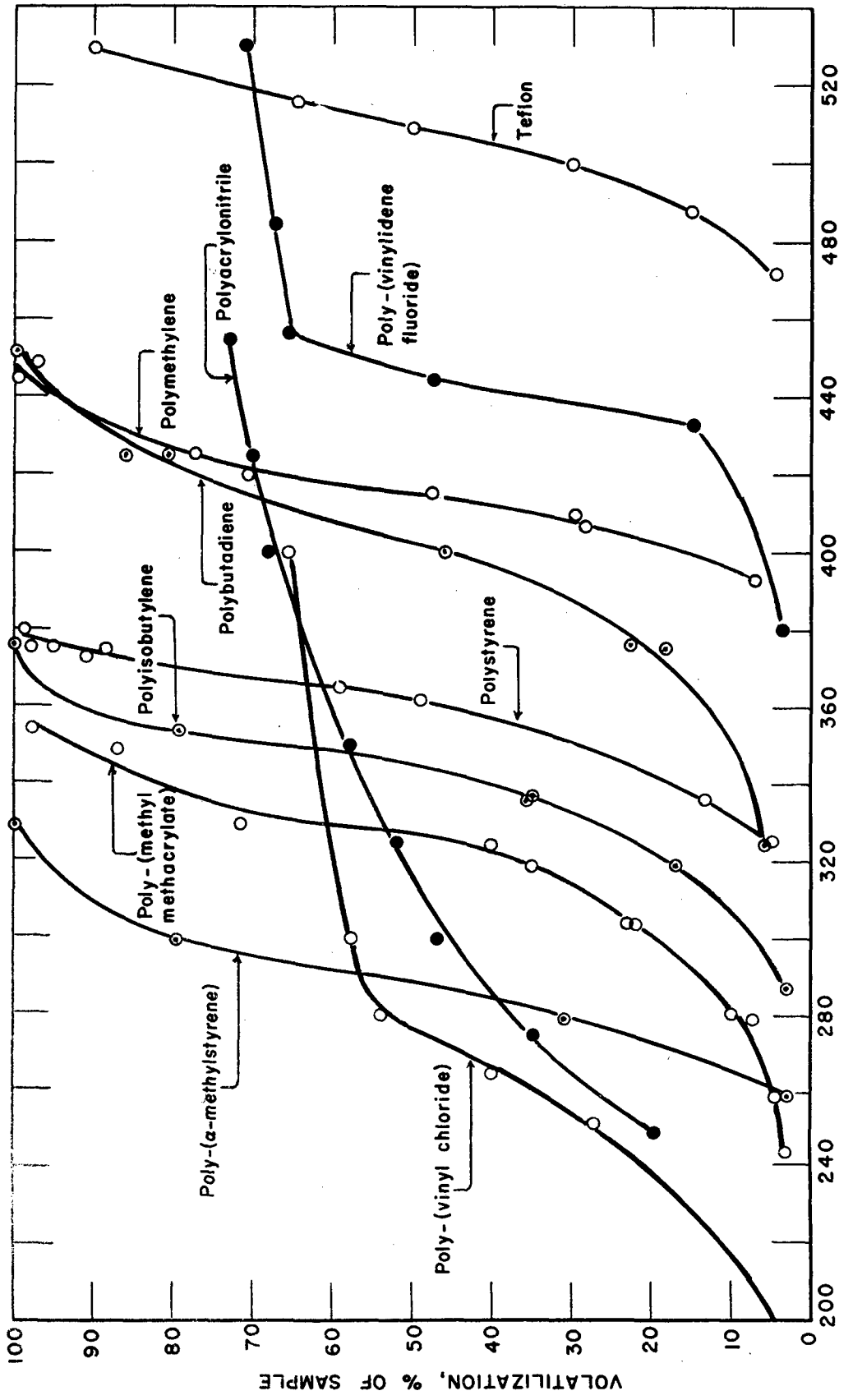


Figure 1. Relative thermal stability of polymers.

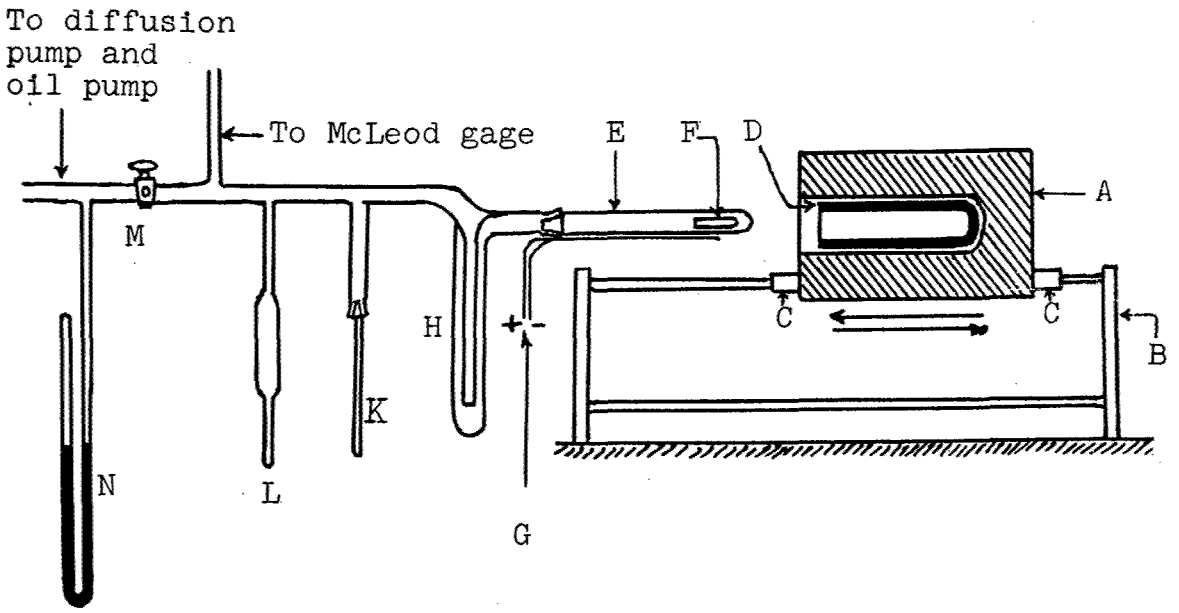


Figure 2. Apparatus for the pyrolysis of polymers at temperatures up to about 900° C.

A, electric furnace, resting on a steel frame B and provided with roller-bearings C so that it can be moved quickly in a horizontal direction; D, stainless steel cylindrical cup serving as an efficient heat distributor; E, fused quartz tube connected to the glass vacuum apparatus by means of a ground joint; F, platinum cylindrical cup open at its left end (the sample is placed in this cup close to its bottom on the right end); G, platinum-platinum rhodium thermocouple held in a fine alundum tube and tied to the fused quartz tube E by means of platinum wire; H, liquid-nitrogen trap; K, Pyrex sample-tube for collecting products of pyrolysis volatile at room temperature, fraction V_{25}; L, sample tube for collecting gaseous products volatile at the temperature of liquid nitrogen, fraction V_{-190}; M, stopcock which is kept closed during pyrolysis and collection of fractions; N, manometer.

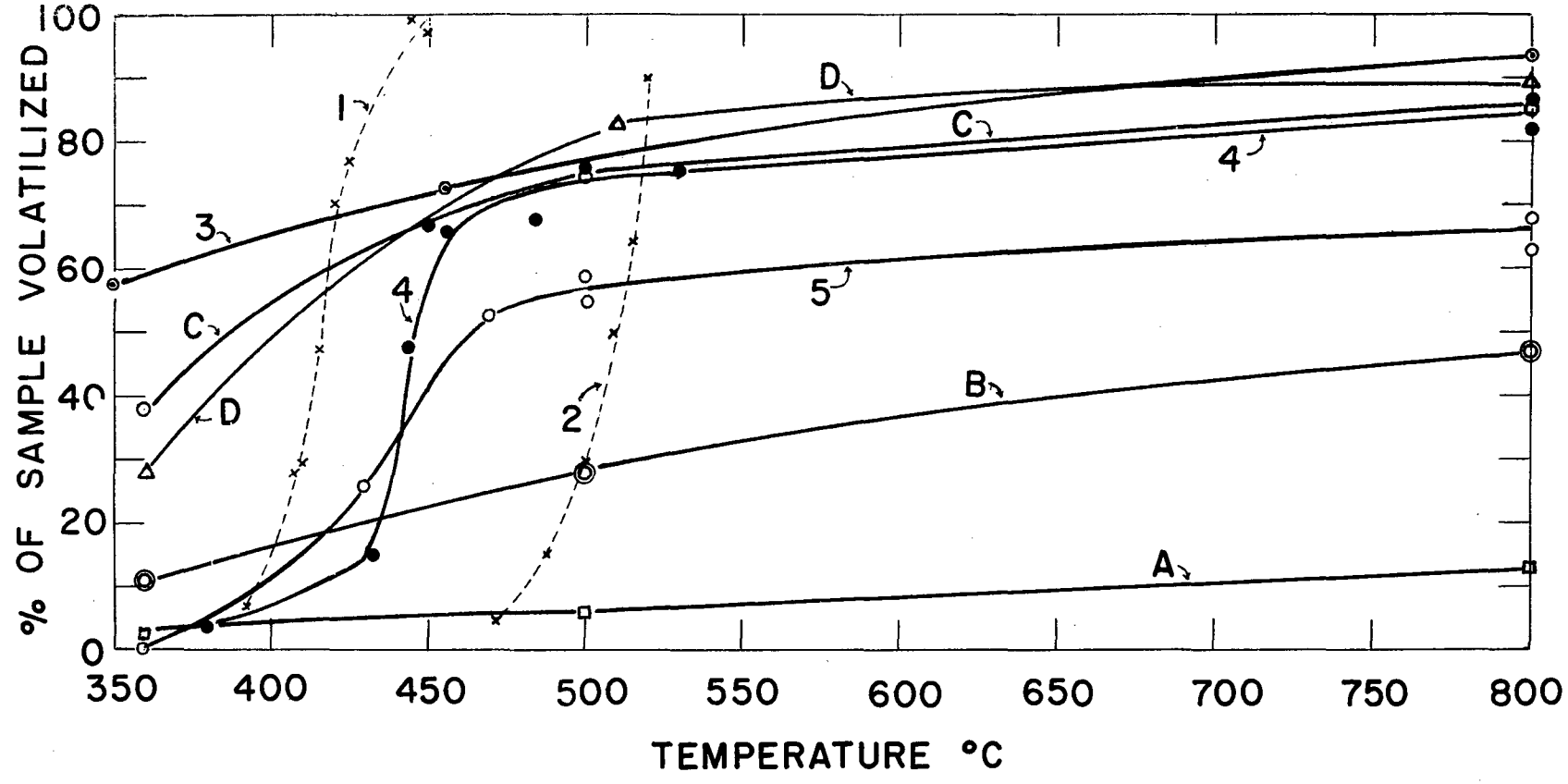


Figure 3. Relative thermal stability of polymers.

1. Polymethylene
2. Poly(tetrafouoroethylene)
3. Polyacrylonitrile
4. Poly(vinylidene fluoride)
5. Poly(trivinylbenzene)

Thermoset plastics

A. Silicone
B. Phenolic
C. Epoxy
D. Vibrin

REFERENCES

[1] F. H. Winslow, W. O. Baker, and W. A. Yager, Proceedings of the First and Second Conferences on Carbon, University of Buffalo, pages 93-102 (1956).

[2] S. Straus and S. L. Madorsky, J. Research NBS 50, 165 (1953).

[3] S. L. Madorsky, S. Straus, D. Thompson, and L. Williamson, J. Polymer Sci. 5, 615 (1950); J. Research NBS 42, 499 (1949).

[4] S. L. Madorsky and S. Straus, J. Research NBS 40, 417 (1948).

[5] S. L. Madorsky and S. Straus, J. Research NBS 53, 361 (1954).

[6] S. L. Madorsky, V. E. Hart, S. Straus, and V. A. Sedlak, J. Research NBS 51, 327 (1953).

[7] R. R. Stromberg and S. Straus, J. Polymer Sci. (in press).

[8] S. Straus and S. L. Madorsky, J. Research NBS 61, 77 (1958).

[9] F. H. Winslow, W. O. Baker, N. R. Pape, and W. Matreyek, J. Polymer Sci. 16, 101 (1955).

[10] F. H. Winslow and W. Matreyek, J. Polymer Sci. 23, 315 (1956).

[11] S. L. Madorsky, V. E. Hart, and S. Straus, J. Research NBS 60, 343 (1958).

[12] H. Staudinger and A. Steinhofer, Ann. 517, 35 (1935).

[13] S. L. Madorsky, J. Polymer Sci. 9, 133 (1952).

[14] S. L. Madorsky, J. Research NBS (in press).

USCOMM-NBS-DC

DIFFERENTIAL THERMAL ANALYSIS AND THERMOGRAVIMETRIC ANALYSIS AS METHODS FOR ASSESSING THE INTRINSIC THERMAL STABILITIES OF EXPERIMENTAL POLYMERS

C. D. Doyle
General Engineering Laboratory
General Electric Company
Schenectady, N. Y.

Introductory Discussion

In this discussion, interest is focused on thermal stability measurement methods which are suitable for the initial evaluation and comparison of experimental high-temperature polymers. Tests of this kind are undertaken primarily in order to guide the direction of subsequent syntheses and to aid in the selection of those new products which are worthy of further examination.

It must be assumed at the outset that only relatively rapid methods can be considered for such screening purposes. Fundamentally definitive methods based on thermodynamic or kinetic concepts of thermal stability are much too time-consuming to be applied as initial comparison tests. This is especially true in the case of polymers, whose degradation reactions may be quite complex. Indeed, polymers which are insoluble and infusible are virtually unamenable to rigorous definitive study even under the best of circumstances. For these reasons, the only procedures which will be discussed in this report are empirical types wherein the temperature range of interest is rapidly scanned for sensible evidence of decomposition of the sample.

It is also assumed that the interpretation of the findings from initial screening tests should not be complicated by questions of eventual practical utilization. Materials are used under so many diverse conditions of function, environment and expected life that no generally applicable criterion of decomposition can be prescribed on the basis of operational requirements. A material which is too short-lived for one intended use may serve quite satisfactorily in another, even at a higher temperature or in a more advanced state of decomposition. (Similarly, specific functional needs determine whether

the melting or softening of a material is disastrous or unimportant.)

A further reason for postponing questions of practical utilization is that most practical atmospheres are reactive. Interaction of the sample with its atmosphere severely complicates the data from screening tests and may even vitiate them completely. If decomposition is observed in terms of weight loss, for example, oxidative weight gain is a potential source of interference if the tests are conducted in air.

Thus, the scope of the present discussion must be further limited to embrace only rapid scanning tests conducted in inert atmosphere. Moreover, the findings from such tests must be interpreted on the basis of experimentally convenient criteria of decomposition rather than in terms of fundamentally definitive or functional considerations.

Procedural Decomposition Temperatures

The measured values of temperature limits determined by dynamic procedures are powerfully dependent upon experimental variables. Variations in the size, shape, or fineness of the sample, for example, are highly influential. An even more powerful variable is the rate at which the sample is heated. This is especially true in the case of activated processes, which occur at higher temperatures when forced to occur at faster rates. Thus, the measured values of decomposition temperatures are particularly dependent upon procedural details.

Further, the measured values of temperature limits determined by empirical procedures are arbitrarily variable because they are based on arbitrarily chosen criteria of failure. Empirical criteria of failure are not altered frivolously, of course, but they are unavoidably subject to change because they can be established only on the basis of experimental evidence. Through trial and error, some recognizable decomposition effect is found and studied in tests on material after material until it is established that the phenomenon occurs consistently and that its meaning is always the same. Thus, because they are of necessity established on the basis of sequential investigation, empirical criteria of decomposition may have to be changed several times before becoming firm.

In view of the powerful effects of procedural details and arbitrarily chosen criteria of decomposition on their measured values, empirically determined and specified temperature limits have been cited as "procedural decomposition temperatures" in the present investigation. The corresponding abbreviation, pdt, is intended to serve as a constant reminder that the cited value has significance only in context with one particular set of experimental conditions and one particular

criterion of failure.

Differential Thermal Analysis and Thermogravimetric Analysis

Procedural decomposition temperatures can be determined in many ways. The simplest method is to heat the sample and observe any visible evidence of decomposition. Usually, however, it is difficult to choose an end point in a visual test, since changes in the appearance of slowly decomposing materials generally occur gradually. As an example of a far more quantitative method, the onset of decomposition in fluids has been observed in terms of vapor pressure by means of the isoteniscope (1).

Present-day differential thermal analysis (DTA)(2) and thermogravimetric analysis (TGA)(3) are instrumented refinements of two very old techniques. In DTA, changes in the sample material are observed in terms of its heat losses or gains as reactions or transitions occur, while in TGA, the residual weight of the sample is continuously measured throughout the heating period.

In DTA, exothermic or endothermic events are observed by placing the sample and an inert reference material side by side in a furnace and measuring any difference in their temperatures as the furnace temperature is increased at a constant rate. When an endothermic process occurs in the sample, its temperature falls below that of the inert reference material. Conversely, an exothermic process causes the sample temporarily to become hotter than the reference material. In either case, when the process is completed, or when its rate becomes sufficiently slow, the difference between the sample and reference temperatures again tends toward zero.

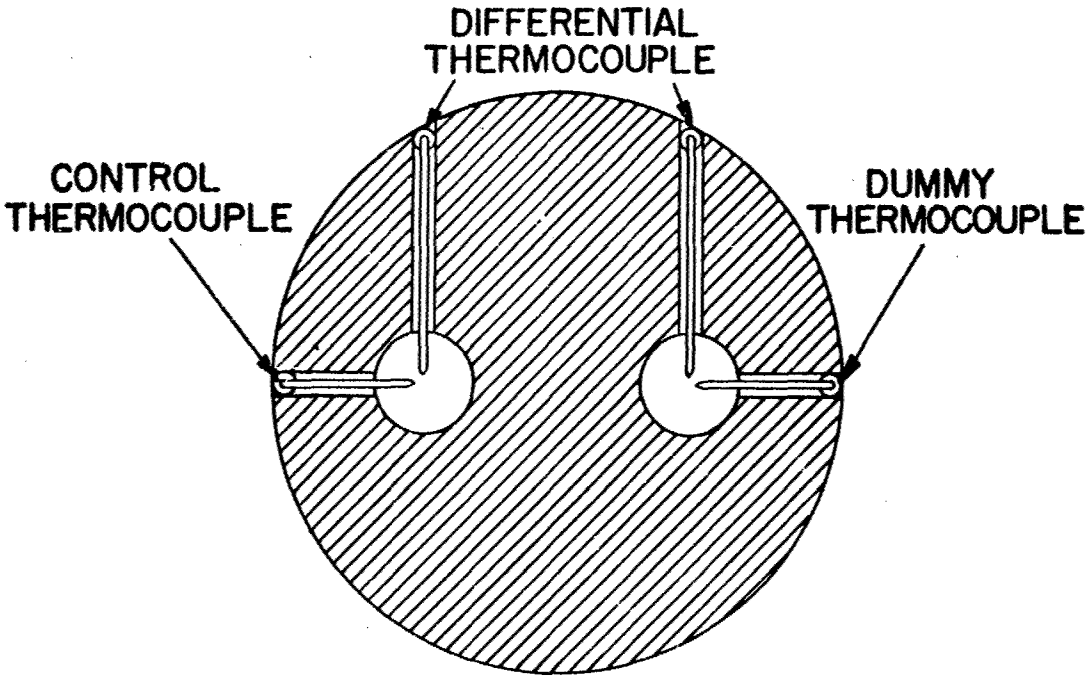
In modern practice, temperature differences are measured by means of a differential thermocouple whose thermal e.m.f. is plotted continuously by a recording potentiometer as a function of time or reference thermocouple e.m.f. or sample thermocouple e.m.f. A typical sample holder is shown in cross section in Figure 1, where it is seen that the thermocouples are arranged for recording the differential e.m.f. and the reference thermocouple e.m.f. The sample holder is positioned within a controlled atmosphere furnace which is based on a design described by Stone (2). In this furnace, DTA runs can be conducted in vacuo or in special atmospheres up to a temperature of 1000°C.

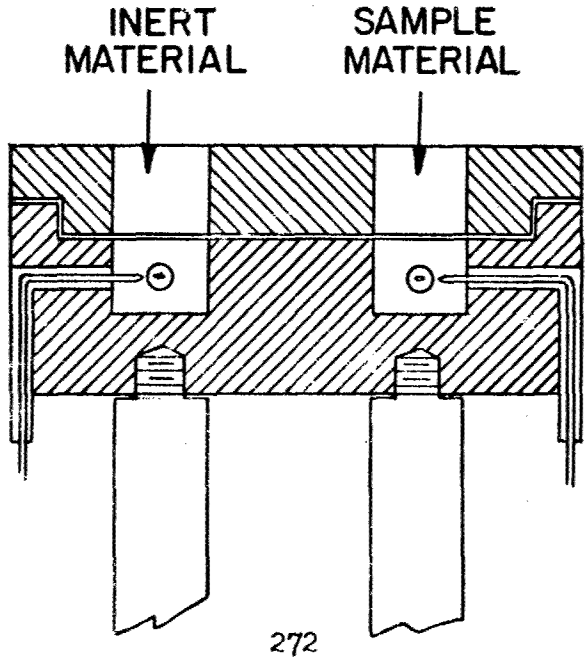
---

1 Ballentine, O.M., WADC TR 54-417 (1954)
2 Smothers, W.J., and Y. Chiang, "Differential Thermal Analysis", Chem. Pub. Co., New York (1958)
3 Duval, C., "Inorganic Thermogravimetric Analysis", Elsevier, New York (1953)

FIGURE 1

DTA SAMPLE HOLDER





Ultimately, the DTA data record is re-expressed as a plot of differential temperature versus sample temperature or reference temperature. The resulting curve displays exothermic and endothermic peaks along the temperature axis, as illustrated in Figure 2.

In present-day TGA, a virtually linear function of the sample's residual weight is recorded automatically on a time base or, more conveniently, on a temperature base. In either case, the ultimate record is a plot of residual weight fraction, W/W_o, versus the environmental temperature in a region near the sample. Illustrative TGA plots are shown in Figure 3.

One of the Chevenard balances used in the present investigation is shown schematically in Figure 4 (4). The balance beam is delicately suspended by means of tungsten wires, and transient motions of the beam are damped out by means of dashpots. The sample crucible is mounted on a quartz rod extending vertically into the controlled atmosphere furnace from one end of the balance beam, while the position-sensing core of a differential transformer is suspended from the other end of the beam. The demodulated output of the differential transformer is automatically plotted against the output of the furnace temperature thermocouple on an X-Y recorder. In the apparatus shown in Figure 4, TGA runs can be conducted in special atmospheres up to a temperature of 1000°C.

Comparison of DTA and TGA as Methods for Measuring pdt's

Because heat is fugitive, the experimental difficulties of DTA are more severe than are those of TGA. Thus, DTA requires a higher degree of sophistication on the part of the operator than does TGA. Even in the hands of sophisticated operators, however, the data records from DTA do not always agree well. In spite of careful technique, irreproducibility of the sort illustrated in Curve A of Figure 2 is frequently encountered. In TGA, on the other hand, reproducibility is easily attained.

An inherent disadvantage of TGA, however, arises from the fact that weight change is not a necessary consequence of decomposition. Thus, DTA is attractive as a potential means of sensing decomposition reactions undetectable by TGA. DTA is also attractive because the occurrence of a peak in the record always indicates that a reaction or transition has occurred in the sample. Weight-loss curves, on the other hand, are confounded if volatile impurities are present in the sample.

---

4 Purchased from Cooke, Troughton and Simms, Inc., 110 Pleasant St., Malden 48, Mass.

FIGURE 2 ILLUSTRATIVE DTA CURVES

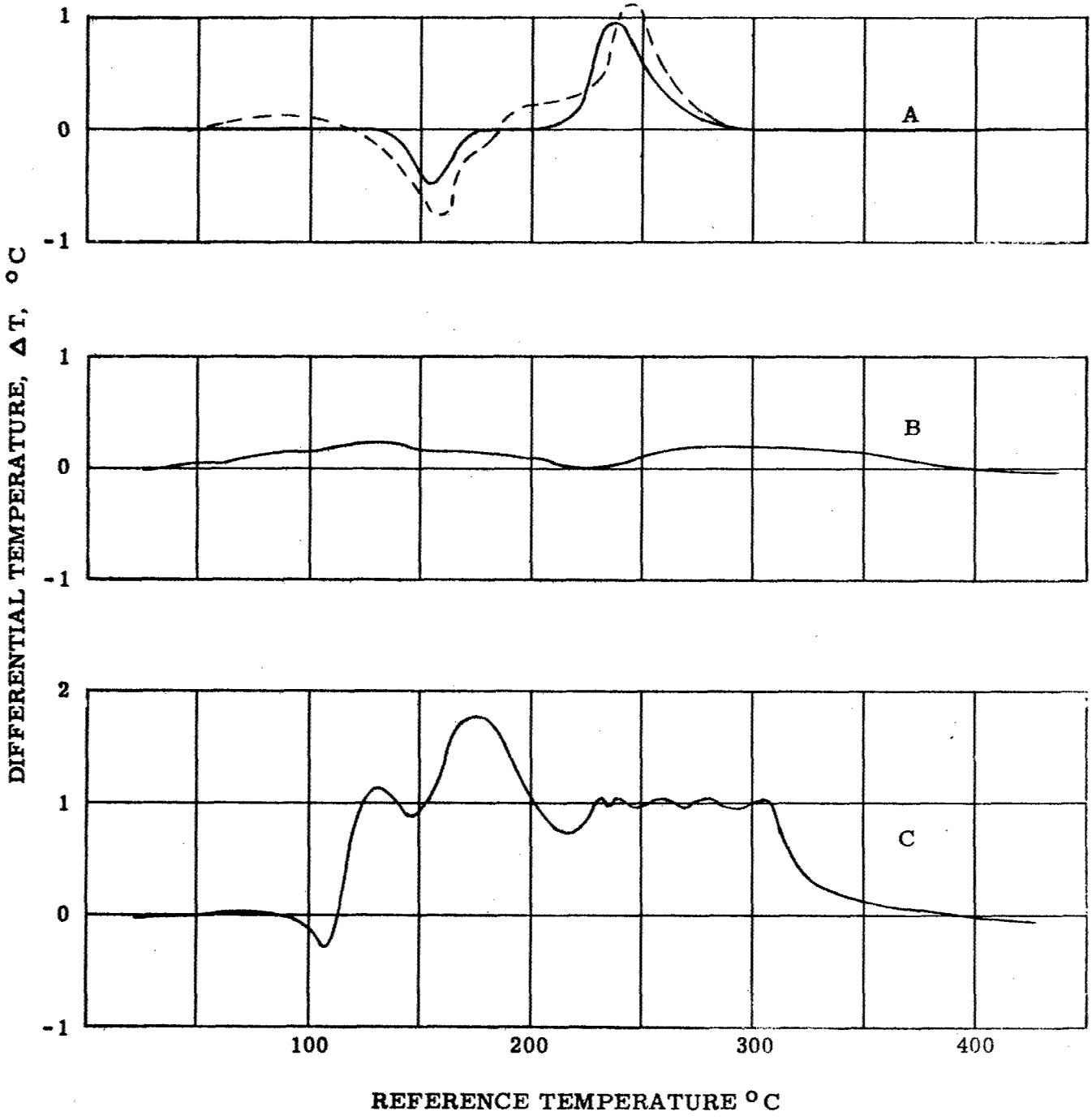


FIGURE 3 ILLUSTRATIVE TGA CURVES

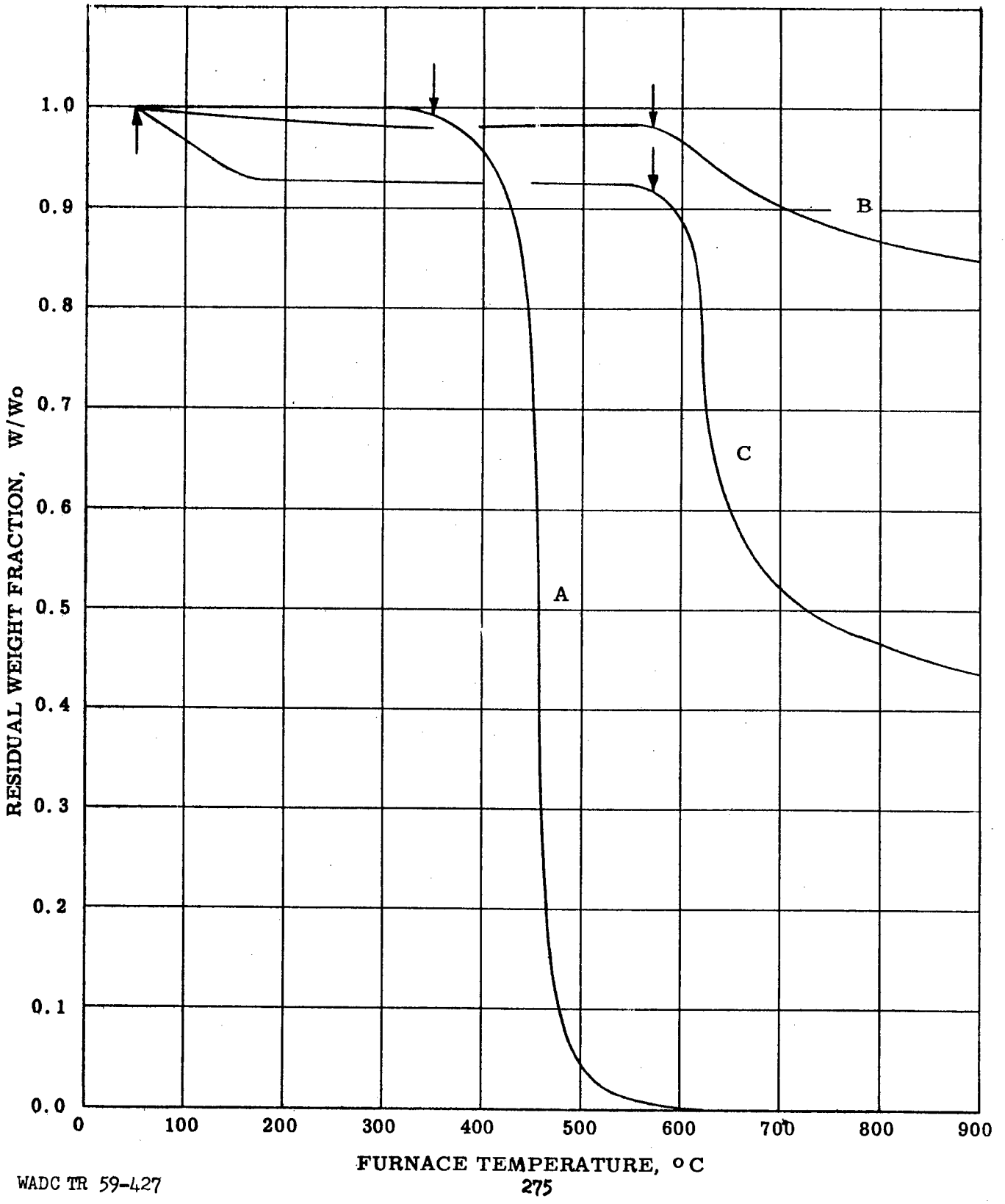
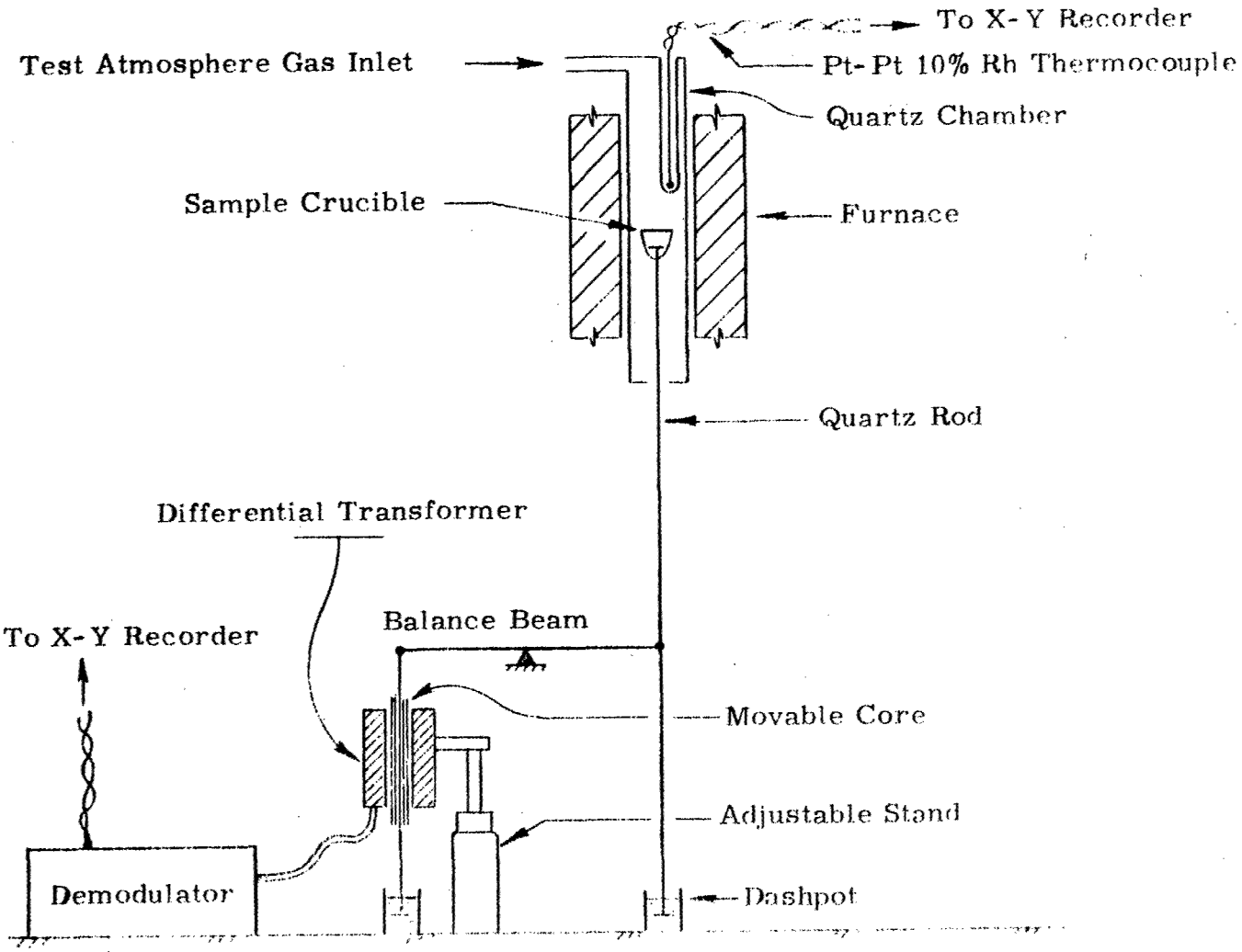


FIGURE 4
SCHEMATIC DIAGRAM OF DIFFERENTIAL TRANSFORMER TYPE
PEN-RECORDING CHEVENARD THERMOBALANCE



Experimental evidence to date, however, indicates that the hoped-for advantages of DTA can seldom be realized in studies of polymers. This is true because the degradation of polymers is frequently accompanied by heat changes which occur over broad temperature ranges, giving rise to flat, ill-defined DTA peaks of the type illustrated in Curve B of Figure 2. It is almost impossible to distinguish such flat or ill-defined peaks in DTA patterns, because they usually display small spurious, irreproducible features over the entire temperature range. Further, many polymers degrade via competing reactions and consecutive reactions whose heat effects interfere, giving rise to partially cancelled, truncated or overlapping DTA peaks, as illustrated in Curve C of Figure 2.

Insofar as the quantitative determination of pdt's for polymers is concerned, DTA does not appear to offer much promise. In cases wherein the data record displays well-defined isolated peaks, pdt's can be located by graphical methods (2), but such cases have rarely been encountered in the present investigation. DTA is still under study, however, for its value as a qualitative corroborative method. When DTA and TGA are conducted at identical heating rates, many helpful comparisons can be drawn on the basis of the corresponding data records.

The findings from TGA, on the other hand, have been more encouraging, in spite of the limited inherent meaning of weight loss data. TGA data records, being highly reproducible, clearly show differences between quite similar materials. Further, TGA records, being cumulative, are easier to relate to the extent of degradation than are DTA records.

Most of the difficulties which have been encountered in TGA studies to date have been those associated with the choice of a suitable criterion of decomposition. No criterion could be prescribed on the basis of cumulative weight loss, for example, because, while some materials may volatilize completely in TGA, others may lose only 10 or 20% of their initial weight, as illustrated by curves A and B in Figure 3.

Up to the present time, an empirical-kinetic end point has been employed. Through trial and error, it has been found that an apparent rate of weight loss of 5% per hour is eventually attained by most sample materials in TGA at 150°C per hour in dry nitrogen. It has also been observed, however, that some samples lose impurities at rates in this neighborhood and at rather low temperatures, as illustrated by Curve C in Figure 3. This source of ambiguity still constitutes a problem. The criterion rate cannot be set much faster, because many materials scarcely attain the 5% per hour rate.

Currently, the problem is side-stepped by citing all of the temperatures at which materials attain the apparent rate

of weight loss of 5% per hour. If other evidence suggests that only one temperature should be cited as the pdt, the confounding temperatures are cited in parentheses. This practice is illustrated in Table 1, wherein typical findings for two conventional polymers and four closely related experimental polymers are presented.

Table 1

Tentative pdt's from TGA at 150° per hour in Dry Nitrogen

Material		pdt, °C
(Poly)methyl Methacrylate		175
Polystyrene		315
Zinc Chelate	RR	430
" "	ROR	(140) 415
" "	RSO_2R	420
" "	RCOR	(105) 380

Summary

DTA is useful primarily as a qualitative method for measuring the intrinsic thermal stabilities of experimental high-temperature polymers. TGA offers promise as a quantitative method, but many more materials must be studied before a criterion of decomposition can be firmly established.

HIGH TEMPERATURE SYNTHESES OF NEW, THERMALLY STABLE CHEMICAL COMPOUNDS

by

Russell C. Phillips

Stanford Research Institute

Introduction

In July 1958, Stanford Research Institute began work under a contract with the Polymer Section, Materials Laboratory, Wright Air Development Center to investigate high temperature (1000°C - 2000°C) reactions which might result in the synthesis of new, thermally stable chemical compounds. The first phase of the program consisted of a critical survey of the literature for pertinent references to chemical reactions carried out at temperatures above 500°C.

On the basis of this literature survey, which was published as Quarterly Progress Report No. 1, and other considerations, four tasks were selected for the experimental phase:

1. Investigation of possible reactions between metals ionized in an electric arc and various organic compounds as a means for direct synthesis of organometallics.

2. Synthesis of symmetrical difluoroacetylene by pyrolysis of halogenated hydrocarbons and by reaction between fluorine atoms and graphite. Difluoroacetylene is expected to be an unstable compound, but might be a precursor of new, thermally stable, fluorocarbon polymers.

3. Synthesis of the postulated spinels $MgSc_2O_4$ and $LiSc_5O_8$, which were expected to have high melting points.

4. Investigation of the refractory boron suboxides.

In view of the immediate objectives of the Polymer Section, however, it was decided early in the program to forego research on the spinels, boron suboxides, and other refractories in favor of an investigation of thiophosphonitrilic polymers.

In this paper, each of the five experimental tasks undertaken in the research program is discussed separately.

Task 1 - Investigation of possible reactions between metals ionized in an electric arc and various organic compounds

At the 10,000°C-range of temperatures readily attainable with a plasma jet, it has been demonstrated that the transition metals can be converted partially to positive ions. Further, it is postulated that these

ions will react with electronegative organic moieties to form organometallic compounds; although this concept is conjectural, it has the tacit support of qualified theoretical chemists. The investigation of this concept is viewed as a difficult, long range research effort. As the results to date are negative, the work will be described only in outline.

The plasma jet, which is a high current density, inert fluid-stabilized electrical arc, is shown schematically in Figure 1. There are two basic methods for introducing the metal into the arc: (1) as a consumable anode, and (2) as a powder or wire introduced into the plasma issuing from the orifice in the cathode. The plasma stream, carrying ionized metal, would impinge upon a rapidly moving stream of organic reactant, either vapor or liquid. This stream would be cooled immediately to minimize thermal degradation.

While awaiting the development and installation of an inert-environment chamber necessary for conducting these experiments with a 25-KW plasma jet, the possibility of achieving the same objective with a submerged arc was investigated. A schematic diagram of the submerged direct current arc assembly is shown in Figure 2.

With this equipment, the organic liquid was circulated at high velocity (6m/sec) through the arc chamber. The arc was struck repeatedly across the consumable electrodes, fabricated of the desired metal reactant. Three systems were investigated, benzene/tungsten, benzene/iron, and cyclopentadiene/iron. Data for typical runs are given in Table I.

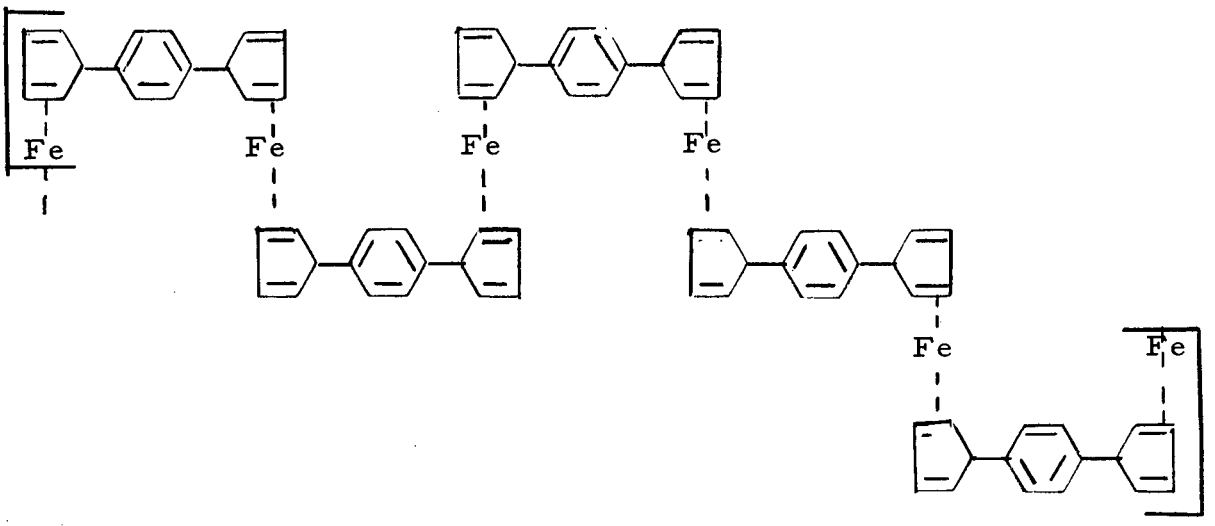
No incontrovertible evidence of organometallic synthesis with this technique has resulted to date, but there were profound effects on the organic liquid. The high boiling fraction obtained indicates polymerization.

Mass spectrographic analysis of the gas produced by the submerged arc in several runs is indicated in Table II. The oxygen (combined and free) found in these samples was accounted for by leakage of air into the system during the rarefaction wave following the veritable explosion every time the arc was discharged. The presence of reactive polymer precursors, such as acetylene, in the product gas was anticipated. The polymerization of these products provides a possible explanation for the high boiling liquid product derived.

Cyclopentadiene was used as a reactant with full knowledge that no ferrocene polymer could possibly result without fortuitous rearrangement of the organic reactant. It served only as a model compound which is known to form organometallic "sandwiches". In ferrocene, more properly biscyclopentadienyliron, the iron is bonded to each of the two

cyclopentadiene molecules through six π electrons. Efforts to form polymers containing the stable ferrocene structure by conventional processing from reactants containing two fused, five-membered rings have not been successful, because such reactants cannot contribute the six π electrons required for each of two bonds with iron.

It was postulated that 1, 4-dicyclopentadienylbenzene, containing a stable, fully conjugated, phenyl linkage would preserve the desired characteristics of the cyclopentadiene ring at each end of the molecule. The ideal reaction between this compound and iron would result in a linear polymer of the type indicated below:

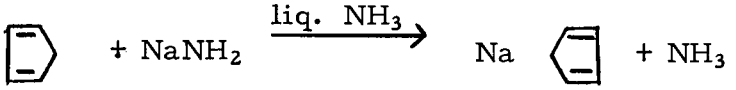


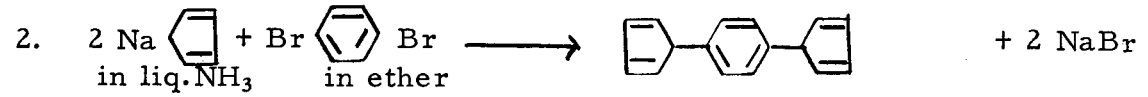
Unfortunately, the seemingly straightforward procedure selected for synthesis of 1, 4-dicyclopentadienylbenzene was not successful*, so the concept has yet to be proved.

This difficulty in obtaining the desired starting material, coupled with the absence of positive evidence of organometallic synthesis, led to termination of the submerged arc work at least temporarily. When and if it is revived, provisions will be made for automatic feeding of the electrodes to maintain a constant arc gap and continuous flow of current, for sighting the arc with a spectograph to establish the degree of metal ionization achieved, and for separation of the products from

---

* Note: The synthesis attempted involved the following reactions:

1. 

2. 

unreacted starting material for recycle. These improvements would permit meaningful material and energy balances and more quantitative interpretation of the phenomena involved.

It is expected, however, that research with the plasma jet, upon completion of its modification, will supersede the submerged arc work.

Task 2 - Synthesis of new fluorocarbons

The thermal stability and unreactivity of highly fluorinated organic compounds has attracted widespread attention and has permitted some novel applications for certain members of the class. Perhaps the most widely publicized of these materials are Teflon, (the tetrafluoroethylene polymer) and Kel-F (the chlorotrifluoroethylene polymer). However, other fluorinated aliphatic hydrocarbon monomers and polymers are serving as unreactive, thermally stable refrigerants, dielectrics, lubricants, insulators, sealants, and heat-transfer agents.

It is significant that the fluorine compounds referred to above belong to the aliphatic, or saturated, class of organic compounds. Perfluoroaromatic compounds, such as hexafluorobenzene and its derivatives, are not mentioned in the industrial literature, and few references are found in the research literature. This apparent lack of interest in perfluoroaromatic compounds is actually caused by the lack of a suitable method of synthesis for any member of the class. In spite of the difficulty encountered in preparing these compounds, a determined effort is being made (24, 38, 40) to evaluate hexafluorobenzene and other perfluorophenyl derivatives as monomers or precursors for thermally stable materials. Further, the thermal stabilities of Teflon and of cuprene, the acetylene polymer, apparently provide the basis for an attempt to prepare polydifluoroacetylene (38).

The commercial synthesis of tetrafluoroethylene is accomplished by the pyrolysis of chlorodifluoromethane (Freon 22) at temperatures above 650°C (24). This reaction is representative of a number of pyrolytic reactions, at temperatures between 500°C and 1000°C, by which low-molecular-weight fluoroalkanes are converted to higher fluorinated alkanes and alkenes (1, 5-7, 10, 14, 15, 29, 30, 32, 38, 40).

Pyrolysis of tribromofluoromethane at 630-640°C is reported by Desirant (13) to yield a mixture of hexafluorobenzene, bromopentafluorobenzene, and tetrabromodifluoroethane. This reaction bears a formal analogy to production of acetylene (including small amounts of benzene) by the pyrolysis of methane and other hydrocarbons in an electric arc at temperatures from 1600°C to 3000°C. The method of pyrolyzing tribromofluoromethane was improved upon by Hellmann and co-workers (21)

and gave yields of up to 55% hexafluorobenzene. The pyrolysis of hexafluorobenzene at 850°C gave perfluorotoluene, $C_6F_5CF_3$ (13).

The pyrolytic procedure is much superior to the tedious classical methods previously used to prepare hexafluorobenzene and related compounds. By these methods, fluorination of benzene, hexachlorobenzene, or other aromatic compounds gave fluorinated cyclohexanes or other saturated ring compounds (18-20, 24, 25, 39). A subsequent dehydrohalogenation or dehalogenation gave hexafluorobenzene or higher fluorinated aromatics.

The unsuccessful attempt of Wall to obtain difluoroacetylene by the decomposition of trifluoroethylene in a low energy electrical discharge (41) is of interest, since difluoroacetylene should be an excellent precursor of perfluorophenyl compounds.

The goal of our experimental work on this phase of the project is to prepare the new compound, difluoroacetylene. Although this compound is not remarkably stable, the interest in it lies in its potential use as a building block for thermally stable materials. Additional interest lies in the fact that one proposed route to these compounds is by way of high temperature pyrolytic reactions. A second proposed route involves direct reaction between fluorine atoms and graphitic carbon.

Tetrabromo-1, 2-difluoroethane is the preferred starting material for the pyrolytic route:

$$\begin{array}{l} Br\ \ Br \\ |\ \ \ \ | \\ F\text{-}C\ -\ C\text{-}F \\ |\ \ \ \ | \\ Br\ \ Br \end{array} \xrightarrow{heat} F\text{-}C{\equiv}C\text{-}F + 2Br_2$$

Tetrachloro-1, 2-difluoroethane is a second choice as a starting material for this reaction.

The proposed synthesis of hexafluorobenzene is analogous to the synthesis of benzene from acetylene (12, p 3), and hexachlorobenzene from dichloroacetylene (27):

$$3\ F\text{-}C{\equiv}C\text{-}F \xrightarrow{Ni(CO)_4} C_6F_6.$$

Possibly difluoroacetylene may not be isolated as an intermediate, and hexafluorobenzene may be a direct product of the pyrolysis of tetrabromo-1, 2-difluoroethane.

A further reaction with difluoroacetylene may also be possible. This reaction, yielding tetrafluorohydroquinone, is analogous to the production of hydroquinone from acetylene, water, and iron carbonyl hydride (12, p 292):

$$4FC{\equiv}CF + Fe(CO)_4H_2 \longrightarrow 2HO\text{-}C_6F_4\text{-}OH + Fe(OH)_2$$

The product anticipated above could lead to very stable, perfluorinated polymers containing ether linkages.

Investigation of the pyrolytic route to difluoroacetylene has been thwarted by the unsuccessful attempts to prepare 1, 2-difluorotetrabromoethane as outlined in Table III. Several comments about these reaction studies are in order.

Pyridine difluoride was prepared by the method described by Simons (37). The addition of fluorine to pyridine at -30°C to -40°C was not smooth, as reported, but was accompanied by occasional sparking at the liquid surface and by the frequent appearance of a flame in the fluorine inlet tube. However, the final solution was somewhat viscous and brown in color, as reported.

The attempted electrochemical fluorination was carried out in an agitated, stainless steel container. The cell was operated at a current density of 0. 02 amp/sq cm and at a potential drop of 35 to 50 volts.

These difficulties in deriving the desired starting material for pyrolysis prompted a modest, concurrent effort to obtain enough difluoroacetylene by more conventional techniques, so that it could be characterized. If the properties of this compound were interesting, accelerated efforts to prepare it by high temperature methods would be justified.

As a model reaction for the proposed low temperature route to difluoroacetylene, the reaction of perchloryl fluoride with sodium phenylacetylide in benzene was investigated.

$$NaC{\equiv}C\phi + ClO_3F \longrightarrow FC{\equiv}C\phi + NaClO_4$$

The infrared spectrum of the crude product agreed with that expected for phenylfluoroacetylene. In view of the instability and reactivity reported for the bromo-and chloroacetylenes, this product was treated with a great deal of caution initially. A micro distillation on the crude product showed a boiling range from 90°C to about 160°C. The residue from this distillation was heated to about 230°C. At the latter temperature decomposition became apparent, but at no time was a vigorous reaction observed.

Therefore, the distillation of the entire lot of crude phenylfluoroacetylene was attempted. Distillation under vacuum, using cumene and finally decalin as scavengers (to increase the recovery of product) gave only the added hydrocarbon and a viscous brown oil. Apparently, thermal polymerization of the substituted acetylene had resulted in the formation of symmetrical trifluorotriphenylbenzene or a linear polymer.

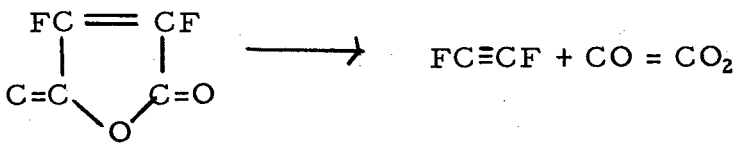
On the strength of the apparent successful reaction with sodium phenylacetylide, disodium acetylide was treated with perchloryl fluoride. The first attempt with disodium acetylide in dimethylformamide solution resulted in extensive decomposition of the solvent. The second run, using diethyleneglycol dimethyl ether as a solvent resulted in the formation of a dark brown residue. The residue, characterized by a bright blue fluorescence, contained no fluorine. The volatile products contained no detectable difluoroacetylene or possible derivatives. The third reaction between disodium acetylide and perchloryl fluoride was carried out in benzene solution. The products of the reaction have not been characterized as yet.

Two additional high temperature routes to the synthesis of difluoroacetylene will also be investigated:

(1) pyrolysis of a metal salt of tetrafluorosuccinic acid

$$NaO_2CCF_2\,CF_2\,CO_2\,Na \xrightarrow{\Delta} FC{\equiv}CF + 2\,NaF + 2\,CO_2$$

and (2) the pyrolysis of difluoromaleic anhydride



$$\longrightarrow \quad FC{\equiv}CF + CO = CO_2$$

The latter procedure is an extension of the recently reported method (26) for the preparation of monofluoroacetylene.

A totally different approach to the synthesis of difluoroacetylene, the atomic fluorination of graphite, is also being investigated. Earlier experiments at Stanford Research Institute in connection with another project reported the detection of acetylene as a major product when evaporated graphite films were exposed to hydrogen atoms produced in an electrodeless discharge through dry molecular hydrogen. In addition, the emission of the CH radical has been detected in similar experiments (3). It was therefore decided to attempt the synthesis of difluoroacetylene by exposing a graphite film to the fluorine atoms produced by a radio frequency discharge in fluorine gas. In order to prevent the further reaction of any difluoroacetylene produced to saturated fluorocarbons, it will be necessary

to carry out the experiment under conditions of low temperature, low fluorine pressure, high conversion to atoms by the discharge, and brief contact times, with efficient trapping of products just past the reaction region. Because of experimental difficulties expected with the fluorine system, the preliminary experiments are concerned with the reaction of chlorine atoms and graphite in order to determine the most desirable operating conditions for isolating the dihaloacetylene. Work is in progress on this phase of the project.

No work has been reported on the reactions of chlorine or fluorine atoms with solids, although the efficiency of various materials, including graphite, for the recombination of chlorine atoms has been studied (36). Wood charcoal, graphite (33), and various carbides (33, 35) burn in an atmosphere of molecular fluorine to give CF_4, C_2F_6, and a smaller amount of higher molecular weight fluoroparaffins. At lower temperature (450°C) fluorine combines with graphite to form $(CF)_x$ (28, 33) which results from migration of the fluorine into the graphite lattice to form interstitial covalent bonds between adjacent graphite layers (8, 28). At higher temperatures $(CF)_x$ decomposes, occasionally explosively, into fluorocarbons and carbon (33). It will, therefore, be necessary to restrict the studies on atomic fluorine to lower temperatures in order to prevent these competing reactions of molecular fluorine.

Although the reaction rate may be accelerated by resistance heating of the graphite, the reaction is not a high temperature one in the narrow sense of the word. In the sense that dissociation of fluorine into its atoms requires energies equivalent to about 10,000°C, this approach is indeed appropriate in a study of high temperature chemistry.

The glass and metal vacuum system now being assembled provides for the continuous flow of dry halogen gas at about 100 microns pressure past an RF coil operated at 17 to 18 megacycles. The dissociated halogen will impinge upon a disc of graphite, previously deposited to a thickness of approximately 2000 Å onto a glass slide by vacuum evaporation. The optical opacity of the graphite will be measured photoelectrically during a run to follow the rate of reaction with the gas. Liquid products will be collected in cold traps and will be analyzed by mass spectroscopy.

Task 3 - Synthesis of postulated spinels, $Mg\,Sc_2O_4$ and $Li\,Sc_5O_8$

Some spinels, most notably magnesium aluminate (MP 2180°C) and magnesium chromate (MP 2135°C) can be classified as refractories. For this reason, a detailed analysis of the methods of preparation and of the properties of spinels was made to judge the feasibility of synthesizing new, thermally stable compounds of this type.

For the purpose of this study, a spinel is defined as a compound crystallizing in a cubic lattice, the unit cell of which contains 32 anions (oxygen or sulfur) and 24 cations. The cations are distributed in the interstices between the anions in such a way that 8 cations lie in the center of a tetrahedron of anions and 16 cations lie in the center of an octahedron of 6 anions. In the so-called "normal" spinel of the 2:3 type, the tetrahedral sites are occupied by divalent metal ions (A^{2+}), while the octahedral sites are occupied by trivalent metal ions (B^{3+}). This leads to the general formula $A^{2+}\ B_2^{3+}\ X_4^{2-}$, where X^{2-} is oxygen or sulfur. Figure 3 is a plan view of the bottom half of a normal 2:3 spinel crystal. The large circles represent anions and the smaller circles are cations.

The discovery by Barth and Posnjak (4) that divalent metal ions could occupy the octahedral sites, led to the so-called "inverse" spinel (2:3 type) with the formula $B^{3+}(A^{2+}\ B^{3+})X_4^{2-}$. Henceforth, where necessary, the ionic distribution will be indicated in the spinel formula by enclosing in brackets the types of ions occupying the octahedral sites. Spinels (2:3 type) were subsequently found (29) that were "intermediate" to these normal and inverse structures, necessitating a general formula $B_{1-x}^{3+}\ A_x^{2}\ (A_{1-x}^{2+}B_{1+x}^{3+})X_4^{2-}$. Thus, the 2:3 type described above can be written as

1. $A^{2+}(B_2^{3+})X_4^{2-}$, $B^{3+}(A^{2+}\ B^{3+})X_4^{2-}$,

   or

   $$B_{1-x}^{3+}A_x^{2+}(A_{1-x}^{2+}B_{1+x}^{3+})\ X_4^{2-}.$$

   Three more spinel types have also been identified. They are:

2. The 4:2 type spinel $B^{4+}\ (A_2^{2+})X_4^{2-}$, $A^{2+}(B^{4+}\ A^{2+})X_4^{2-}$,

   or

   $$B_x^{4+}\ A_{1-x}^{2+}(B_{1-x}^{4+}A_{1+x}^{2+})X_4^{2-}$$

3. The 6:1 type spinel $B^{6+}\ (A_2^{1+})\ X_4^{2-}$, $A^{1+}(B^{6+}\ A^{1+})X_4^{2-}$,

   or

   $$B_x^{6+}\ A_{1-x}^{1+}(B_{1-x}^{6+}A_{1+x}^{1+})X_4^{2-}$$

4. The 3:1 type spinel $B_2^{3+}(A^{1+}\ B_3^{3+}(X_8^{2-}$, $A^{1+}\ B^{3+}\ (B_4^{3+})X_8^{2-}$,

   or

   $$B_{2-x}^{3+}\ A_x^{1+}\ (B_{2+x}^{3+}A_{1-x}^{1+})X_8^{2-}$$

From an extensive review of the properties of existing spinels, the following primary criteria were established for searching for new high melting spinels:

1. Spinels with high melting points are prepared from high melting constituent oxides.

2. The Goldschmidt ionic radii of metal ions in known spinels range from 0.78 to 1.03 Å for the divalent metal ions, from 0.57 to 0.93 Å for the trivalent metal ions, and from 0.44 to 0.74 Å for the tetravalent ions. The likelihood of finding new, thermally stable, oxidic spinels containing metal ions with radii outside these limits is remote.

3. As a rule, the melting points of spinels are directly proportional to the summation of the negative standard enthalpies, ΣH (or negative heats of free energy ΣF), of the constituent oxides.

A review of high melting point oxides containing metal ions having radii within the prescribed limits revealed that scandia (Sc_2O_3) is the only candidate not yet reported as a spinel constituent. Scandia, containing a trivalent metal ion could form 2:3-type or 3:1-type spinels.

Consideration of the possible spinel-forming oxides with which scandia could be combined, showed that MgO, with a melting point of 2800°C is the best constituent with a divalent metal ion; among the oxides with a monovalent metal ion, Li_2O has the highest melting point (1700°C). Both of these potential combinations have larger calculated negative $\Sigma\overset{\Delta}{H}$ and $\Sigma\overset{\Delta}{F}$ values than any of the spinels with known melting points. Table IV contains the known information about the two potential compounds, Mg Sc_2O_4 and Li Sc_5O_8 together with some estimated properties (in parentheses).

Prior to the diversion of effort from the refractories, five experiments were performed to investigate the synthesis of Mg Sc_2O_4. Data on these experiments are presented in Table V. No magnesium scandate ($MgSc_2O_4$) was synthesized; however, these preliminary experiments served to bracket the temperature region (1600-2200°C) that offers the greatest promise for synthesis.

The source of heat used was a small National Research Corporation (NRC) vacuum melting furnace equipped with a specially fabricated tungsten heating element of the size and shape indicated in Figure 4. This element, installed in the furnace and surrounded with proper radiation shielding, reached temperatures in excess of 2500°C.

Samples were prepared by dissolving 1:1 mol ratios of the pure oxides in nitric acid, evaporating the excess liquid, and heating to 200°C. The resultant solid was reground to pass a 200-mesh screen and pelleted in a chromium-plated die using approximately 0.5% water as a binder. These pellets were presintered at 200-700°C for four or more hours in a muffle furnace.

The reaction procedure was to place the presintered pellet in the inverted cone of the special heating element inside the NRC furnace. The furnace chamber was evacuated and the heating element and sample were slowly raised to reaction temperature. If a partial vacuum was desired, as in the fifth experiment, the vacuum and diffusion pump valves to the furnace chamber were closed and highly purified (>99.999%) argon was bled into the furnace chamber to establish the desired pressure. After the desired reaction time, the sample and heating element were slowly cooled below 1000°C; then the power was shut off and rapid cooling ensued.

The magnesia-scandia pellets used in the first two experiments were reacted at 1590°C and 1570°C for 4 and 5 hours, respectively: a pressure of 2×10^{-5} mm Hg was maintained inside the NRC furnace during the reaction period. The X-ray diffraction analysis of these pellets both before and after reaction showed no magnesia (MgO) lines, although recrystallization of scandia at 1500+°C was indicated. This lack of diffraction pattern for MgO was due to formation of amorphous MgO in the preparation and to the use of a reaction temperature too low to allow recrystallization.

The third experiment was a successful attempt to synthesize magnesium aluminate ($MgAl_2O_4$) spinel by the technique used in the first two experiments. The only changes were a shorter reaction time (2 hours) and a higher reaction temperature (1710°C).

The fifth and last experiment was an attempt to form $MgSc_2O_4$ at 2070°C. A higher partial pressure of argon was used to reduce the expected volatilization of MgO. The X-ray diffraction analysis showed that no crystalline MgO was left in the sample after reaction. This was confirmed by emission spectrographic analysis which indicated magnesium in the deposit on the shielding but no magnesium in the reacted sample. The MgO either reacted with the tungsten heating element or was volatilized from it by the high temperature, despite the use of only a partial vacuum in the NRC furnace (250 mm Hg pressure).

Initial experiments designed to synthesize $MgSc_2O_4$ were unsuccessful. However, these experiments were of an exploratory nature designed principally to test the capabilities of the technique. For instance, the failure to reach the proper temperatures in the first two experiments was the

result of insufficient shielding. There is still a good chance that the reaction of magnesia with scandia to form the spinel would occur somewhere between 1590°C and 2070°C.

One additional experiment was run to establish the melting point of scandia, which has never been reported in the literature. In this case the pellet was prepared directly from the 99.8% pure scandia powder supplied by Research Chemicals, Incorporated. The fusion point as measured by optical pyrometer was 2350°C. However, this value is probably not reliable to better than $\pm$ 50°C.

It is expected that the interrupted investigation of scandate spinel synthesis will be reactivated as a separate research program.

Task 4 - Investigation of refractory boron suboxides

In the course of a previous investigation, a new material with the probable formula B_7O was obtained from a sample submitted by American Potash and Chemical Company. According to elemental analysis carried out at Stanford Research Institute, it contained only traces of Mg and N_2 and had the analytical formula $B_{6.6}O$. Its diffraction pattern, obtained with an X-ray goniometer, did not fit any of the patterns of the known boron modifications or boron oxides. Furthermore, partial dissolution of the material did not change the X-ray pattern (16).

These results could be reasonably explained by assuming a new compound, B_7O, contaminated by about 2% of B_2O_3. However, it also could be a compound, $B_{13}O_2$, or B_6O contaminated with B, or, alternatively, a new modification of B containing a fair amount of amorphous B_2O_3. It was therefore decided to establish unequivocally the identity of the material by further application of X-ray methods. Assurance that a unique boron suboxide exists was needed before extensive efforts to synthesize such a compound could be justified.

X-ray powder photographs were taken in the Philips powder camera (r = 5.74 cm) with Cu K_a radiation. Fairly sharp lines were obtained over the whole range, including the back reflection range, an indication of a high degree of order in the structure. The spacings d derived from the observed positions of the reflections are reported in column 3 of Table VI.

On careful inspection of the spacings, it was discovered that all the reflections could be indexed on the basis of an orthorhombic unit cell

a = 8.20(4)A b = 5.35(4)A c = 5.13(0)A

The density of the material was determined experimentally by flotation as d = 2.64(4) g/cu cm.

In columns 5 and 4 of Table VI the indices of the reflections and spacings calculated from the given unit cell dimensions are reported. The agreement between observed and calculated spacings is very satisfactory, the differences being within the limit of accuracy of the experimental measurements. This success in indexing the observed reflections proves, without doubt, that the X-ray pattern arises from one homogeneous phase only. Possible impurities are present in small amounts and/or in amorphous form.

From the unit cell dimensions and the density, the molecular weight of the sample was calculated. If one assumes that 4 molecules are present per unit cell, which is very likely for an orthorhombic cell, one obtains M_{obs} = 89.7. The molecular weight of B_7O, calculated from the atomic weights, is M_{calc} = 91.7.

The agreement is also satisfactory, and even more so if one considers possible errors in the experimental data. The experimental density is expected to be low because of the suggested presence of the low density contaminant, B_2O_3 and also because minute air inclusion is difficult to eliminate in the grains of the sample used in the flotation method. Since molecular weight is directly proportional to the density of the crystal, one would expect the observed molecular weight to be less than the calculated. These considerations thus make it unlikely that the compound is $B_{6.5}O$ (or $B_{13}O_2$) with a calculated molecular weight of 86.3, about 4% smaller than the experimentally observed value.

Thus, the existence of the boron suboxide, B_7O, has been proven rather conclusively. The structure of B_7O is postulated to be closely related to that of elemental boron, as is the structure of boron carbide, B_4C. In elemental boron, the boron atoms are arranged in icosahedra (12B) which are tied into a three-dimensional network by additional B-B bonds between the icosahedra (20) (22). Similarly, in B_4C (which is better written as $B_{12}C_3$), chains of C_3 are found in the interstices of a three-dimensional network of boron icosahedra (11, 42).

It is suggested that B_7O is structurally $B_{12}(BO)_2$, in which the 12 boron atoms form a three-dimensional network similar to that in $B_{12}C_3$, and BO groups are located in the interstices. X-ray data on single crystals would be needed to confirm this proposed structure.

The work on B_7O was terminated before it had been synthesized in the present program. The experimental approach was to have been one in which pellets of a stoichiometric mixture of B_2O_3 and metallic boron

would be distributed over the length of a thermal gradient furnace. The temperature at the center of the hearth would be about 1400 °C, and at the extremes about 700°C. A current of argon would be passed through the furnace. Periodically, the samples would be removed for X-ray analysis and then returned to the furnace until evidence of B_7O formation was found. This would establish the proper time-temperature relation for synthesis and would permit duplication of these conditions on a larger scale.

(Note: A paper reporting the identification and characterization of B_7O has been accepted for publication in Acta Crystallographica.)

Task 5 - Synthesis of thiophosphonitrilic compounds

The current high level of interest in inorganic polymers containing a backbone of -P = N- units has been stimulated, at least in part, by the thermal stability and elastomeric nature of phosphonitrilic chloride polymers. In an effort to impart hydrolytic stability to these polymers, Bilbo (9) and Audrieth (2) have investigated the replacement of the chlorine with S and SH respectively. One point of departure was Bilbo's finding that heating thiophosphoryl triamide at 500°C yielded a thiophosphosoamidine rather than $[SPN]_x$. The solid triamide, $SP(NH_2)_3$, was prepared at Stanford Research Institute by the ammonolysis of $SPCl_3$[4, 5] in order to study the effect of pyrolysis at 1000°C to 2000°C with very short residence times. The approach is to expose a pellet of the triamide at the focus of an arc-image furnace or to feed the powder into a plasma jet.

Formation of polymeric $[SPN]_x$ directly from the elements and/or simple combinations of the elements at high temperatures is more in keeping with the present investigation and has a higher priority than pyrolysis of $SP(NH_2)_3$. Equipment similar to that developed by the Tennessee Valley Authority for synthesis of phosphorus nitrides from the elements in an electric discharge was assembled for this purpose. (17, 23). Figure 5 is a sketch of the equipment.

Phosphorus sesquisulfide, P_4S_3, was prepared by heating a stoichiometric mixture of the elements slightly above 100°C, followed by distillation. Nitrogen, purified by passing through copper turnings at 500 °C, was directed over the surface of molten P_4S_3 held at 320°-325°C (BP408°C). The gas stream flowed into the reaction chamber, a 5-L Pyrex flask, and reaction occurred across the arc between the two tungsten electrodes. A solid was deposited on the walls of the flask, which was held at 500°C. Effluent gas was passed through copper turnings at 500°C to remove phosphorus and sulfur.

If the reaction between phosphorus sulfide and nitrogen in the electric arc does not yield thiophosphonitrilic compounds of interest, reactions among the elements and between phosphorus nitride and sulfur (or sulfides) will be investigated.

The contributions of the following investigators to the research program are acknowledged with gratitude: Dr. David L. Chamberlain (fluorocarbons), F. Alan Ferguson (spinels and thiophosphonitrilics), Dr. Bruce King (fluorination of graphite with atomic fluorine), Dr. Raphael A. Pasternak (boron suboxide).

Table I
SUBMERGED ARC EXPERIMENTS

Exp. No.	Electrodes: Metal	Electrodes: Wt. Loss (g)	Circulating Fluid	Circulating Fluid: Weight (g)	Circulating Fluid: Conversion to High Boiling Fraction (%)	Electrical Discharge: No. of Discharges	Electrical Discharge: Total Time (sec)	Electrical Discharge: Total Energy Supplied (Joules)	Volume of Gaseous Products (ml)	Electrode Metal in High Boiling Fraction
1	tungsten	-	benzene	~250	-	5	-	-	-	none
2	tungsten	-	benzene	~3500	-	12	-	-	-	none
4	iron	0.78	cyclopentadiene	~500	-	7	-	-	-	Trace
5,6	iron	1.02	cyclopentadiene	~500	-	15	-	-	~380	Trace
7	iron	0.75	benzene	250	1.3	6	0.4	280	~460	Trace
8	iron	0.21	cyclopentadiene	405	17.5	4	0.4	345	~480	Trace

Table II

MASS SPECTROGRAPHIC ANALYSIS OF GAS SAMPLES FROM SUBMERGED ARC EXPERIMENTS

Component	Vol. % Exp. No. 5-6 Cyclopentadiene	Exp. No. 7 Benzene	Exp. No. 8 Cyclopentadiene
H_2	(70. 0) *	67. 0	41. 8
CH_4	4. 8	1. 7	4. 4
C_2H_2	1. 1	3. 7	0. 3
C_2H_4	0. 5	0. 5	0. 2
C_6H_6	0. 4	7. 2	--
Cyclopentadiene	0. 1	--	16. 5
Dicyclopentadiene	--	--	0. 4
Other cyclic compounds	--	--	0. 3
A	0. 2	--	4. 8
CO	(5.)	(14)	1. 8
CO_2	--	0. 2	14. 5
N_2	(9. 0)	(3. 0)	6. 6
H_2O	(5. 9)	(1. 5)	(6. 3)
O_2	2. 6	1. 0	1. 9

* Brackets indicate approximate values

Table III

REACTIONS INVESTIGATED FOR ADDITION OF FLUORINE TO TETRABROMOETHYLENE

Reactant	Solvent	Catalyst	Reaction Conditions
PbF_4	Chloroform	None	
PbF_4	Chloroform	BF_3	
PbF_4	Chloroform	Anhyd. HF	
PbF_4	Anhyd. HF	None	
Pyridine difluoride	Pyridine	None	-25°C
Fluorine	Anyhd. Acetonitride	None	Electrochemical Cell
Fluorine	Glacial Acetic Acid	None	Electrochemical Cell

Table IV

PROPERTIES OF PROPOSED NEW THERMALLY STABLE SPINELS
$MgSc_2O_4$ and $LiSc_5O_8$

Spinel:	$MgSc_2O_4$	$LiSc_5O_8$
Type:	2:3 (normal)	3:1
Melting Point of Constituent Oxide, °C:		
$\underline{A}_2O$		1700
$\underline{A}O$	2800	
$\underline{B}_2O_3$	2350 ± 50[a]	2350 ± 50[a]
Unit Cell Dimension, Å:	(8.7)	
Ionic Radii, Å, of:		
$\underline{A}$	0.78	0.78
$\underline{B}$	0.83	0.83
No. of 3d electrons		
$\underline{A}$	0	0
$\underline{B}$	0	0
Σ H	-554.8	-584.8[b]
Σ F	-525	-555.6[b]

a. Experimentally determined value
b. Values of Σ_H and Σ_F for $LiSc_5O_8$ are per one-half mole to make them comparable with other spinels.

TABLE V

SPINEL SYNTHESIS REACTION CONDITIONS
(pelleting pressure 1.25×10^5 lb/sq in.)

Exp. No.	Pelleted Material	Pellet Size wt (g)	Pellet Size dia (cm)	Pellet Size length (cm)	Temperatures (°C) Pellet	Temperatures (°C) Filament	Reaction Time	Reaction Furnace Pressure (mm Hg.)	Analytical Results X-ray Diffraction Lines Found for:	Analytical Results Emission Spectrogram
1	$MgO-Sc_2O_3$	0.2157	0.47	0.60	1590	1935	4 hr	2×10^{-5}	Sc_2O_3	-
2	$MgO-Sc_2O_3$	0.1703	0.47	0.47	1570	1925	5 hr	1×10^{-5}	Sc_2O_3	-
3	$MgO-Al_2O_3$	0.2206	0.47	0.70	1710	1895	2 hr	5×10^{-4}	$MgAlO + Al_2O_3 + MgO$	-
4	Sc_2O_3	0.20	0.47	0.50	2350	2350	20 min	5×10^{-4}	-	
5	$MgO-Sc_2O_3$	0.369	0.47	0.90	2070	2170	4-1/2 hr	250 (argon)	Sc_2O_3	W, Sc but no Mg

Table VI

OBSERVED AND CALCULATED SPACINGS OF B_7O

Line	Intensity*	Spacings (A) d_{obs}	Spacings (A) d_{calc}		Indices hkl
1	m	4.343	4.349		101
2	s	4.114	4.102		200
3	m	3.715	3.704		011
4	w	2.679	2.677		020
5	vs	2.571	2.565		002
6	vs	2.284	2.280		121
7	w	2.251	2.242		220
8	w	2.178	2.175		202
9	vw	2.049	2.051		400
10	w	1.855	1.852		022
11	vw	1.737	1.744		130
12	w	1.691	1.688		222
13	w	1.649	1.651		131
14	vw	1.640	1.637		230
15	s	1.464	1.465		032
16	m	1.448	1.450		303
17	s	1.430	1.435		331
18	vw	1.403	1.400	1.399	313, 520
19	m	1.340	1.339		040
20	m	1.282	1.282		004
21	vw	1.274	1.272		240
22	w	1.261	1.267		104
23	w	1.244	1.247		014
24	vw	1.238	1.235		033
25	vw	1.221	1.221	1.224	133, 204

*s= strong, m = medium, w = weak, v = very

Table VI
(Continued)

Line	Intensity*	Spacings (A) d_{obs}	Spacings (A) d_{calc}		Indices hkl
26	vw	1.189	1.187		042
27	w	1.158	1.157		024
28	w	1.142	1.142	1.140	701, 242
29	vw	1.121	1.121		440
30	vw	1.090	1.087		404
31	m	1.026	1.025	1.027	800, 442
32	m	1.007	1.007	1.007	424, 810
33	vvw	.9916	.9903	.9929	722, 514
34	vvw	.9277	.9259		044
35	vw	.9098	.9092		723
36	w	.8917	.8923		060
37	m	.8776	.8791	.8794	061, 803
38	w	.8691	.8699		505
39	v w	.8558	.8550		006
40	w	.8450	.8440		444
41	vvw	.8350	.8368		206
42	vw	.8253	.8255		262
43	vw	.8153	.8160	.8143	306, 026
44	vw	.8068	.8067		316

*s= strong, m = medium, w = weak, v = very

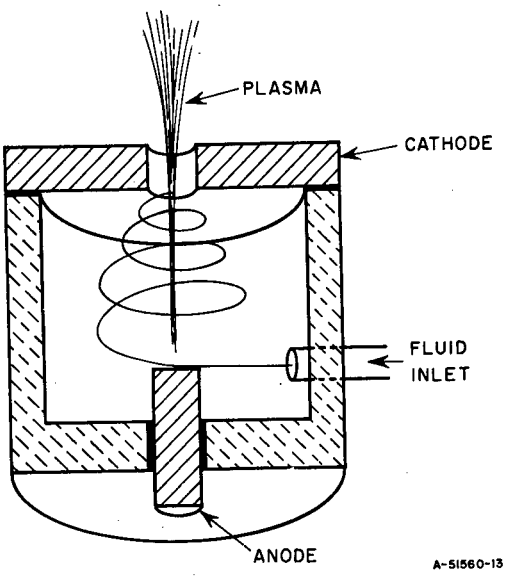


FIG. 1

SCHEMATIC DIAGRAM OF
PLASMA JET

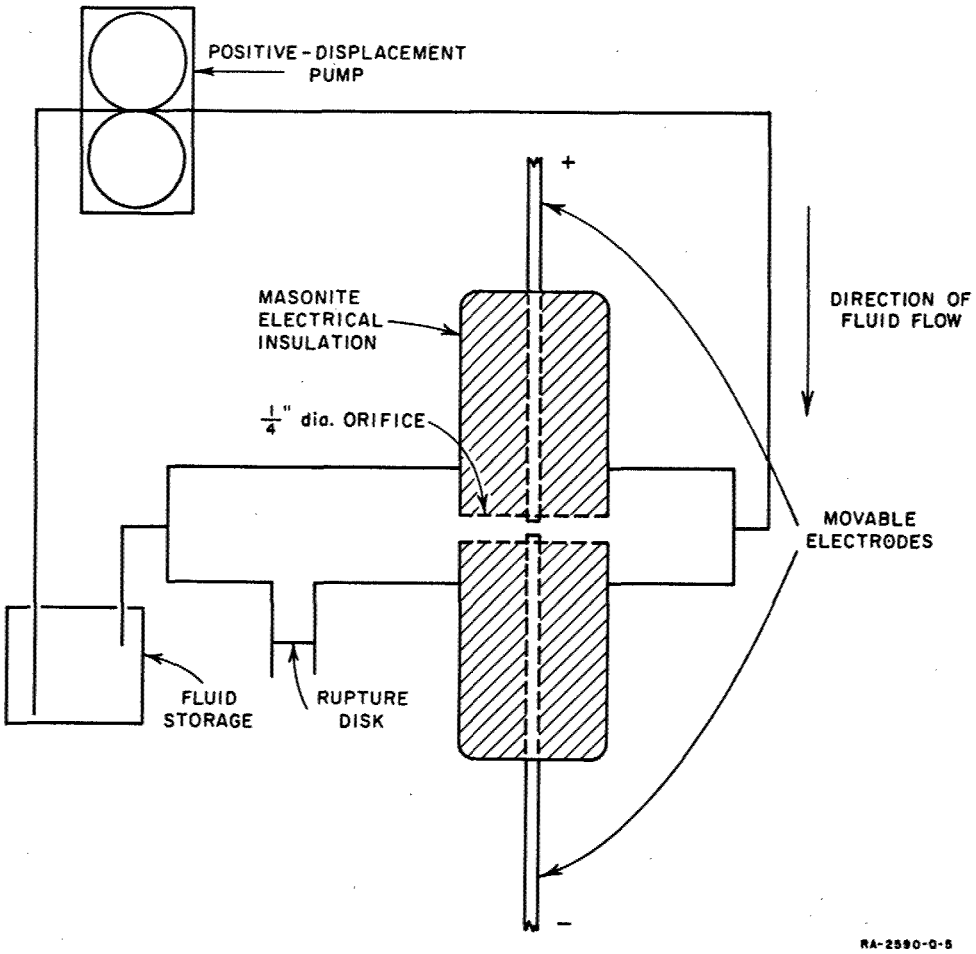


FIG. 2

SCHEMATIC OF SUBMERGED ARC EQUIPMENT

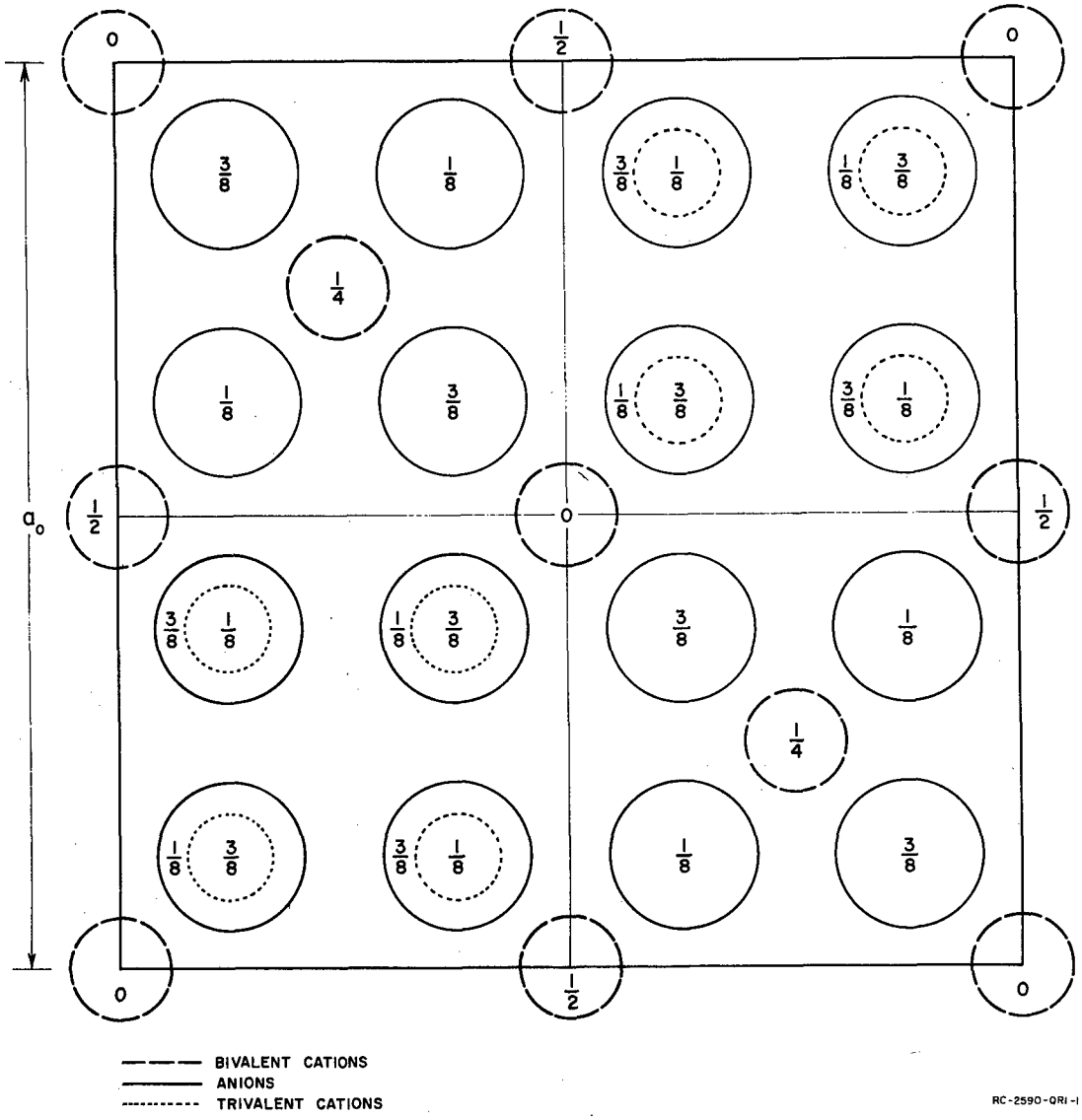


FIG. 3

NORMAL SPINEL CRYSTAL
Schematic Representation of Bottom Half of Crystal
Plan View. Not to Scale

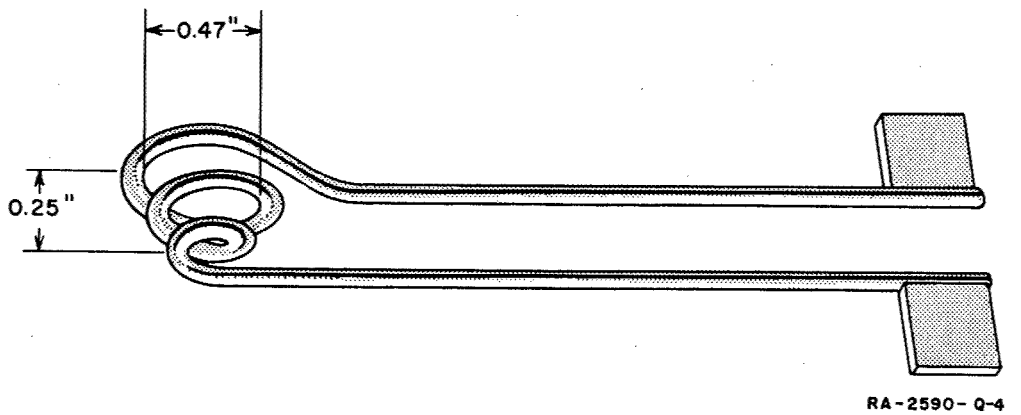


FIG. 4

SPECIALLY CONSTRUCTED HEATING ELEMENT
FOR NRC FURNACE

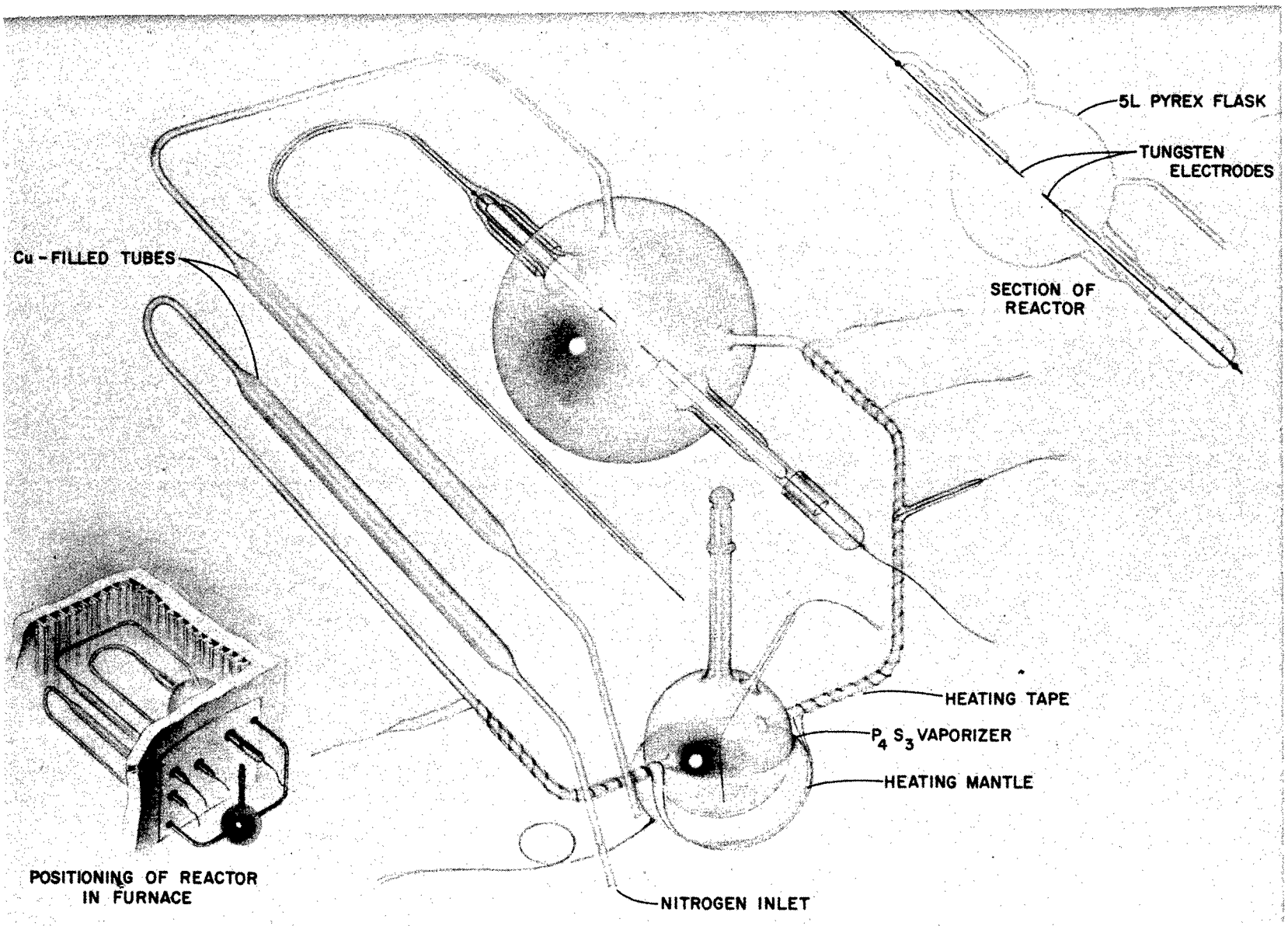


FIG. 5

ASSEMBLY OF EQUIPMENT FOR SYNTHESIS OF SPN IN AN ELECTRIC ARC

BIBLIOGRAPHY

1. Aynsley, E. E., and R. H. Watson, J. Chem. Soc., 1955, 576-7.

2. Audrieth, L. F., Quarterly Progress Report under Contract AF 33(616)-5486, June 1958, p. 44.

3. Avramenko, L. E., J. Phys. Chem. USSR, 20, 1299 (1946).

4. Barth, T. F. W., and E. Posnjak. Z. Krist. 82, 325-41 (1932) (in English).

5. Benning, A. F., B. Downing, and D. Park, U. S. Pat. 2,394,581 (1946).

6. Benning, A. F. and J. D. Park, U.S. Pat. 2,384,449 (1945).

7. Benning, A. F. and E. G. Young, U. S. Pat. 2,615,926 (1952).

8. Bigelow, L. A., Chem. Rev., 40, 83 (1947).

9. Bilbo, A. J., in a report prepared by R. L. Rau, Wright Air Development Center Technical Report 58-160, June 1958, p. 46.

10. Booth, H. S., W. L. Mong, and P. E. Burchfield, Ind. Eng. Chem. 24, 328-31 (1932).

11. Clark, H. K. and J. L. Hoard, J. Am. Chem. Soc. 65, 2115 (1943).

12. Copenhaver, J. W., and H. Bigelow, Acetylene and Carbon Monoxide Chemistry, Reinhold Publ. Corp. (1949).

13. Desirant, Y., Bull. classe sci., Acad. roy. Belg. 41, 759-6 (1955).

14. Downing, F. B., and A. F. Benning, U.S. Pat. 2,384,821 (1945).

15. Downing, F. B., A. E. Benning, and R. C. McHarness, U.S. Pat. 2,551,573.

16. Eding, H. J., Wright Air Development Center, AF 33(616)-2271, Supplement 3(55-1368) (1956).

17. Elmore, K. L., Chief of Research Branch, Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Alabama, private communications.

18. Fear, E. J. P. and J. Thrower, J. Appl. Chem. (London) 5, 353-8 (1955).

19. Godsell, J. A., M. Stacey, and J. C. Tatlow, Nature 178, 199-200 (1956).

20. Haszeldine, R. N. and F. Smith, J. Chem. Soc. 1956, 783-4.

21. Hellmann, M., E. Peters, W. J. Pummer, and L. A. Wall, J. Am. Chem. Soc. 79, 5654-6 (1957).

22. Hoard, J. L., R. E. Hughes, and D. E. Sands, J. Am. Chem. Soc. 80, 4507 (1958).

23. Huffman, E. O., et al, Synthesis of Phosphorus Nitrides, J. Amer. Chem. Soc. 76, 6239 (1954).

24. McBee, E. T., W. B. Ligett, and V. V. Lindgren, U. S. Pat. 2, 586, 364, Feb. 19, 1952.

25. McBee, E. T., V. V. Lindgren, and W. B. Ligett, Ind. Eng. Chem. 39, 378-80 (1947).

26. Middleton, W. J. and W. H. Sharkey, J. Am. Chem. Soc., 81, 803 (1959).

27. Ott, E. and G. Dittus, Ber. 76B, 80-4 (1943).

28. Palin, D. E. and K. D. Wadsworth, Nature, 162, 925 (1948).

29. Pummer, J. and L. A. Wall, Paper presented at the Fifth Joint Army Navy Air Force Conference on Elastomers Research and Development, Dayton, Ohio, Oct. 15-17 (1958).

30. Rogers, Gail C. and George H. Cady, J. Am. Chem. Soc 73, 3523-4 (1951).

31. Romeijn, F. C., Philips Research Repts. 8, 304-20 (1953).

32. Ruff, O., and O. Bretschneider, Z. anorg. allgem. Chem. 210, 173-83 (1933).

33. Ruff, O., O. Bretschneider, and F. Ebert, Z. anorg. allgem. Chem., 217, 1 (1934).

34. Ruff, O. and O. Bretschneider, Z. anorg. allgem. Chem., 217, 19 (1934).

35. Schumb, W. C. and J. R. Aronson, J. Am. Chem. Soc., 81, 806 (1959).

36. Schwab, G. M. and H. Friess, Z. Electrochem., 39, 586 (1933).

37. Simons, J. H., ed. Fluorine Chemistry, v. 1, Academic Press, Inc. New York, p. 421 (1950).

38. Simons, J. H., H. Pearlson, and R. James, U. S. Pat. 2, 494, 064 (1950).

39. Smith, R. P. and J. C. Tatlow, J. Chem. Soc. 1957, 2505-11.

40. Thornton, V., B. Burg, and H. I. Schlesinger, J. Am. Chem. Soc. 55, 3177-82 (1933).

41. Wall, L. A., Nat'l. Bur. Stds. Rept. 5A-185, July 24, 1953.

42. Zhadanov, G. S. and N. G. Sevast'yanov, Compt. rend. acad. sci. USSR, 32, 432 (1941).

SYNTHESIS OF 1000°F. STABLE FLUIDS

J W. Dale, I. B. Johns, E. A. McElhill, and J. O. Smith
Monsanto Chemical Company

Advanced aircraft and missiles are being subjected to ever-increasing temperature levels and this requires materials of ever-increasing thermal stability. One such need is for base stock fluids which are stable to 1000°F. To obtain the high-temperature performance it will probably be necessary to sacrifice some low-temperature performance and room temperature has been selected as the target melting point.

In attempting to prepare this 1000°F. base stock fluid, we have taken a fairly basic physical chemical approach to the problem. The work has been divided into two parts; first, the thermal stability of a number of representative, fairly simple chemical structures has been determined without regard to boiling point, freezing point, or other properties. This phase of the work has been largely completed and will form the main basis of this report. The second part of the work involves the methods which may be used to couple these basic structures into thermally stable liquids. This part of the work is just getting underway and will be discussed only briefly.

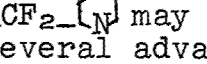
The thermal stability of the compounds was measured in two ways, depending on the physical state of the compound. Vapor phase thermal stability was determined by heating the vapor of the compound at atmospheric pressure in a closed system until decomposition occurred. The decomposition was determined by measuring the volume change of the vapor. The system was flushed with nitrogen so that the compound was always maintained in an inert atmosphere.

The thermal stability of the compounds in the liquid, or condensed, phase was determined in an inert atmosphere in an isoteniscope. The isoteniscope is simply an instrument used to measure vapor pressure over a range of temperatures. If the vapor pressure of a compound did not change with time at a given temperature, the compound was assumed to be stable at this temperature. The lowest temperature at which the vapor pressure of the compound changed appreciably with time was taken as the decomposition temperature of the compound These are simple and reliable methods for determining thermal stability. It is difficult to imagine a case in which a compound decomposes without either an increase or a decrease in vapor pressure or volume. Infrared and ultraviolet spectrography and vapor phase chromatography were used to detect decomposition products.

In the following parts of the report the compounds will be discussed in order of decreasing thermal stability as follows: (1) fluorine-containing materials, (2) aromatics, (3) nitrogen compounds, (4) a silicon compound, (5) phosphorus compounds, (6) ferrocene, and (7) boron compounds. Table I summarizes the results obtained in the vapor phase and Table II, the results in the liquid or condensed phase. The final part of the report will touch on some general considerations about thermal stability.

Fluorine-Containing Compounds. Hexafluorobenzene was the most stable compound tested in the vapor phase, being stable at 1200°F., the upper limit of the equipment. Perfluorocyclohexane also is very stable decomposing between 1150 and 1200°F. This is even more impressive in view of the fact that the compound was only 80% pure The perfluorocyclohexane was made by direct fluorination of cyclohexane, and the reaction was not complete, only about 80% of the hydrogen being replaced.

It is believed that fluorine compounds may possibly be made into 1000°F. fluids. It is possible to make compounds of the type C_6F_5MgBr and $C_6F_4Br_2$ By means of these reactive groupings it may be possible to link the perfluoro residues together to form thermally stable fluids In addition it is possible to form cyclic perfluoroalkanes from the corresponding hydrocarbons by direct fluorination.

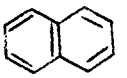
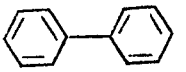
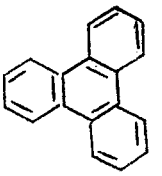
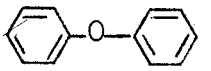
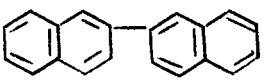
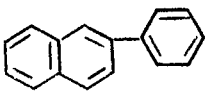
Although it is probably better to have no hydrogen in the fluorocarbons to prevent decomposition of the molecule by evolution of HF, an exception to this may exist in the case of certain nitrogen-containing compounds, e.g. 2-trifluoromethylpyridine, . There is some interaction in this compound between the nitrogen and fluorine, since the nitrogen loses its basic nature Preliminary tests on this compound[a] gave encouraging but not conclusive results. Compounds of the type  may have unusual stability. The fluorocarbons offer several advantages in addition to thermal stability. They are resistant to oxidation and are good lubricants. They suffer from the disadvantage of having a poor

---

(a) This material was kindly furnished by Professor George Janz of Rensselaer Polytechnic Institute

viscosity-temperature relationship, but this may possibly be overcome by the proper selection of molecule shape and make-up.

Aromatics. Benzene itself is stable to 1100°F. in the gas phase, and a number of compounds containing benzene rings are stable in the 950°F.-1000°F. range in the condensed phase as shown in the following extract from Tables I and II.

Compound	Formula	Decomposition Temperature, °F. Vapor	Condensed
Naphthalene		1150-1200	1050
Benzene		1100	—
Biphenyl		950-1000	1010
Triphenylene		—	980
Diphenyl ether		—	1000
2,2'-Binaphthalene		—	965
2-Phenylnaphthalene		—	945

These results agree in general with those of other workers* which show that decomposition in the liquid phase takes place at a lower temperature than in the gas phase. This is to be expected because of the greater number of collisions per unit time for the liquid. If a direct dependence of reaction rate on concentration (unimolecular reaction) is assumed, then the number of molecules reacting per unit volume in the liquid phase should be about 10^2 times the number of molecules react-

* Madison and Roberts, Ind. Eng. Chem. 50, 237-50 (1958).

per unit volume in the gas phase at atmospheric pressure*. If equally sensitive measures of reaction are used in the gas and liquid phases, then reaction should be detected at a lower temperature in the liquid than in the gas phase. Of course, it is possible that the mechanism of reaction in the liquid phase is different from that in the gas phase.

It is possible to translate very approximately these differences in amount of reaction at a given temperature to differences in temperature at a given amount of reaction. Taking the decomposition of hexaphenylmelamine as shown in Figure 1 as a typical reaction with an activation energy of decomposition of 62,000 calories/mole, it will be noted that, in the 950°F. region, reducing the temperature by about 150°F. reduces the reaction rate constant by 10^2. The results obtained with naphthalene are roughly in agreement with this figure. Biphenyl is the one exception to the rule found to date. It is as stable in the liquid as in the vapor state. The reason for this is not known.

A generalization which may be made concerning decomposition reactions involving the benzene ring is that ring rupture is not observed. The usual reaction is loss of hydrogen from the ring followed by a dimerization of the fragments left behind.

There is a good possibility that a material with stability in the 950°F.-1000°F. range and boiling above 1000°F. can be made from condensed aromatics. One or two naphthyl groups attached to triphenylene should have the desired boiling point and good thermal stability. A third naphthyl added to 2,2'-binaphthalene should also have the desired high-temperature properties. Naphthyl and phenyl groups joined together may also have interesting possibilities. These materials however all melt considerably above room temperature. By combining them in various mixtures, various lower melting eutectics may be formed.

Unfortunately ter- and quater-phenyl formed by adding one or two phenyl groups to diphenyl are less stable than biphenyl by almost 100°F. An even more marked loss in stability, amounting to about 150°F., is incurred when a phenoxy group is added to diphenyl ether. If suitable groups for linking benzene rings together could be found, there would be a good possibility of developing fluids with the desired high- and low-

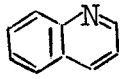
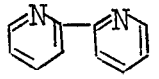
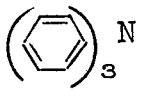
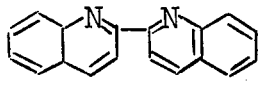
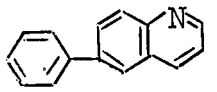
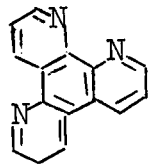
---

* The molar volume of naphthalene at 800°F. and atmospheric pressure = $22,400 \times \frac{698}{273} = 57,200$ cc. The molar volume of liquid naphthalene at 800°F. $\sim \frac{130}{0.5} \sim 260$ cc.

$\frac{\text{Concentration in liquid}}{\text{Concentration in vapor}} \sim \frac{57,200}{260} \sim 2.3 \times 10^2$.

temperature properties. This will be discussed in greater detail later.

Nitrogen-Containing Compounds. A number of five- and six-membered resonance stabilized rings containing non-adjacent nitrogen atoms showed great stability in the vapor phase but gave disappointingly low results in the liquid phase, as shown in the following extract from Tables I and II.

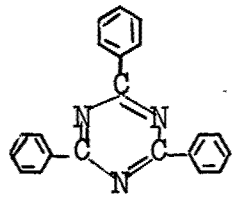
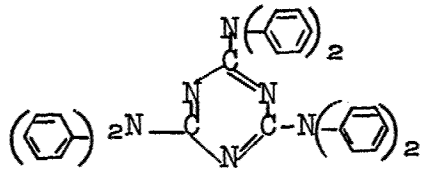
		Decomposition Temperature, °F.	
Compound	Formula	Vapor	Condensed
Quinoline		1200	950-1000
Pyridine		1150-1200	—
Imidazole		1150-1200	—
Pyrimidine		1150-1200	—
2,2'-Bipyridine		1150-1200	900
Triphenylamine		—	935
2,2'-Biquinoline		—	920
6-Phenylquinoline		—	900
1,2,6-Tripyridinobenzene		—	900

It appears that approximately 900°F. is the top stability limit of the resonance stabilized nitrogen heterocyclics in the liquid phase. These compounds, in general, are lower melting than their benzene analogues, and it may be possible

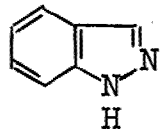
to gain low-temperature performance, at some sacrifice of high-temperature performance, by use of nitrogen heterocyclics.

Triphenylamine was the most stable nitrogen compound tested in the liquid phase. This type of nitrogen linkage may be of use in joining benzene rings to form compounds stable in the 900°F. region.

The triazine ring is of considerable interest because trichlorotriazine is a convenient compound for synthetic manipulation. The triazine ring appears to decompose in the 850-870°F. region, as shown in the following:

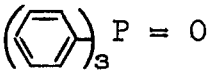
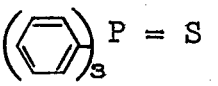
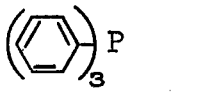
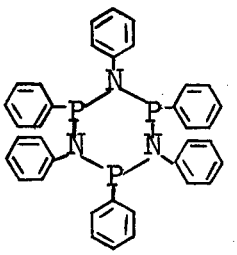
Compound	Formula	Decomposition Temperature, °F. (Condensed Phase)
Triphenyl-s-triazine		870
Hexaphenylmelamine		850

Resonance stabilized ring compounds containing adjacent nitrogen atoms are relatively unstable, as shown in the following extract from Table I.

Compound	Formula	Decomposition Temperature, °F. (Vapor Phase)
Indazole		less than 900°F.
1,2,4-Triazole		less than 800°F.

Silicon-Containing Compounds. Silicon-containing compounds are being investigated by other workers, so only one type of compound was tested, diphenyldiphenoxysilane, in order to get a direct comparison with other materials in our program. This material decomposed at approximately 900°F. in the liquid phase. Silicon appears to offer an attractive way of coupling benzene rings to form fluids stable at least to 900°F.

Phosphorus Compounds. There is considerable interest in phosphorus containing materials as high-temperature fluids. A number of these compounds have been screened in this work and of those tested it appears that ~850°F. is the top limit of usefulness as shown in the following:

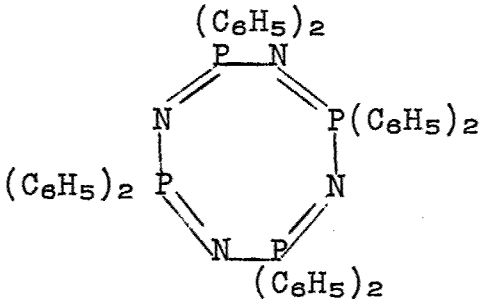
Compound	Formula	Decomposition Temperature, °F. (Condensed Phase)
Triphenylphosphine oxide		850
Triphenylphosphine sulfide		715
Triphenylphosphine(a)		705
Hexaphenylphosphazole		665

(a) E. S. Blake, WADC Report 57-437.

The phosphazole ring does not appear to be particularly stable. An interesting comparison exists between the stability of hexaphenylphosphazole and the tetramer of diphenylphosphinic nitride*. The probable structure of which is:

---

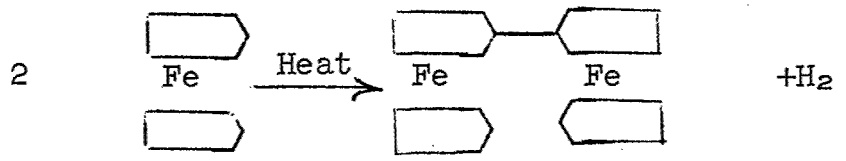
* Diphenylphosphinic nitride tetramer was kindly supplied by Dr. C. P. Haber, Chem. Section, U. S. Naval Ordnance Lab.



The tetramer decomposed at 820°F. The higher stability of the tetramer demonstrates the effect of type of bonding on thermal stability and may reflect the high stability of pentavalent phosphorus compounds.

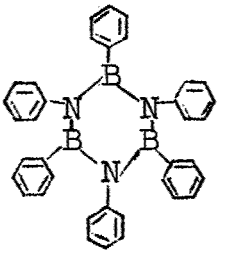
Ferrocene. The ferrocenes are an interesting new class of compounds of good thermal stability. Ferrocene itself had a top limit of stability of about 850°F.

The ferrocene decomposition product appeared to form by the following reaction:

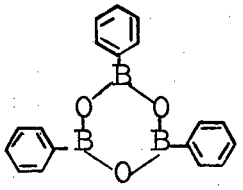


Infrared and u.v. analyses of the decomposition product indicated that the ferrocene structure was still present, with some extra absorptions added. Elemental analysis and molecular weight determination confirmed the presence of the dimer. The dimer appears to explode in air at approximately 400°F. This decomposition of ferrocene by loss of hydrogen indicates that to form a ferrocene with a stability greater than 850°F., the hydrogens of the ferrocenes should be replaced by more stable groups.

Boron Compounds. Two types of boron compounds have been investigated. Hexaphenylborazole



decomposed at 815°F. indicating that B-N ring system does not have outstanding thermal stability. Triphenylboroxole

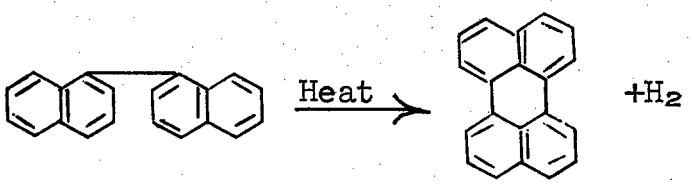


decomposed at 665°F., indicating a relatively low stability for the B-O ring system.

Generalizations and Conclusions. A number of generalizations may be drawn from these results.

1. Thermally stable molecules have high bond energies. For example, the most stable compound tested in this work was hexafluorobenzene with a C-C bond of ~100 Kcal. and a C-F bond energy which may be as high as 145 Kcal. Benzene ring compounds, stable in the 950°F.-1000°F. range have, in addition to the C-C bond at ~100 Kcal., the C-H bond with ~100 Kcal. However, not all molecules with high bond energies are stable; certain other factors are necessary.

2. Thermally stable molecules should have all paths of easy elimination of simple fragments blocked. When in certain positions, hydrogen is eliminated easily. This type of hydrogen arrangement should be avoided. For example, 2,2'-binaphthalene decomposes at 945°F. whereas 1,1'-binaphthalene decomposes at 845°F. The 1,1'-compound probably decomposes by the following reaction:

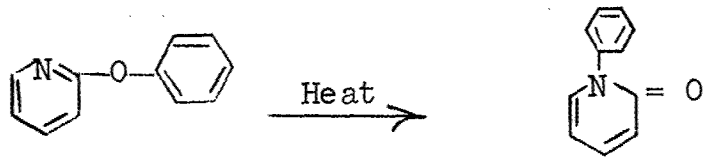


which is blocked in case of the 2,2'-compound, since a new benzene ring cannot be formed.

Another example, is hexaphenylmelamine which decomposes at 850°F. whereas triphenylmelamine, with available hydrogens, decomposes at ~660°F. (E. S. Blake, WADC Technical Report 57-437.).

Other more complicated rearrangements can also occur. 1-Phenylimidazole, a liquid at room temperature, quantitatively rearranges to 2-phenylimidizole, a high-melting solid, at 890°F., in the vapor phase. Also, 2-Phenoxypyridine rear-

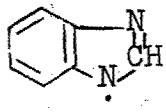
ranges to the pyridone at 850°F. as follows:



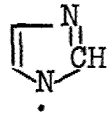
The pyridone is unstable at 850°F.

3. Resonance stabilized structures have great stability. In most of the decomposition reactions studied in this work, the resonance stabilized rings have remained intact. Usually hydrogen is eliminated, or the bond joining the rings together is broken. It appears that the C-C bond in the benzene ring is thermally stable at 1000°F.

4. For great thermal stability compounds should be avoided which can furnish stabilized free radicals or resonance stabilized decomposition products. As an example, imidazole decomposes at 1150-1200°F. in the vapor phase, whereas benzimidazole decomposes at 750-805°F. The difference is probably due to the greater resonance stabilization of the radical



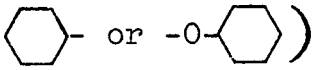
compared with



The greater the resonance stabilization of the resulting radical, the easier the removal of the hydrogen.

Another example is possibly furnished by the compounds obtained on linearly joining together benzene rings. Biphenyl is stable to 1000°F., while ter- and quater-phenyls are stable to about 900°F. A possible explanation of this may be that the radical $C_6H_5.C_6H_4.C_6H_4$- is more stable than $C_6H_5.C_6H_4$-, and thus terphenyl loses a hydrogen more readily than diphenyl. The same condition exists with phenyl ether which is stable up to 1000°F., while the polyphenyl ethers decompose 150° to 200°F. lower.

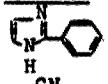
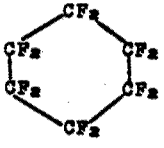
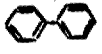
One answer to this problem may be to provide "insulating" groups between the benzene rings. Groups such as $-CF_2-$, $-C(CN)_2-$, $-\underset{\underset{R}{|}}{B}-$, $-O-\underset{\underset{R}{|}}{B}-O-$, $-\underset{\underset{R_2}{|}}{Si}-$, and $-O-\underset{\underset{R_2}{|}}{Si}-O-$ (where R =

 may have this characteristic.

5. For good thermal stability molecules should be avoided that can "unzip." The molecule should be composed of groups which can act as "stoppers," e.g. — -, -O— —O-, R, R, R O-Si-O, -B-, -N-, etc. A molecule containing "stoppers" must R decompose link by link and cannot go by a chain mechanism. A simple example of a molecule which can "unzip" is polyisobutylene which goes to isobutylene on heating, or teflon which gives tetrafluoroethylene.

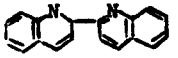
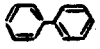
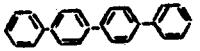
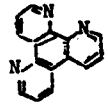
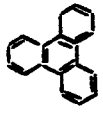
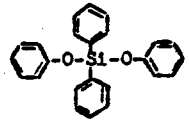
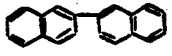
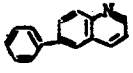
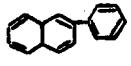
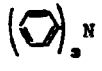
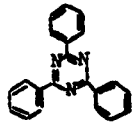
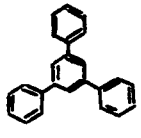
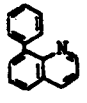
This work was sponsored by the Materials Laboratory, Wright Air Development Center. Dr. Christ Tamborski and Mr. George Baum are the project engineers.

TABLE I
THERMAL STABILITY OF COMPOUNDS IN THE VAPOR PHASE

Compound	Formula	Decomposition Temp., °F.(a)	Compound	Formula	Decomposition Temp., °F.(a)
Hexafluorobenzene (in monel apparatus)		over 1200	2-Phenylimidazole		1100
Quinoline		1200	Benzonitrile		1060-1120
2,2'-Biyridine		1150-1200	Toluene		1050-1100
Pyridine		1150-1200	Benzothiazole		1025-1050
Imidazole		1150-1200	Thiazole		1000
Perfluorocyclohexane (80% pure) in monel apparatus		1150-1200	Biphenyl		950-1000
Pyrimidine		1150-1200	Benzimidazole		750-800
Naphthalene		1150-1200	Indazole		under 900
Thiophene		1100-1150	1,2,4-Triazole		under 800
Benzene		1100			

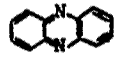
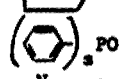
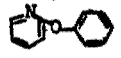
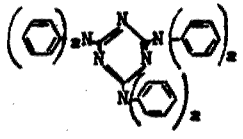
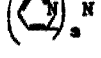
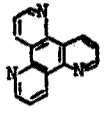
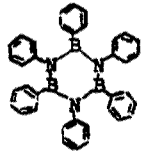
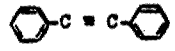
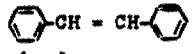
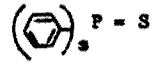
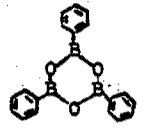
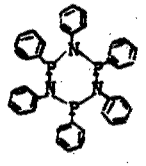
(a) Temperature at which decomposition rate is appreciable.

TABLE II
THERMAL STABILITY OF COMPOUNDS IN THE CONDENSED PHASE

Compound	Formula	Decomposition Temp., °F. (a)	Compound	Formula	Decomposition Temp., °F. (a)
Naphthalene (critical temp., 896°F.)		1050	2,2'-Biquinoline		920
Biphenyl (critical temp., 982°F.)		1010	p-Quaterphenyl		900-940
Quinoline		950-1000	2,2'-Bipyridine		900
Diphenyl ether		~1000	1,2,6-Tripyridinobenzene		900
Triphenylene		980	Diphenyldiphenoxysilane		900
2,2'-Binaphthalene		965	6-Phenylquinoline		900
2-Phenylnaphthalene		945	1-Phenylimidazole		890
Triphenylamine		935	Triphenyl-s-triazine		870
1,3,5-Triphenylbenzene		930	8-Phenylquinoline		870

(a) Temperature at which decomposition rate is ~1%/hr.

TABLE II (CONT.)
THERMAL STABILITY OF COMPOUNDS IN THE CONDENSED PHASE

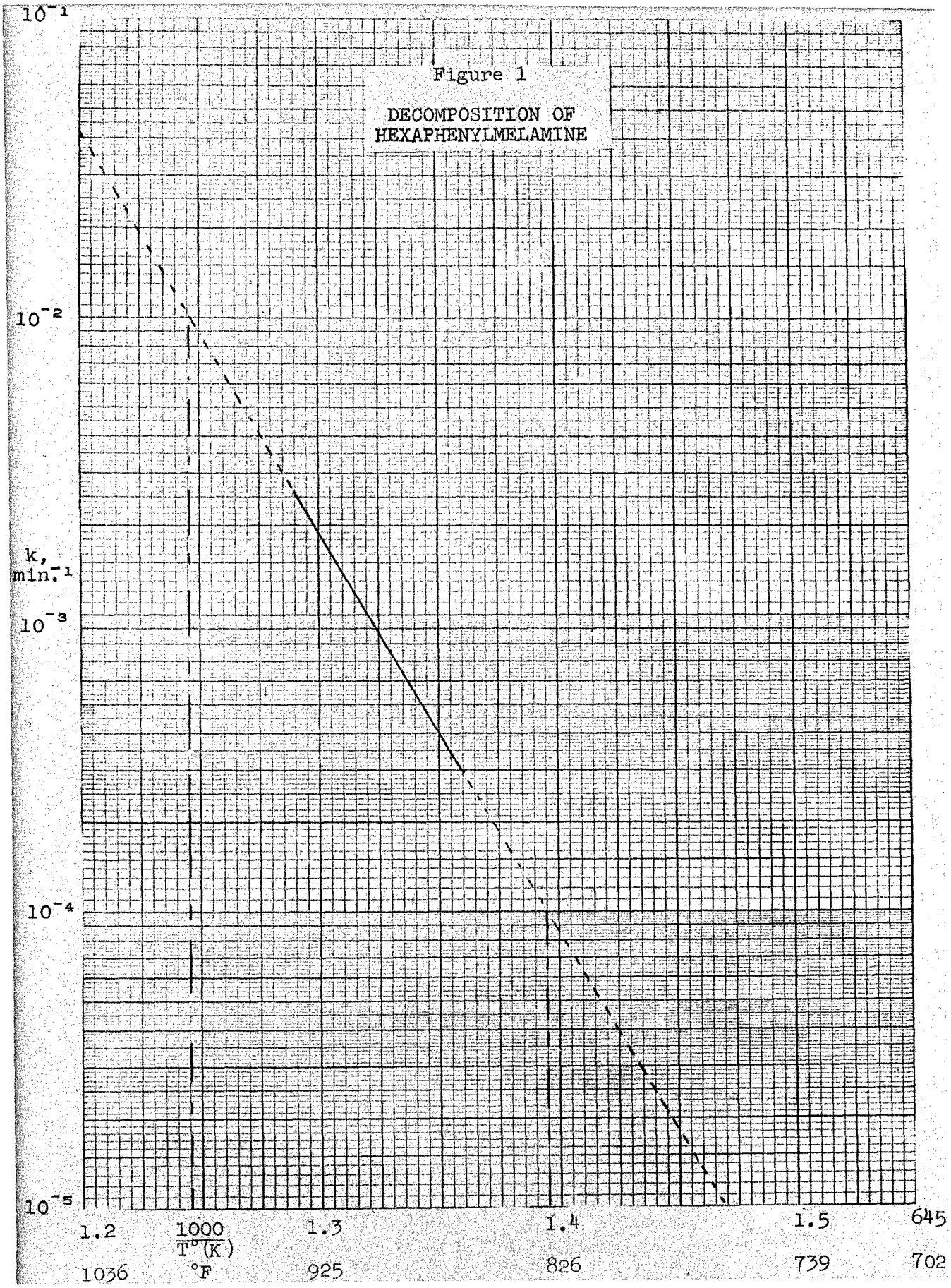
Compound	Formula	Decomposition Temp., °F.
Phenazine		~850
Ferrocene		850
Triphenylphosphine oxide		850
2-Phenoxypyridine		850
Hexaphenylmelamine		850
Hexaphenylbenzene		845
Coronene (b)		845
1,1'-Binaphthalene		845
Tri(2-pyridyl)amine		845
1,5,9-Tripyridinobenzene		825
Hexaphenylborazole		815
Diphenylacetylene		790
Stilbene		785
Triphenylphosphine Sulfide		715
Triphenylboroxole		675
Hexaphenylphosphazole		665

(a) Temperature at which decomposition rate is 1%/hr.

(b) Sample kindly furnished by Professor Melvin J. Newman of Ohio State University.

Figure 1

DECOMPOSITION OF HEXAPHENYLMELAMINE



INVESTIGATIONS into the RADIATION CHEMISTRY of POLYPHENYL FLUIDS

by

Josef J. M. Schmidt
and
George E. Bohner

Denver Research Institute
University of Denver
Denver 10, Colorado

April 1959

I. OBJECTIVE

The research program conducted at the Denver Research Institute, University of Denver, has as its objective investigations into the relations between the chemical structure of a number of alkyl polyphenyl compounds and polyphenyl ethers and the radiolytic degradation of these compounds under the influence of high intensity gamma radiation.

II. INTRODUCTION

It is well known that aromatic and/or polyaromatic hydrocarbons such as benzene or biphenyl show superior radiation stability as compared to aliphatic and/or alicyclic hydrocarbon compounds of comparable molecular weight. It is generally assumed that this stability is connected with the strongly resonating nature of the aromatic structure which will allow for a rapid energy dissipation in the molecule, other than by bond rupture, reducing thus considerably the degree of degradation and/or polymerization.

Similar phenomena have been observed with higher homologous derivatives of benzene, viz., polycondensed aromatics such as napthalene and other polynuclear aromatics such as polyphenyl and polyphenyl ether compounds. These exhibit even higher radiation stability than benzene itself. Indeed, the latter two groups of compounds have become of considerable interest as potential base materials for radiation stable organic fluids and/or reactor coolants.

Previous investigations have also shown that aromatic or polyaromatic hydrocarbons such as benzene or polyphenyls etc., when in mixtures with aliphatic or alicyclic hydrocarbons such as n-hexane or cyclohexane will protect the latter to an extent against radiolysis from energy ionizing radiation. This protective effect has been attributed to transfer of least stable molecule to the more stable aromatic or polyaromatic compound. Because of the lower excitation potential and ionizing potential of the aromatic compound as compared with those of e.g., cyclohexane it is possible that any one of the two routes of transfer may be energetically operative.

It was therefore, of interest to investigate the problem, whether direct attachment of e.g., aliphatic chains in covalent bonding to the aromatic or polyaromatic system would eventually or even further enhance the protective role of the latter. By allowing for a greater probability of any energy transfer from the activated alkyl side chain to the aromatic system it could be conceived that if this transfer and dissipation of energy is sufficiently fast it would eventually prevent the scission of the attached hydrocarbon at some of its more sensitive points. If this were the case, then it was furthermore of interest to determine whether

and to what degree various structural parameters such as position of the alkyl groups, chain length and degree of branching will be effective and what the most probably breakdown mechanism of these various structures might be.

Alkyl polyphenyl type compounds have been chosen as model substances for a number of reasons, but mainly because of the relatively high radiation stability of the parent polyphenyl compounds in themselves, the absence of heteroatoms (such as oxygen in e.g., polyphenyl ethers) which could further complicate the number and type of scission products and familiarity with this group of compounds from previous experimental work. There is also a more practical reason for such choice, namely, that alkylation of polyphenyls and/or polyphenyl ethers can render these compounds liquid at lower temperatures, a desirable property if such products are to be used as base fluids in radiation enviornment.

The present study was therefore undertaken in the hope of obtaining more detailed information on the relation between the chemical structure and radiolytic degradation of alkyl aromatic and alkyl polyaromatic compounds and ultimately eventually some more concise information on the process of energy transfer and breakdown mechanism.

Information of this sort may ultimately allow a more definite deduction of the most radiolytically stable structure among these classes of compounds.

1. Sample Material

Sample material was secured whenever possible from commercial sources. Since the commercial market offers only a limited number of liquid alkyl aromatic and alkyl polyphenyl compounds (these being almost exclusively alkyl benzenes) a number of derivatives had to be prepared or were drawn from D.R.I.'s own stock.

The alkyl aromatic compounds chosen for preparation and study were such that all were liquids at room temperature. As first approach to the problem mono-n-alkyl derivatives were investigated with C_7 as maximum chain length to maintain greatest fluid temperature range and optimal thermal stability. The materials received and/or synthesized were tested for purity and, if indicated, purified by vacuum distillation and adsorption column chromatography until gas liquid chromatography indicated 99.7% or greater purity.

2. Sample Preparation

Before irradiation, the samples were deaerated by repeated evacuation and freezing and sealed under a vacuum or Argon. The sample was placed in the source and allowed to remain during the radiation period. The temperature at the point of irradiation was 30°C. Sample volumes of 50 ml and 100 ml were prepared for irradiation.

3. Irradiation

The purified and prepared compounds ere irradiated in the Denver Research Institute's Co^{60} radiation source. The geometry of the source allows the irradiation at a dose rate of 4.4×10^5 r/hr. and a maximum volume of 600 ml.

The radiation intensity was measured by the cerric sulfate method and all doses reported have been calculated from dosimetry data before and after each irradiation period.

III. ANALYTICAL EVALUATION

A major task of the program was to be concerned with the separation and the identification of the various breakdown products and/or polymeric materials resulting from the irradiation of the compounds. These included gaseous, liquid and solid polymeric materials. Because of the closely related and/or polymeric nature of many of these high boiling materials only few techniques were amenable for their analysis.

1. Gas Analysis

After the irradiation period the free volume gas was collected and the gas volume measured. The gas was then analyzed for composition up to C_6 hydrocarbons using a Beckman GC-2 gas chromatograph. The various gas yield values were then calculated from this analysis.

2. Liquid Phase Analysis

It was assumed early in the research that vacuum distillation would probably not permit separation of all the yield products and conceivably could change the character of any thermally unstable yield materials. For these reasons, other methods of fractionation had to be chosen. These methods are briefly discussed below:

(a) Adsorption and Partition Column Chromatography

Column adsorption and partition chromatography has been investigated first as a possible method of separation of the liquid fractions. Although this method allows the separation of various polyphenyl compounds of a wider difference in molecular weight it is unsatisfactory for the separation of the more related homologous members of alkyl derivatives. After considerable effort, no method was found that would adequately separate various alkyl polyphenyl homologs by column chromatography.

(b) Countercurrent Distribution Methods

A two-hundred tube Craig type countercurrent distribution apparatus available at Denver Research Institute has been utilized in separating the yield materials from irradiated polyphenyl hydrocarbons. Although this method shows only moderate success to actually

separate the yield components it will successfully concentrate several components into fractions, relatively free of parent material. In the case of polymeric yield products, this concentration will permit other methods of characterization to be utilized.

(c) Gas Liquid Partition Chromatography

For such materials that will traverse a column at 220°C in a reasonable period, a Beckman GC-2 chromatograph has been used for the detection of radiolytically producted products and the determination of $-G_m$ values (molecules of parent disappearing per 100 ev energy absorbed) for the lower boiling hydrocarbons. Any lower boiling scission product formed in the high boiling materials can also be detected with this method of using a back-purge to remove the high boiling material from the column.

A high temperature gas chromatograph was constructed for use in conjunction with the alkyl-terphenyl analysis. The maximum temperature of operation of the instrument is limited at the present time to the column partitioning material. The following materials at 300° to 320°C give adequate resolution to terphenyls and their alkyl homologs:

(1) High vacuum silicone grease (2) Asphalt (3) Polyethylene (4) Irradiated Polyethylene (5) Apiezon L.

For the identification of the individual peaks the fractions were collected. Careful examination of such fractions for eventual contamination with traces of partitioning material is, however, required since it was observed that some fractions can be contaminated with partitioning liquid at temperatures as low as 280°C. Operation of the instrument at reduced pressure does not improve resolution but creates additional problems in gas flow control and fraction collection.

However, high temperature gas-liquid chromatograph has been to date the most feasible and successful method of separation and it is expected that application of capillary column as developed by Golay and ionization detectors will considerably improve its resolution and efficiency. Columns used to date and operating at 320°C column temperature have not been able to resolve polymeric materials from the irradiated alkyl-terphenyls, although these materials are known to be present and were separated by the countercurrent distribution methods.

Because of the small amounts of degradation or polymerization compounds present in the irradiated material a number of other micro methods had to be developed for the characterization of these fractions.

(d) Other Methods

Various other micro analytic methods presently developed are being used to characterize fractions of irradiated materials obtained from countercurrent distribution and gas chromatographic separations. Such methods include micro density, index of refraction and exact micro molecular weight methods; these are being at present used to characterize these fractions by the well known relationship of these properties to various structural characteristics of hydrocarbons. These data may yield a rather concise picture of the type of breakdown products present in irradiated intervals.

Infrared spectroscopy in the form of differntial analysis has been successfully applied to the characterization of the various fractions separated by GLC from the irradiated material, even in cases where fractions may have been contaminated with traces of partitioning material.

IV. DISCUSSION

1. General Remarks

Although the material and data gathered to date is still too inconclusive to allow the postulation of a more concise degradation mechanism and the establishment of a mode of energy transfer and dissipation, certain basic trends could be established which eventually may lend themselves to a quantitative formulation of a specific and well defined radiolytic breakdown mechanism of the alkyl polyphenyl and polyphenyl ether derivatives under investigation.

Values obtained to date from the irradiation of various alkyl aromatic and alkyl polyphenyl materials are presented in Tables I to V and shall be discussed briefly further below. For the sake of simplicity only those values considered of significance at this stage of the investigations have been presented in these tables.

The G values shown are the yields of the corresponding molecules or group of compounds as molecules per 100 ev of energy with $G_{sci.}$ (G scission) being molecules detected and/or identified with molecular weights less than the target material; the value G_{poly} (G-polymer) on the other hand represents molecules of greater molecular weight than the target material. The $-G_m$ value represents the number of target molecules disappearing per 100 ev of energy absorbed.

The following observations from the tables are particularly noted:

(1) The gasyields of the alkyl-aromatics are very much less, as expected, than the yields from the normal or cyclic aliphatics. In the alkyl-aromatics, hydrogen is the primary gasious yield component; forming about 90% of the gas in the alkyl benzenes and greater than 95% of the gas in the irradiated alkyl-polyaromatics. The other prime component in the gas phase was methane.

(2) The gas yield from all the alkyl-polyphenyls is relatively constant and very low, being generally in the region of 0.06. The only exception to the above is the yield from the 3-hepty-o-terphenyl which is 0.11. This value, may be significant in connection with structure-stability relationships.

(3) The irradiation of normal and cyclic aliphatic hydrocarbons shows a strong predominance of polymeric product formation compared to that of scission product formation. This indicates that the radicals formed by hydrogen scission from the molecule preferentially recombine with other radicals rather than the removed hydrogen. A strong indication that this is true can be seen in the detection of bicyclohexyl and related hydrocarbons in irradiated cyclohexane.

(4) The resonating structures of benzene markedly reduces the gas yield and the disappearance of parent material when compared to hexane and cyclohexane. The reduction in the amount of yield gas (hydrogen) may, however, not be a true indication as to the number of target molecules being affected during irradiation. Lowered hydrogen yields may be the direct result of hydrogen use in saturating or partially saturating decomposing aromatic rings. Trace quantities of biphenyl and bicyclohexyl have been identified in an irradiated benzene. The only source of hydrogen for the formation of the latter would be from hydrogen cleaved from a benzene molecule. The presence of biphenyl and bicyclohexyl also shows that formed radical combination is a preferred mode of radical stabilization.

A benzene insoluble material (trace quantity) has been isolated and partially characterized by melting point (slow sublimation above 250°C) and infrared spectroscopy as being a polyphenyl of greater molecular weight than terphenyl and consisting primarily of 1,2-aromatic substitution indicating that ortho polymerization must prevail.

(5) The irradiation of the alkyl benzenes (Table II) show an interesting set of data that might indicate a significance in side chain length. The $-G_m$ values for propyl and butyl benzenes are quite low and that of hexyl benzene is high. Biphenyl and bicyclohexyl have been identified in the yield products of the latter. This would suggest a possible cyclization reaction occurring when the alkyl chain is sufficiently long to permit strain free ring closure. Another possible mechanism accounting for the formation of the identified materials would be the complete scission of the alkyl chain with the formation of a phenyl radical which could combine with another (as indicated in 4, above) phenyl radical to yield biphenyl. The formed alkyl radical from the scission could yield cyclohexane with a resulting formation of bicyclohexyl as indicated also (3) above.

No higher molecular weight materials have as yet been detected

in the propyl and butyl benzene by GLPC methods.

(6) In the alkyl biphenyls, (Table III) degradation is of the order found in the alkyl terphenyl series. The $G_{(gas)}$ and $-G_m$ values of the 2 and 4 substituted alkyl biphenyls are not significantly different but may indicate positional dependence of radiolytic break-down. A higher molecular weight product has been detected by GLPC in the 2-heptyl biphenyl but is not yet characterized.

(7) The irradiation of alkyl substituted o - and m - terphenyls shows slight but distinct differences in their $G_{(gas)}$ and $-G_m$ values depending on the type of the parent isomeric terphenyl. This reflects in general the increase in radiation stability of the parent compounds from the angular o- terphenyl to the p - terphenyl compound. The ortho terphenyl derivatives is also the only terphenyl compound from which decomposition products could be resolved more definitely by a GLC - column operating at 320° C. This material has been tentatively identified by IR as being a partially hydrogenated alkyl-o-terphenyl in which the ring containing the alkyl side chain is subjected to partial hydrogenation.

(8) It could be shown that some of the degradation products of benzene, hexylbenzene and 3-heptyl-o-terphenyl are saturated or partially saturated forms of the target material or dimers of the target compound. If this mechanism should prevail in other types of polyphenyls, it is very possible that the high temperature GLPC (320°C) columns presently used are not resolving the formed products from the parent material. It is known that a polyethylene column operating at 320°C will not resolve a mixture of 4'-heptyl-m-terphenyl and its fully saturated analog 4'-heptyl-m-tercyclohexyl but will resolve alkyl terphenyls differing by CH_2 in the alkyl chain. For these reasons it is suspected that partially saturated target material is formed from gamma irradiation and is not being detected by present GLPC methods.

(9) Based on viscosity changes, the irradiated 4'-heptyl-m-terphenyl compound (Table V) must be assumed to undergo polymerization the degree of which increases viscosity directly in proportion to, the increased radiation dose. This appears to be of significance in that with $-G_m$ (disappearance of the parent compound) being pracitcally constant, the polymer formed must be resistant to further changes since the viscosity increase is a linear function of the total dose.

If a dimerization is assumed, the most likely product formed would be a dialkyl-hexaphenyl compound; this material would be very unlikely to traverse a GLPC column at 320°C. Counter-current distribution separation of the aforementioned compound after exposure to an overall dose of 4.4×10^8 r (Table V, Column 5) yielded a small amount of resinous material; by IR spectroscopy it could be determined that this material is by all probability a higher homologog of the parent material. This compound could not be detected by

GLPC. The molecular weight of this compound is being determined at the present time and should indicate the number of units in this material.

(10) Lower dose irradiation of 4'-heptyl-m-terphenyl in the order of 5×10^5 and 5×10^6 roentgens gave abnormally high $-G_m$ values (Table V column 1 and 2). These values cannot be explained at the present time but are reproducible data as far as high temperature GLPC analysis is concerned.

(11) It has also been observed that the 4'-propyl-m-terphenyl and the irradiated in air 4'-heptyl-m-terphenyl show increased values for the parent compound after irradiation. It is assumed that this is due to the formation of materials that are eluted with the parent compound in the GLPC analysis. The possible separation of this material by other methods is being investigated at the present time.

TABLE I

IRRADIATION DATA FROM MISCELLANEOUS COMPOUNDS

	Compound		
	Nexane	Cyclohexane	Benzene
Dose, erg/gr. x 10^{-10}	.532	.744	.887
Dose, (100 ev) x 10^{-22}	.083	.128	.18
$G_{(gas)}$	3.8	4.18	.0683
G_{H2}	2.73	4.14	.055
G_{CH4}	.23	.04	.01
$G_{(sci.)}$	.33	trace	ND*
$G_{(poly.)}$	.95 (a)	.14 (b)	(c)
$-G_m$	9.9	16	1.2

* None detected; $-G_m$ = number parent molecules disappearing per 100 e v energy adsorbed

(a) contains detected hydrocarbons up to C_{12}

(b) is primarily a bicyclohexyl type material

(c) trace amounts of polymeric material identified as biphenyl, bicyclohexyl and an insoluble material identified by infrared as A 1-2 disubstituted aromatic, probably an ortho polyphenyl

TABLE II

IRRADIATION DATE FROM ALKYL BENZENES

	Compound		
	Propylbenzene	Burylbenzene	Hexylbenzene
Dose, erg/g x 10^{-10}	.599	0.897	1.187
Dose (100 ev) x 10^{-22}	0.126	0.172	0.643
$G_{(gas)}$	0.262	0.207	0.685
G_{H_2}	0.238	0.162	0.250
G_{cH4}	.024	0.011	0.031
$G_{(sci.)}$	(a)	ND *	(b)
$G_{(poly)}$	ND	ND	(b)
$-G_m$	1.75	0.76	7.9

*ND None detected

(a) Hexane and benzene detected in trace amounts

(b) Biphenyl G = .05; bicyclohexyl 0 = .02

TABLE III

IRRADIATION DATA FROM ALKYL BIPHENYLS

	Compound		
	2 heptylbiphenyl	2 heptylbiphenyl	4 heptylbiphenyl
Dose, ergs/gr x 10^{-10}	0.985	4.11	3.71
Dose (100 ev) x 10^{-22}	.208	1.27	1.98
Viscosity change			
cs. at 100°F	.33	1.73	.67
cs. at 210°F	.09	.28	.14
$G_{(gas)}$	—	0.095	0.062
G_{H_2}	—	0.092	0.060
G_{CH_4}	—	0.001	0.001
$G_{(sci.)}$	ND*	ND	ND
$G_{(poly)}$	.32(a)	(b)	ND
$-G_m$	2.36 (1.67)(b)	0.709	0.314

* ND None detected

(a) This material does not traverse an Apiezon column at 220°C but does at 300° C. The $-G_m$ has a different value under these conditions.

(b) 1.33% of the irradiated material is polymeric as determined on a polyethylene column.

TABLE IV

IRRADIATION DATA FROM MISCELLANEOUS ALKYL-TERPHENYLS

	Compound				
	3-heptyl-o-terphenyl	3 heptyl-m-terphenyl	4'propy-m-terphenyl	4'nonyl-m-terphenyl	4'heptyl-m-terphenyl*
Dose, ergs/gr x 10^{-10}	0.929	1.28	1.088	0.870	.964
Dose, (100 ev)x 10^{-22}	0.517	0.35	0.301	0.245	0.59
Viscosity Change					
cs. at 100°F	14.663	14.969	8.28	11.43	2.78
cs. at 210°F	0.437	0.639	.10	0.22	0.069
$G_{(gas)}$	0.112	0.076	.0195	0.049	0.084
G_{H_2}	0.107	0.074	00.0186	0.045	0.081
G_{CH_4}	0.002	0.001	0.003	0.002	0.002
$G_{(sci.)}$	ND	ND	ND	ND	ND
$G_{(poly)}$	(a)	—	ND	ND	ND
$-G_m$	1.68(b)	—	-0.52(b)	0.73(b)	3.54(c)

ND None detected

(a) 11.2% of the irradiated material is of higher molecular weight and boiling point than the parent compound. IR indicates these compounds (two species) may be partially hydrogenated parent compound.

(b) Determined from irradiated polyethylene column

(c) Determined from silicone grease column

* This material is different from that reported in Table V. This contains about 0.5% m-terphenyl.

TABLE V

DATA FROM THE IRRADIATION OF 4'-HEPTYL-M-TERPHENYL TO VARIOUS DOSE

	Levels					
	1	2	3	4	5	6*
Dose, ergs/gr x 10^{-10}	.0052	0.050	0.495	1.604	3.85	0.724
Dose, (100 ev)x 10^{-22}	0.0012	0.012	0.131	0.565	0.325	0.162
Density Change	0	0.0012	0.0019	0.0022	0.0032	0.0016
Viscosity Change						
cs. at 100°F	-1.677	3.014	4.898	9.042	18.334	2.261
cs. at 210°F	-0.151	0.058	0.121	0.298	0.724	0
$G_{(gas)}$	0.073	0.043	0.058	0.076	—	0.045
G_{H_2}	0.073	0.045	0.053	0.074	—	0.041
G_{CH_4}	ND	ND	0.003	0.002	—	0.002
$G_{(sci.)}$	ND	ND	ND	ND	ND	ND
$G_{(poly)}$	ND	ND	ND	ND	ND	ND
$-G_m$	(218)	(592)	1.02	0.78	1.18	0.7

ND None detected

* Irradiated in presence of air

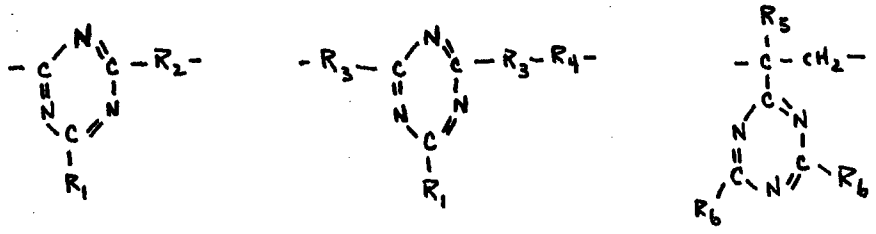
Materials Laboratory Polymer Research

Dr. G. Ehlers

In addition to the contractual research program of the Polymer Section, some internal work has been done in the field of thermally stable resins. One of these studies is concerned with the synthesis of organic polymers comprised of various substituted triazine nuclei.

The purpose of this investigation is the synthesis of three principal types of polymers in which the triazine nucleus is contained within the repeating unit. This may be represented by the following general formulae:

Figure 1



where R_1 is Alkyl, aryl, or perfluoroalkyl

R_2 is $-NR_7-$ (R_7 is H, alkyl, aryl), $-R_7N-\overset{\overset{Z}{\|}}{C}-NR_7-$ $(Z = O, S)$

R_3 is ; ; $-(CH_2)_n-$; $-\underset{\underset{R_7}{|}}{N}-(CH_2)_n-$ $(n \geq 1)$

R_4 is $-\overset{\overset{O}{\|}}{C}-NH-CH_2-$; $-\overset{\overset{O}{\|}}{C}-O-CH_2-$

R_5 is H, CN, C-OET, Alkyl, aryl, triazinyl

R_6 is OH, aryl, alkyl, alkoxyl, phenoxyl

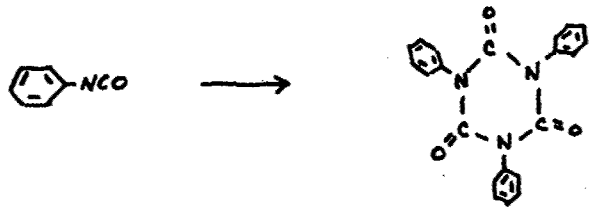
The work to date has been mainly concerned with the synthesis of the corresponding monomers. Cyanuric Chloride has been used as the starting material in almost every case.

These polymers, especially those in which the repeating unit is that

represented by (A) and (B) are expected to have good thermal characteristics because they satisfy our present concepts regarding thermal stability. The resonance energy of the cyanuric nucleus has been reported as 82.5 kcals/mole as compared to 39 kcals/mole for the benzene nucleus. It is generally implied that chemical systems possessing a high resonance energy usually exhibit good thermal stability. The stability of the linkages, as well as the total resonance energy of the repeating unit, is generally enhanced if the linkages themselves can take part in the resonance. This is the case in most of the groups mentioned above. Polymers in which the repeating unit is represented by (A) have been synthesized. Although these polymers exhibit good thermal stability as expected, continued research is necessary in order to improve the mechanical properties which are rather poor. The synthesis of polymers in which the repeating unit is represented by (C) will provide valuable comparative information on the effect(s) of various substituted triazine nuclei on the polymer properties.

Additional work on polymers containing the triazine nucleus is based on the fact that isocyanates, more specifically phenylisocyanates give isocyanurates upon treatment with the proper catalysts (Fig. 2). This offers a possible synthesis of polymers from diisocyanates, which contain

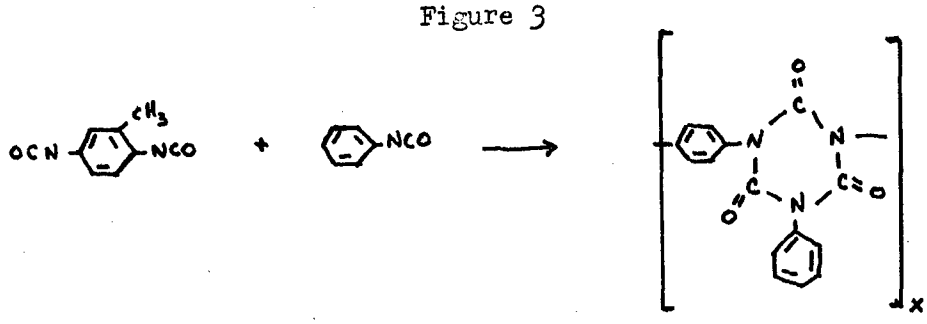
Figure 2



linked triazine rings. Of the known catalysts, and some others, which were tried, pyridine, with epichlorohydrin as a solvent, proved to be the most effective for the cyclization at room temperature. Alkaline catalysts, especially sodium methylate, form the same product at temperatures of approximately 80°C. If, however, pyridine alone, or pyridine and epichlorohydrin, both in catalytic amounts, were applied, another compound formed which proved to be carbanilide, probably due to the presence of some water. The epichlorohydrin was never found to react with the isocyanate.

Toluene -2,4 diisocyanate was used to synthesize polymers following the approach outlined above. With both sodium methylate and epichlorohydrin-pyridine as catalysts brittle resins were obtained. They were insoluble and non-melting and appeared to be crosslinked systems of relatively low molecular weights which still contained free isocyanate groups. In an attempt to obtain linear polymers, phenylisocyanate was added in hopes of incorporating it into the molecular as shown in Figure 3.

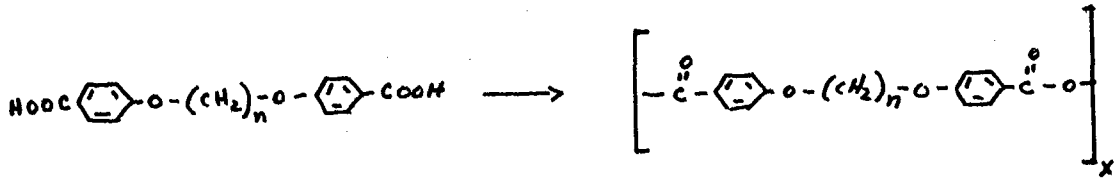
Figure 3



The resulting resin was still brittle, insoluble and non-melting, however, analysis strongly indicated that the suggested structure had been obtained. The fact that the material did not even partially melt at the melting temperature of triphenylisocyanurate indicated that a co-polymer and not a mixture of both cyclization products had been obtained. This information might be important for future trials with diisocyanates of a more flexible structure which then might result in more promising polymers.

The synthesis of fiber-forming and hydrolytically stable poly-anhydrides by Conix (Figure 4) prompted further investigation in this field.

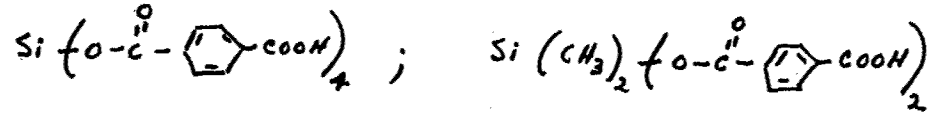
Figure 4



Attempts were made to obtain polymeric anhydrides by treating maleic, pyromellitic and butanetetracarboxylic acids with acetic anhydride or acetyl chloride. However, even with more severe conditions than are normally used for anhydride synthesis, no products other than the monomeric anhydrides were obtained. Terephthalic acid was then selected as a starting material for a potentially thermally stable polyanhydride. After trying several methods, finally the treatment of an equivelant mixture of terephthalic acid and terephthaloyl chloride, in toluene with pyridine present, gave a solid reaction product. According to its melting and physical behavior, this material appeared to be a well-defined, possibly low molecular weight, polyanhydride of terephthalic acid.

Attempts to combine terephthalic acid with aliphatic dicarboxylic acids to yield polyanhydrides with a higher degree of flexibility, gave powdery, ill-defined products. The reaction of terephthalic acid with chlorosilanes, in the presence of pyridine, resulting in monomeric reaction products rather than a polyanhydride from terephthalic and silicic acids (Figure 5).

Figure 5

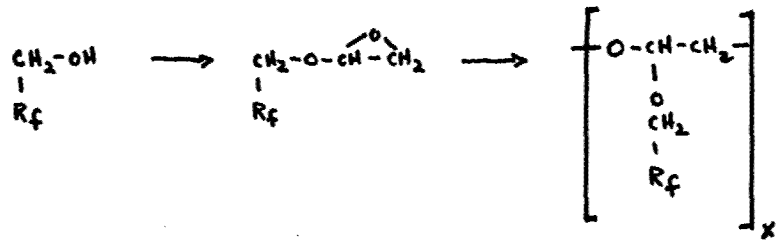


With phosphorus oxychloride, the terephthalic anhydride was formed as well as an additional compound of $POCl_3$ and pyridine.

From Conix' work, the work reported above, and other references, it appears that the dicarboxylic acids used as starting materials should be mainly aromatic. In addition, the diacids should have a certain chain length and flexibility in order to give polyanhydrides of hydrolytic stability, thermal stability and good mechanical properties. However, if higher molecular weight diacids are used, the effect of the anhydride group should be significantly reduced. Therefore, it appears doubtful if this approach will give any materials with new and different properties.

At the present time, some studies are underway on fluorinated polyethers. Fluorinated mono-and dialcohol are epoxidized by reaction with epichlorohydrin and the resulting mono-and di-glycidylethers are polymerized with the aid of catalysts (Figure 6). Structures with $(-O-CH(Rf)-CH_2)$ as the repeating unit would be expected

Figure 6



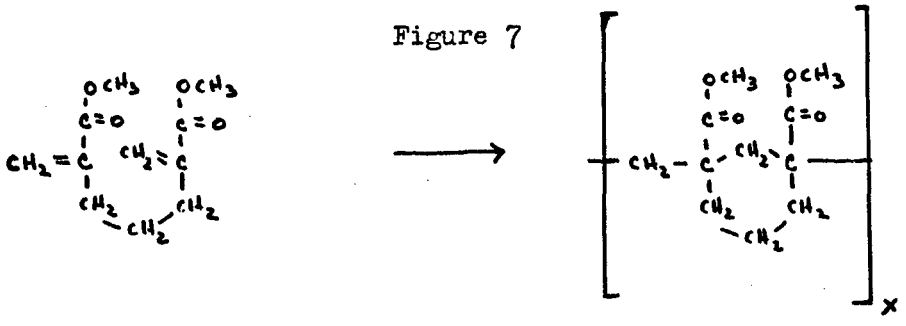
with fluoroalkyl groups (R_f) either as side groups or crosslinkages. The use of epoxy compounds containing carbon-carbon double-bonds would allow the curing of the above linear structures by conventional means. These experiments will also be extended to new derivatives of polyepichlorohydrin and polyepibromohydrin.

The formation of macromolecular having cyclic recurring units in the backbone of the polymer chains will be the subject of two other speakers at this conference. These are Professor G. B. Butler of the University of Florida, who has been concerned with polymerization of the diallyl ammonium halides, acrylic anhydride, and other monomers, and Professor C. S. Marvel of the University of Illinois who has been investigating the polymerization of α,α'-dimethylene pimelic and α,α'-dimethylene adipic acids, the methyl and ethyl esters and amides of

these acids, 2,6-dicyano-1,6-heptadiene, 2,6-diphenyl-1,6-heptadiene, and other monomers. Professor Butler has proposed a mechanism (involving an inter-intra-molecular propagation reaction) for the polymerization of these monomer types to give largely linear polymers, rather than the highly crosslinked structures usually resulting from the polymerization of divinyl compounds.

Results from the preliminary evaluation of some of these polymers indicate an increase in thermal stability over that of conventional plastic materials. The polymers from free radical polymerization of α,α'dimethylene pimelic and α,α'dimethylene adipic acids and their methyl and ethyl esters have been generally characterized as white powders, which when cast from solution form hard, transparent films with softening points greater than 100°C. A need exists in the Air Force for transparent plastics having serviceability at these and higher temperatures. In order to more fully characterize the pimelate polymers as to overall performance, a quantity of poly (dimethyl-α,α'dimethylene pimelate) was prepared and an evaluation of this material was made in the Materials Laboratory, WADC. The structure of the monomer and the resulting polymer are shown in Figure 7.

Figure 7



Details on the preparation of this polymer are as follows: bulk polymerization; 0.1% benzoyl peroxide; container-a mold of dimensions 6" x 2½" x ¼"; reaction time, 3 days at 50°C, followed by 8 hours at 100°C. The polymer was obtained as a sheet having a slightly yellow color. Table I lists the results of the evaluation carried out on this material compared with the specifications of poly (methylmethacrylate). As may be noted, the physical properties of the pimelate polymer show, in most cases, marginal improvements over the methacrylate polymer. However, these marginal improvements on the first trial are encouraging. The low values for the % luminous transmittance and high value of haze are due primarily to minor processing difficulties and offer no serious handicap to the use of this polymer. It is felt that significant improvements in these properties can be made by suitable modifications in the polymerization reaction. For example, it would be expected that both the proportion of crosslinked units and the molecular weight will exert a significant effect on the physical properties of the polymer. With more information on the nature of the polymerization reaction it should be possible to vary both of these quantities. In addition, copolymerization of the pimelate monomers with other vinyl monomers might be expected to alter the physical properties. To provide the necessary background for such modifications a study of the polymerization of dimethyl-α,α'-dimethylene

pimelate has been started. This study is designed to yield needed information on the variation in polymer structure with polymerization variables such as amount and type of initiator, monomer concentration, temperature, etc. The first part will deal with the bulk and solution polymerization kinetics. Other parts will deal with emulsion polymerization and copolymerization. Preliminary results on the solution reactions indicate a faster overall polymerization reactions for this monomer than is obtained with styrene on the esters of acrylic or methacrylic acid.

Table I

Physical Properties of Poly (Dimethyl-α', α'Dimethylene Pimelate) and Poly (Methyl Methacrylate).

	Pimelate	Methacrylate
Color	light yellow	colorless
Heat Distortion Temp. (°C)	114	110
Luminous Transmittance (%)	80.5	90
Haze (%)	13.4	3.0
Flexural Strength (psi)	11,500	16,000
Notched	8,750	11,000
Modulus ($x10^{-5}$)	3.86	4.5

The poly(methylmethacrylate) used for comparison is probably the best available (ie., MIL-P-8184A) and contains some crosslinked units.

MATERIALS LABORATORY FLUIDS RESEARCH

Stanley I. Goldberg
Wright Air Development Center

Research efforts of the Materials Laboratory in the area of thermally stable fluids are primarily concerned with investigations of various organo-metallic systems. Studies in certain aspects of organo-silicon chemistry are being performed by Dr. Helen Lloyd and Mr. George Baum. Capt. Fred Ford and Mr. George Moore are investigating the properties of compounds consisting of various bonding combinations of Group IV and/or Group V elements, while the writer is concerned with materials derived from ferrocene. In addition Dr. Lloyd is also studying reactions of some perfluorinated materials.

Since a detailed account of all these research activities would lead to a presentation too lengthy for the present purpose; and since a brief description would be inadequate, this discussion will be limited to results obtained from our work in the field of ferrocene chemistry. A further limitation will consist in considering the ramifications of only one reaction sequence of ferrocene which was studied in the Materials Laboratory during the past eighteen months.

This reaction sequence (Figure 1) - lithiation of ferrocene, followed by treatment of the mixture of lithioferrocenes with a trialkylhalosilane - has not only given rise to an interesting fluid, but has led to a number of contributions to the chemistry of ferrocene as well.

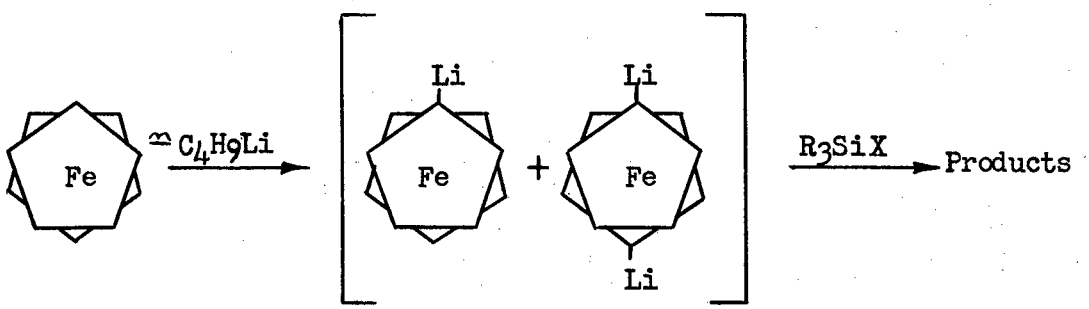
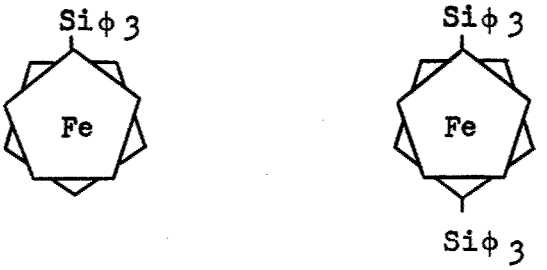


Figure 1

The two-step sequence, shown in Figure 1, was first reported by Benkeser et al.[1] in 1954. These authors obtained, by treatment of the mixture of lithioferrocenes with triphenylchlorosilane, two silylferrocenes -

triphenylsilylferrocene (I) and a derivative which contained two triphenylsilyl groups, to which they assigned the structure, 1,1'-bis(triphenylsilyl)-ferrocene (II).



I II

Designation of the latter as a heteroannular-substituted product was primarily based upon the fact that carbonation of the lithioferrocenes produced, in addition to ferrocenecarboxylic acid, a dicarboxylic acid which possessed properties identical to those reported for a dicarboxylic acid derivative of ferrocene by Woodward and Rosenblum.[2] These latter workers had assigned the heteroannular structure to their diacid because it was obtained from hypoiodite oxidation of diacetylferrocene-A, which structure they had deduced as 1,1'diacetylferrocene.

These structural postulations were subsequently strengthened by results reported by Nesmeyanov et al.[3] The Russian workers were able to show, by means of destructive hydrogenation followed by characterization of the cyclopentane derivatives obtained, the heteroannular orientation of ferrocenedicarboxylic acid and diacetylferrocene. However, in none of these investigations was any mention made of direct comparisons of the compounds obtained in each laboratory. Criteria for the identifications were limited to literature-reported physical constants.

Confirmation of these structural postulates was obtained from the results of investigations carried out in the Materials Laboratory. In this work comparisons of derivatives were made directly since all compounds used were prepared in this Laboratory.

The reaction sequence shown in Figure 1 was used to prepare two different silylferrocene which were both disubstituted. In each case the identical compound was obtained by means of the "sandwiching reaction" of the correspondingly substituted cyclopentadiene. This work, therefore, afforded rigorous proof of structure for the disubstituted silylferrocenes obtained via lithiation of ferrocene. In addition, it was found that disodioferrocene, prepared from treatment of ferrocene with phenylsodium, also gave rise to the heteroannularly oriented product. These reactions are summarized in Figure 2.

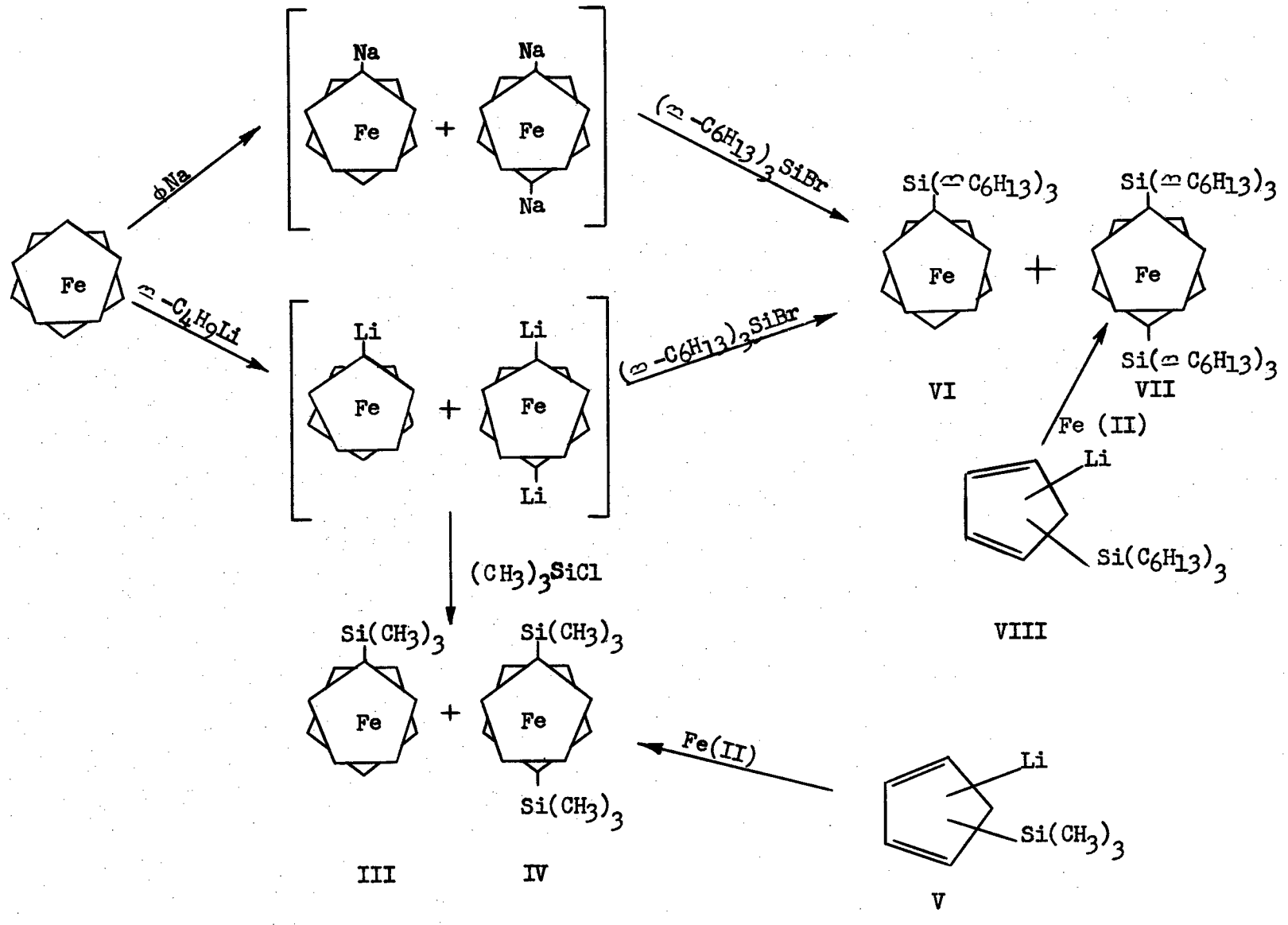

Fe
ΦNa
Na
Fe
Na
+
Fe
Na
(n-C6H13)3SiBr
Si(n-C6H13)3
Fe
+
Fe
Si(n-C6H13)3
VI
Si(n-C6H13)3
VII
n-C4H9Li
Li
Fe
Li
+
Fe
Li
(n-C6H13)3SiBr
Fe (II)
Li
Si(C6H13)3
VIII
(CH3)3SiCl
Si(CH3)3
Fe
Si(CH3)3
+
Fe
Si(CH3)3
III
IV
Fe(II)
Li
Si(CH3)3
V

Figure 2

Treatment of trimethylsilylcyclopentadienyllithium (V) with iron (II) chloride by Martin Vogel gave rise to 1,1'-bis(trimethylsilyl)-ferrocene (IV), previously obtained by Rausch, Vogel and Rosenberg[4] in this Laboratory via the lithioferrocenes. Reaction of tri-n-hexylbromosilane with the lithiated ferrocenes was found by Dr. Dana Mayo to produce tri-n-hexylsilylferrocene (VI) and a bis(tri-n-hexylsilyl)-ferrocene. The latter was shown by the writer to be 1,1'-bis(tri-n-hexylsilyl)-ferrocene (VII) when treatment of tri-n-hexylsilylcyclopentadienyllithium (VIII) with iron (II) chloride produced the identical compound. In addition, the disubstituted silylferrocene obtained from reaction of the sodioferrocenes with tri-n-hexylbromosilane was shown by the writer to be identical to VII.

Thus, unequivocal structure assignments of IV and VII were made, and direct, non-degradative-type evidence for the steric course of the two metalation reactions of ferrocene was obtained.

During distillation of the crude reaction product produced from treatment of a mixture of lithioferrocenes with tri-n-hexylbromosilane, Dr. Mayo isolated a very small amount of an orange-colored crystalline material. Additional quantities of this material were obtained when the reaction was repeated. In a collaborative effort, Dr. Mayo and the writer undertook the structural elucidation of this interesting compound.

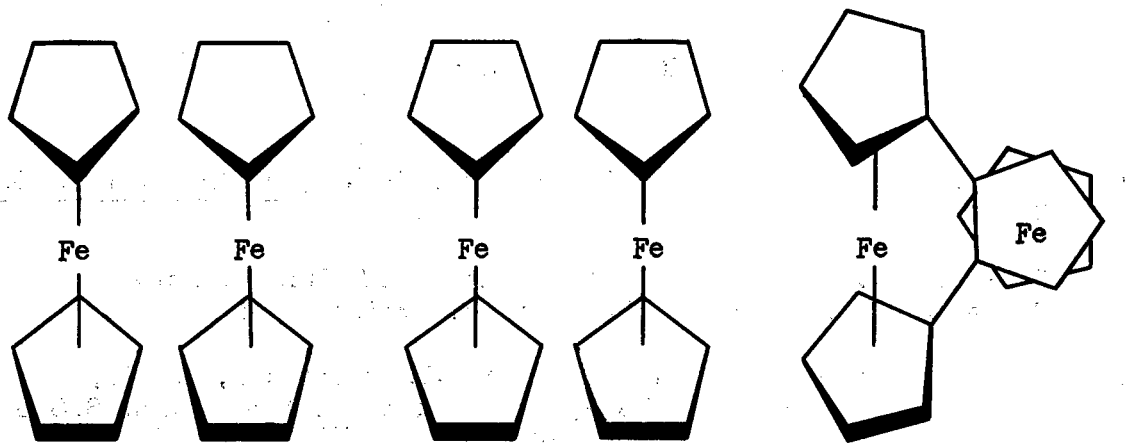
The product was carefully chromatographed on alumina, and it was further purified by repeated recrystallizations from benzene-petroleum ether. The pure compound melted at 227.5-229.0°C. (uncorr.) when observed in a carefully evacuated capillary tube. Attempts to melt it in the presence of air resulted in its decomposition at about 200°C.

Although the material gave rise to an ultra-violet spectrum which was quite different from that of ferrocene, its infrared spectrum possessed striking similarities to the corresponding spectrum of ferrocene, particularly in the C-H stretching region. Only one band at 3.26 μ was present, and only one band at 3.25μ is found in that region of the ferrocene spectrum. This was taken to mean that only C-H bonds of the ferrocene-type were present in the compound. Combustion data were in agreement with this view since an empirical formula close to a multiple of $C_{10}H_{9.3}Fe$ was indicated. Molecular weight values, carefully determined in camphor and in the absence of air, were 385 and 389. Similar determinations in naphthalene confirmed these values.

All of the evidence at this stage of the work, therefore, was only consistent with the formulation of a molecule which contained two ferrocene nuclei bonded to each other in some manner.

Since the mechanism for the formation of the compound was obscure, it was necessary to consider the three structures shown in Figure 3 as being possible within the limitations established by the analytical data.

The presence of absorption at 9 and 10 microns in the infrared spectrum of the material allowed for the rejection of structure X (9-10 Rule[2]). In spite of the fact that the calculated hydrogen content of structure IX was



IX X XI

Figure 3

in better agreement than that of structure XI with the measured value, it was not considered satisfactory to eliminate structure XI on this basis alone.

Conclusive evidence which allowed for an unambiguous structure assignment was obtained by means of a quantitative treatment of the 9-10 Rule.

In order to use this technique, it was first necessary to prove the feasibility of a quantitative relationship for the 9-10 Rule on an intermolecular basis. This was accomplished with the use of fourteen known ferrocene derivatives. It was found that, within the proper concentration range, a linear relationship exists between the intensity of the 9- and/or the 10-band and the number of unsubstituted cyclopentadienyl rings present.

Application of this technique to the unknown ferrocene derivative clearly showed the compound to possess two unsubstituted cyclopentadienyl rings and, therefore, established its structure as that of IX.

This compound, structure IX, for which the name, diferrocenyl, is suggested, represents the first and simplest example of direct bonding between ferrocene nuclei.

The quantitative applicability of the 9-10 Rule - demonstrated in this work - is believed to hold the promise of becoming a valuable guide in the structural elucidation of multi-nuclear ferrocene derivatives.

REFERENCES

1. Benkeser, R. A., Goggin, D. and Schroll, G., J. Am. Chem. Soc., 76, 4025(1954).

2. Woodward, R. B. and Rosenblum, M. in M. Rosenblum's "Doctoral Dissertation," Harvard University, 1953.

3. Nesmeyanov, A. N., Perevalova, E. G., Golovnya, R. V., Nikitina, T. V. and Simukova, N. A., Izvesta Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 6, 739(1956).

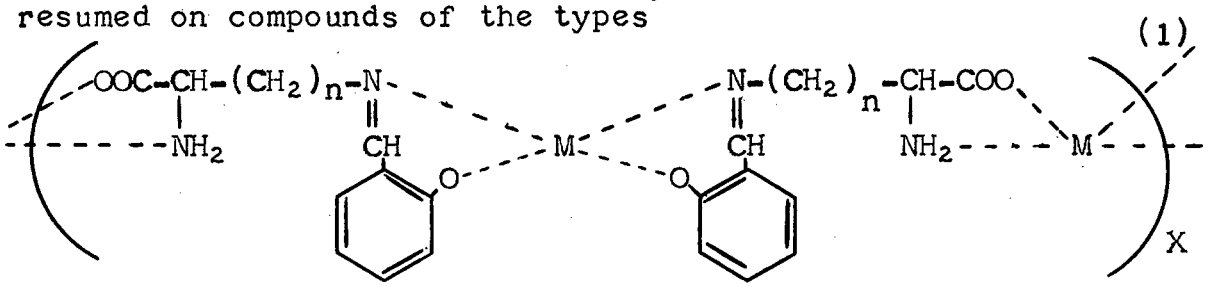
4. Rausch, M., Vogel, M. and Rosenberg, H., J. Org. Chem., 900(1957).

COORDINATION POLYMERS

John C. Bailar, Jr.

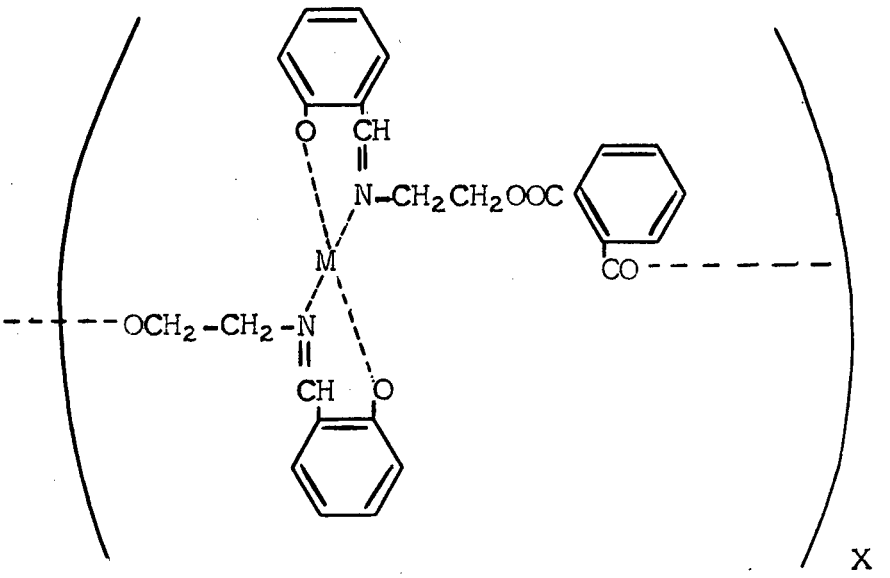
University of Illinois

Recent work in our laboratories has been devoted to the study of coordination polymers from bis-8-hydroxyquinolines, bis-aminophenols, bis-diphenols, and bis-salicylic acids. Within the last few weeks, in the hope of learning more about the mechanism of coordination polymerization, work has been resumed on compounds of the types



(1)

and



(2)

The various projects will be discussed in that order.

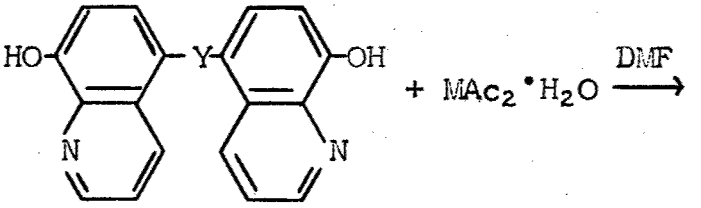
I. COMPLEXES OF bis-8-HYDROXYQUINOLINES (with Dr. M. L. Judd).

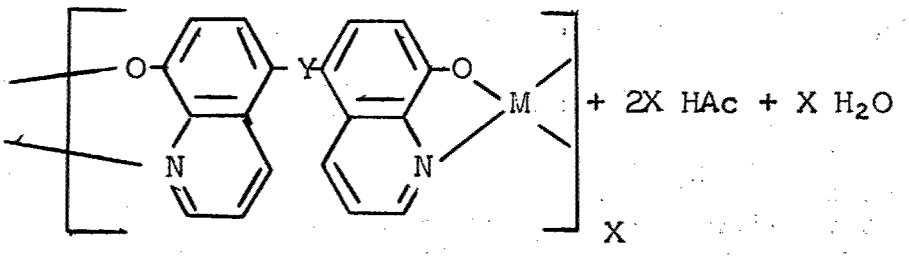
As a class, the bis-(8-hydroxyquinolines) are ideally suited to the preparation of inorganic coordination polymers. The ligand is thermally stable, as shown by the observation that all the bis-(8-hydroxyquinolines) investigated were stable at their melting points in the vicinity of 300°C. The delocalization of the bonding electrons in the molecule should reduce dipole-dipole attractions among the various polymer chains, thereby enhancing the possibilities of obtaining a plastic material. Evidence that these compounds

will form stable donor atom--metal ion bonds is provided by the known stability of complexes of 8-hydroxyquinoline.

One of the most important attributes of this class of compounds is that they are stable at their melting points. The biggest single drawback of inorganic polymers prepared in this study and in similar studies is their physical form; that is, they are powders. This is probably not related to the structure of the polymer but rather to the method of preparation employed. When it is desired to polymerize a compound which decomposes before it melts, it is necessary to carry out the reaction in a solvent. As the one property held in common by all coordination polymers appears to be their insolubility, the polymer grows until it becomes insoluble, and then precipitates from the solution, invariably in the form of a fine powder. However, when the ligand to be polymerized by treatment with metal ions is stable at its melting point, the reaction may be carried out by melt polymerization. This method overcomes to some extent the problem of insolubility and may well lead to materials which are elastomers rather than powders. Of the ligands investigated in this study, only the bis-(8-hydroxyquinolines) are stable at their melting points.

The general reaction which has been used thus far for the formation of these polymers is

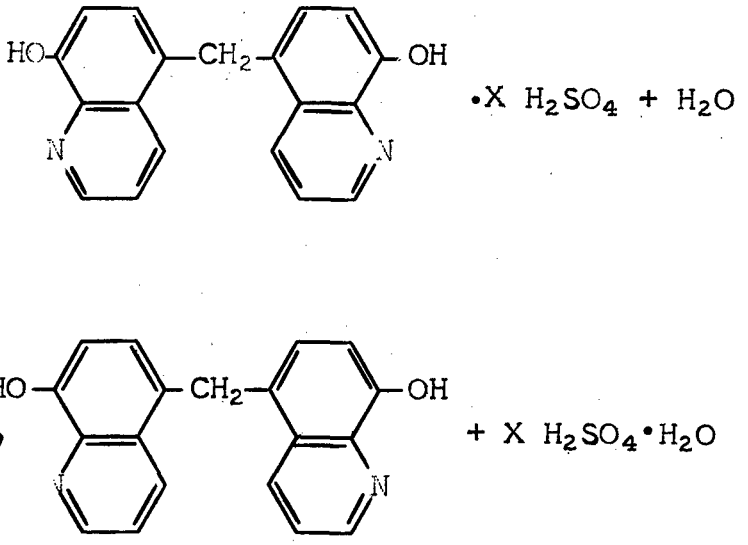




where Y stands for $-CH_2-$, $-SO_2-$ or simply a bond connecting the two rings, M for copper(II) or zinc(II) and DMF for dimethylformamide. The individual systems will be discussed separately.

A. bis-(8-Hydroxy-5-quinolyl)-methane

There are several descriptions of this compound in the literature (3). However, these reports are inconsistent in their description of the material and provide only meager experimental details. The article by Schuller appeared to provide the most promising method for preparing the compound; however, two attempts to obtain the product as described by Schuller were unsuccessful. Failure to reproduce Schuller's work may perhaps be attributed to the fact that his description of the process does not indicate the amounts of chemicals, the temperatures used, or the time required for the reaction. The compound was eventually obtained by a variation of the method. The method consists of dropping formaldehyde into a cold solution of 8-hydroxyquinoline dissolved in sulfuric acid and isolating the product as a hydrogen sulfate salt of indefinite composition by pouring the reaction mixture into a large quantity of water. Extensive fractional crystallization of this hydrogen sulfate salt failed to yield a product of definite composition. It was noticed that whenever a sample was dissolved in water, a small amount of white material remained undissolved. This white material was identified by analysis as bis-(8-hydroxy-5-quinolyl)-methane. This suggests that an equilibrium exists in the system:



Dissolving the salt in water causes the equilibrium to shift to the right, and accounts for the precipitation of the bis-(8-hydroxy-5-quinolyl)-methane. This mechanism also explains why fractional crystallization failed to produce a clearly defined hydrogen sulfate salt of this base. Neutralization of the salt yielded the desired bis-(8-hydroxyquinoline). As it is possible for the reaction between 8-hydroxyquinoline and formaldehyde to link together more than two

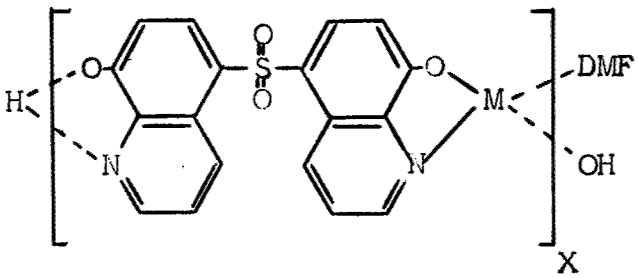
8-hydroxyquinoline molecules, it was necessary to confirm the identity of the product by molecular weight measurements. This was done by measuring the boiling point elevation of nitrobenzene. The experimental molecular weights of 307 and 308 agree well with the value of 302 calculated for bis-(8-hydroxy-5-quinolyl)-methane.

The copper and zinc complexes of this compound were prepared by mixing solutions of the ligand in dimethylformamide with solutions of the metal acetates in the same solvent. The copper complex is a brown-yellow powder and the zinc compound is a green-yellow powder. Elemental analysis gave no indication of the nature of the terminal groups.

B. bis-(8-Hydroxy-5-quinolyl)-sulfone

This compound was prepared in 54 per cent yield by means of a Skraup reaction on bis-(3-amino-4-hydroxyphenyl)-sulfone. The commercially available bis-(4-hydroxyphenyl)-sulfone was nitrated by the method of McLean (4) to give bis-(3-nitro-4-hydroxyphenyl)-sulfone. This material was reduced by treatment with sodium dithionite to yield the desired bis-(3-amino-4-hydroxyphenyl)-sulfone. The copper and zinc complexes of this material were prepared in the same way as those of bis-(8-hydroxy-5-quinolyl)-methane. The copper complex is a green-yellow powder while the zinc complex is a bright yellow powder.

The analysis of these compounds indicates that the polymers are of the form



DMF = dimethylformamide

where the average value of X is three. This assumption is supported by the results obtained with the polymers of bis-(3-amino-4-hydroxyphenyl)-sulfone.

C. bis-(8-Hydroxy-5-quinolyl)

This material was produced in 48 per cent yield by means of a Skraup reaction on bis-(3-amino-4-hydroxyphenyl), which was prepared from bis-(4-hydroxyphenyl) by nitration, followed by reduction of the dinitro compound. bis-(4-hydroxyphenyl) was obtained by the diazotization and subsequent

hydrolysis of benzidine. The copper and zinc complexes of this material were prepared in the same way as those of the other bis-(8-hydroxyquinolines). The copper complex is a brown powder while the zinc complex is a drab-yellow powder. The elemental analysis gave no indication of the nature of the terminal groups.

D. 2,2-bis-(8-Hydroxy-5-quinolyl)-propane

Several attempts were made to prepare this material by means of a Skraup reaction on 2,2-bis-(3-amino-4-hydroxyphenyl)-propane. This was prepared from 2,2-bis-(4-hydroxyphenyl)-propane which is sold under the trade name of Bisphenol-A. This was nitrated to give 2,2-bis-(3-nitro-4-hydroxyphenyl)-propane, which was then dissolved in warm aqueous ammonia and reduced to the amine by the addition of solid sodium dithionite. Although there is some evidence that the Skraup reaction proceeded as expected, efforts to isolate the desired product were unsuccessful.

E. bis-(8-Hydroxy-5-quinolyl)-sulfide

Airon and Wagle (5) report that treatment of 8-hydroxy-quinoline with sulfur monochloride gives a small yield of bis-(8-hydroxy-5-quinolyl)-sulfide along with chlorinated 8-hydroxyquinolines. Efforts to repeat this work were unsuccessful.

F. Thermal Stability Studies of bis-(8-Hydroxyquinoline Polymers

The six polymers discussed above were heated in a stream of nitrogen in the thermogravimetric balance. The decomposition temperatures of these polymers are shown in Table I. The decomposition temperatures of the copper and zinc complexes of 8-hydroxyquinoline are included for the purpose of comparison.

TABLE I

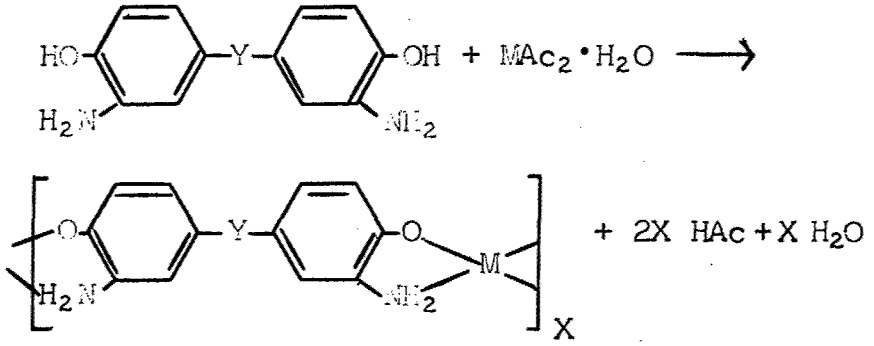
DECOMPOSITION TEMPERATURES OF METAL-bis-(8-HYDROXYQUINOLINE) POLYMERS AND METAL-8-HYDROXYQUINOLINE COMPLEXES

Metal	Ligand	Decomposition Temperature
Copper(II)	bis-(8-Hydroxy-5-quinolyl)-methane	240°C.
"	bis-(8-Hydroxy-5-quinolyl)-sulfone	280°C.
"	bis-(8-Hydroxy-5-quinolyl)	240°C.
"	8-Hydroxyquinoline	300°C.
Zinc(II)	bis-(8-Hydroxy-5-quinolyl)-methane	240°C.
"	bis-(8-Hydroxy-5-quinolyl)-sulfone	320°C.
"	bis-(8-Hydroxy-5-quinolyl)	300°C.
"	8-Hydroxyquinoline	300°C.

As a class, these compounds are more stable to heat than any of the others investigated in this study. This may be attributed to the delocalized bonding of the quinoline structure and the strong coordination ability of the 8-hydroxyquinoline group. In two cases it is seen that the zinc polymers are more stable than the corresponding copper polymers. This is perhaps due to the fact that zinc has a fixed valence of two, while copper can exhibit a valency of either one or two. This variable valency on the part of copper could possibly lead to the catalytic oxidation of the material in which it is included. The greater stability of those polymers containing the sulfone linkage indicates that this group has a desirable inductive effect.

II. COMPLEXES OF bis-AMINOPHENOLS (with Dr. M. L. Judd)

The formulas of the bis-(o-aminophenols) indicate that they should be capable of reacting with divalent, four coordinate metals to yield linear polymers. Several of these potential polymer forming reactions were undertaken with what appears to be some degree of success. The reaction which leads to the formation of polymers is



where Y represents $CH_3-\dot{C}-CH_3$, $-SO_2-$ or simply a bond connecting the two phenyl groups.

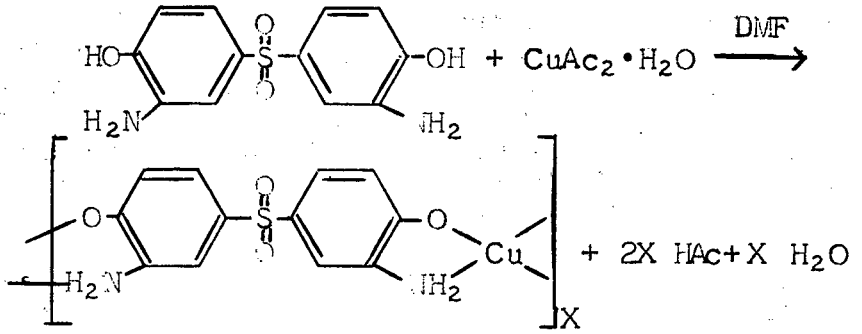
As a class, the metal complexes of these ligands are extremely insoluble, drab colored powders. The complexes are easily destroyed by both acids and bases.

A. 2,2-bis-(3-Amino-4-hydroxyphenyl)-propane

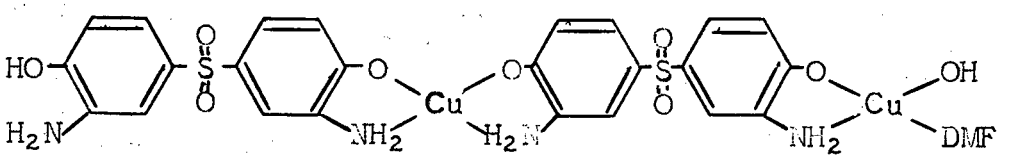
The copper complex of this ligand was obtained as a fine gray precipitate by the reaction of the aminophenol dissolved in methanol with a solution of copper acetate monohydrate in the same solvent. A polymer of a high degree of polymerization is indicated by the analysis, which gives no indication of end groups. In short polymer chains, the end groups are significant and show up in the elemental analysis.

B. bis-(3-Amino-4-hydroxyphenyl)-sulfone

The copper(II) complex of this material was prepared in two ways. The first consisted of the simple mixing of dimethylformamide solutions of the aminophenol and copper acetate monohydrate. Analysis of the gray material which precipitated from this reaction did not correspond to that formulated for an infinite polymer which would result from the reaction.



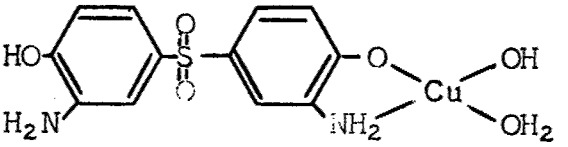
Thinking that possibly the rapidly forming precipitate had occluded impurities in its lattice and that these caused the poor analysis, the reactants were mixed by slow diffusion in dimethylformamide. The material prepared in this manner was shown by analysis to be identical to that prepared by simple mixing. This consistency of results indicates the existence of a stoichiometric compound. A structure agreeing with the analysis found is as follows:



DMF = Dimethylformamide

This preparation was repeated, allowing aqueous solutions of copper acetate and the sodium salt of the aminophenol to react. It was hoped that this method of preparation would yield the same type of structure as above but with a water molecule replacing the DMF.

The analysis of the product obtained agrees most closely with the nonpolymeric structure



It is probable that the decreased chain length is due to the decreased solubility of the copper-aminophenol complex in water.

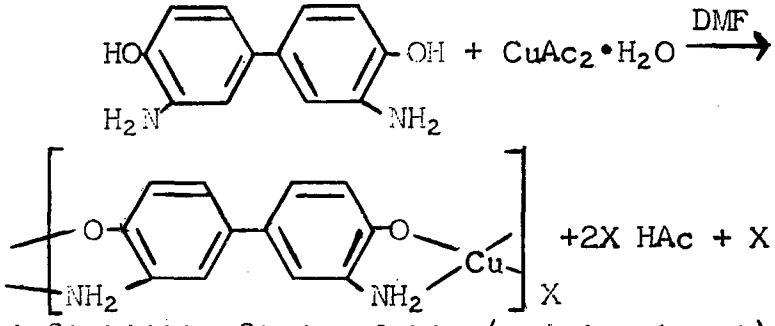
The proposal that a dimethylformamide molecule occupies one of the coordination sites on the terminal copper atom is a purely speculative one based only on elemental analysis. Yet it is to be expected that some group would occupy this coordination position,as copper has a strong tendency to fulfill its coordination number of four. In all probability the other aminophenol-metal ion coordination polymers have a similar terminal structure but due to their greater chain length the presence of these groups is not detected by elemental analysis. It is interesting to note that in the series of bis-(8-hydroxyquinoline)-metal ion coordination polymers which was studied, the polymers containing the ligand bis-(8-hydroxy-5-quinolyl)-sulfone also showed the presence of dimethylformamide end groups.

There is,then,some evidence to indicate that complexes containing the sulfone linkage achieve a much smaller degree of polymerization than the other systems investigated. A possible explanation is based upon the relative solubilities of the various polymer systems. As the reaction between metal ion and tetrafunctional ligand is functionally capable of proceeding as long as the needed building blocks are available, a polymer chain should continue to grow until it becomes insoluble and precipitates from the solution. It is proposed that the apparent lack of formation of long polymer chains by the systems containing sulfone linkages is simply a matter of solubility. This speculation is supported by the observation that for both the bis-(o-aminophenols) and the bis-(8-hydroxyquinolines), the compound which contained the sulfone linkage was the least soluble of the series. If this solubility relationship is retained when these compounds are polymerized, it offers an explanation for the inability of the sulfone containing polymers to attain a high degree

of polymerization.

C. bis-(3-Amino-4-hydroxyphenyl)

The copper complex of the aminophenol was prepared by mixing hot dimethylformamide solutions of the reactants



D. Thermal Stability Study of bis-(o-Aminophenol) Polymers

The three polymers discussed above were heated in a stream of nitrogen in the thermogravimetric balance. The decomposition temperatures of these polymers are shown in Table II.

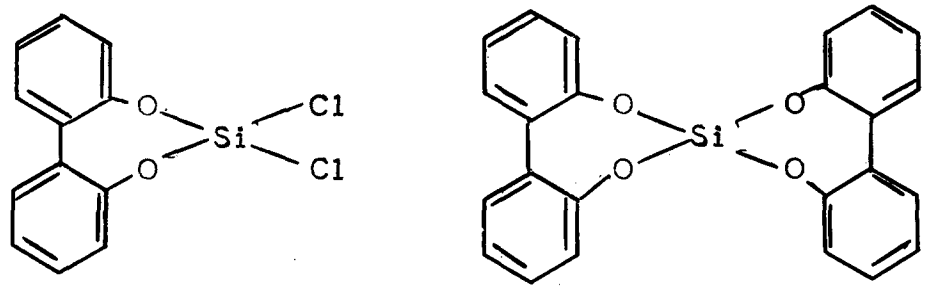
TABLE II

DECOMPOSITION TEMPERATURES OF COPPER(II)-bis-(o-AMINOPHENOL) COMPLEXES

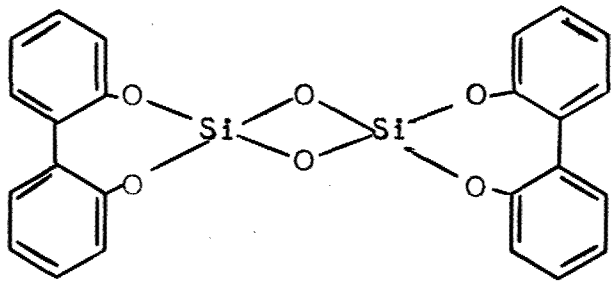
bis-(o-Aminophenol)	Decomposition Temperature
2,2-bis-(3-amino-4-hydroxyphenyl)-propane	240°C.
bis-(3-amino-4-hydroxyphenyl)-sulfone	240°C.
bis-(3-amino-4-hydroxyphenyl)	240°C.

III. COMPLEXES OF bis-DIPHENOLS (with Mr. John McLean).

2,2'-Dihydroxybiphenyl has been shown to react with silicon tetrachloride (6) to give very stable products of the types



and



This suggests that bis-diphenols containing phenolic groups ortho to each other might give stable polymers.

Several methods have been investigated in attempts to prepare suitable tetrols for the synthesis of silicon-containing polymers. These investigations have brought only limited success because the isolation of desired products from starting materials and side products has proved to be extremely difficult.

1. Synthesis of 2,2-bis-(3,4-Dihydroxyphenyl)propane.- Two methods which can be used for this synthesis have been found. The first gives pure product but the yields are very small. The second gives better yields but the purification of the product is more difficult.

a. Acid Hydrolysis of the Diazonium Salt of 2,2-bis-(3-Amino-4-hydroxyphenyl) propane.- A cold solution of the diazonium salt was prepared and added dropwise to boiling fifty per cent sulfuric acid. Only small amounts of the tetrahydroxy compound can be prepared in this manner because of the vigorous foaming of the reaction mixture. While it is possible to control this foaming with conventional antifoaming agents, it is not practical because such a large amount of antifoaming agent is required that purification of the product becomes a major problem. Attempts to hydrolyze the diazonium salt under milder conditions yielded an infusible coupling product.

b. Condensation of Pyrocatechol and Acetone.- bis-Phenols are prepared commercially by condensing phenols with carbonyl compounds in the presence of a mercapto-substituted aliphatic carboxylic acid catalyst. Although use of this method has been restricted to dihydroxy compounds, it has been found to be applicable to tetrahydroxy compounds as well. Pyrocatechol, acetone, hydrochloric acid and mercapto-succinic acid were suspended in ethylenedichloride and the mixture was stirred for 72 hours at room temperature. The brown product was recrystallized twice from ethanol-water mixtures. Analysis indicated that this material contained slight amounts of impurities which were not removed by this

purification procedure. An attempt was made to increase the yield from this reaction by substituting β-mercaptopropionic acid for mercaptosuccinic acid and acetic acid was substituted for ethylenedichloride as a reaction medium. The latter modification was adopted to allow the reaction to be carried out in solution rather than in suspension. Both of these modifications proved fruitless, as no reaction took place under the conditions mentioned.

2. Synthesis of 3,3',4,4'-Tetrahydroxydiphenyl Sulfone.- Preparation of the diazonium salt followed by acid hydrolysis produced only the coupling product when the same conditions used in the synthesis of 2,2-bis-(3,4-dihydroxyphenyl)propane were employed. Fortunately, foaming was not a problem in the hydrolysis of the diazonium salt of the sulfone. This permitted wide variations in the reaction conditions in studies of the control of the coupling reaction. Ordinarily, coupling reactions can be minimized in diazotization reactions by increasing the acidity of the reaction mixture. There is an upper limit to the concentration of the acid which can be used; high concentrations tend to degrade the starting material into cleavage products during the hydrolysis. An optimum acid concentration has not been found which leads to the desired product.

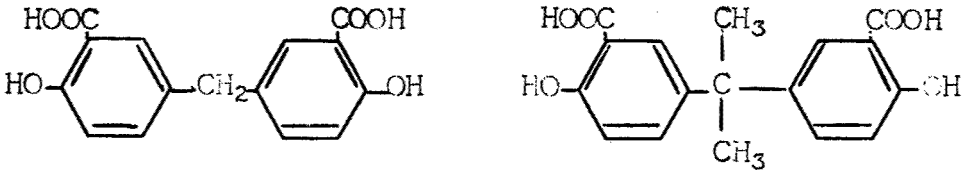
3. Attempted Synthesis of 2,2',6,6'-Tetrahydroxybiphenyl.- 2-Lithium resorcinol di-2-pyranyl ether was prepared by an exchange reaction between phenyl lithium and resorcinol-di-2-pyranyl ether. The corresponding iodo compound was conveniently prepared by the reaction of iodine with the lithium compound. When the iodo compound was subjected to the conditions of the Ullmann reaction, an exothermic reaction took place. However, no suitable solvent has yet been found which would extract the 2,2',6,6'-tetrahydroxybiphenyl from the reaction mixture.

Recently, however, we have found that 2,2',6,6'-tetramethoxybiphenyl can be demethylated to the corresponding tetrol in the presence of a great excess of aluminum chloride, and we shall soon be able to report on the reaction of the latter substance with silicon tetrachloride.

IV. COMPLEXES OF bis-SALICYLIC ACIDS (with Mr. John McLean).

Copper-3-phenylsalicylate is a well known copper complex which is used as a textile preservative in the dye industry. This compound greatly increases the durability of fabric exposed to weather and gives it outstanding thermal stability. The desirable properties of this substance have led to an investigation of the possibility of incorporating a molecule of this type into a metal-containing polymer. Two model salicylic acid derivatives have been prepared and

their reactions with metal ions and with silicon tetrachloride have been investigated.



1. Synthesis of Methylene Disalicylic Acid (I) and its Reactions with Metal Ions (7).- Methylene disalicylic acid can be prepared easily by the formal condensation of formaldehyde and salicylic acid in the presence of a strong mineral acid. This reaction leads to a mixture of the 5,5-, 3,5-,and 3,3-isomers. Separation is unnecessary, since all of the isomers are suitably substituted for polymer formation with metal atoms. This compound was dissolved in ethanol and added to boiling solutions of nickel, copper and zinc salts in methanol. All three metal salts gave immediate precipitates. These precipitates were soluble in aqueous ammonia. In the cases of nickel and zinc, the metals were removed through treatment with ammonia. The ammonical solution of the copper compound remained colorless, which indicates that no copper tetrammine ion was formed and that the copper compound is stable toward this type of decomposition. The thermal stability of these complexes is surprisingly low. The correct stoichiometry of the compounds could not be worked out with the information obtained from elemental analysis. Since both methanol and ethanol were used in the synthesis it is possible that random coordination of the two alcohols could account for the analytical figures which have been obtained. It seems quite certain that solvent molecules are attached to the metal atoms in the chain. The terminal metal atoms may be coordinated to firmly bound groups such as OH, which stop chain growth.

When an ether solution of silicon tetrachloride was dropped into a boiling suspension of methylene disalicylic acid and ether, a condensation ensued as was evidenced by evolution of hydrogen chloride. Molecular weights of such polymers, based on analytical data, range from 1600 to 4500. Although this polymer can be decomposed by prolonged heating (220°C. for three days gave 3% weight loss) it is believed that more stable polymers can be made by choosing more nearly homogeneous reaction conditions. Since methylene disalicylic acid is only slightly soluble in absolute ether, a more suitable solvent is being sought.

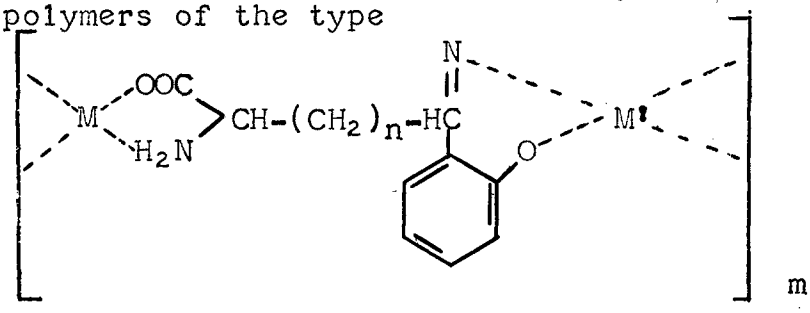
V. WORK ON THE MECHANISM OF COORDINATION POLYMERIZATION (with Mrs. Lu-chi Chen and Mrs. J. M. Moraghan).

The reactions which it was thought would lead to the formation of long chain coordination polymers have given

instead very short chains. If valuable products are to be obtained, we must discover why chain growth stops, and devise methods of making it continue. The most probable reasons for the failure of the chains to grow are:

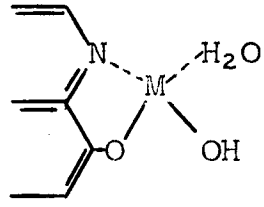
1. Insolubility of the growing polymer. This can, perhaps, be overcome by introducing solubilizing groups into the coordinating molecule.

2. Aquation and hydrolysis of "end" metal atoms. In regard to the first of these Rau's study (1) of the formation of polymers of the type



in which M and M' represent divalent, 4-covalent metals (Cu^{++}, Ni^{++}, Pd^{++}), is being extended. In the cases investigated by Rau, chain growth ended when the molecule contained three metal atoms. Repitition of Rau's work, under a variety of conditions, has led to polymers of somewhat greater molecular weight, but it is evident that high molecular weights will not be achieved by the methods which have been used thus far. It has also been observed that when two different metals are used in the formation of polymers of this type, interchange takes place readily.

Several bits of evidence indicate that in some cases, at least, the growth of a coordination polymer in aqueous medium is stopped by the attachment of water and hydroxyl groups to the end metal atom. Thus, bis-8-hydroxyquinoline derivatives seem to contain the end group



Techniques of forming the polymers in non-coordinating solvents or in weakly coordinating solvents (ethers, esters, etc.), or in the absence of solvents, are being sought.

BIBLIOGRAPHY

1. Robert Rau, Thesis, University of Illinois (1955).
2. John C. Bailar, Jr., K. V. Martin, M. L. Judd and John McLean, W.A.D.C. Technical Report 57-391 (Part II), August 1958; ASTIA Document No. 155799.
3. H. J. Schuller, J. prakt. Chem. [2], 88, 180 (1913); Soc. pour l'ind. chim. a Bale, Swiss 208,000 (March 6, 1940); Brit. 536, 367, (May 13, 1941); Noelting, E., Chimie et Industrie, 8, 758 (1922).
4. WADC Technical Report 58-51, University of Illinois, December, 1957.
5. Airon, J. W., and Wagle, D. S., J. Univ. Bombay, 23, Part 3, Sci. No. Sect. A., No. 36, 29 (1954); C. A., 49, 10272 (1955).
6. R. Von Schwartz and W. Kuchen, Z. anorg. allgem. Chem., 279, 84 (1955).
7. E. Clemmensen and H. C. Heitman, J. Am. Chem. Soc., 33, 737 (1911).

Thermally Stable Coordination Polymers

May 28, 1959

University of California, Los Angeles
W..C. Drinkard, Jr., D. N. Chakravarty

Polymers exibiting a high degree of thermal stability have recently become a subject of prime interest. Encouraging results have been obtained but more work is needed to bring our understanding to a practical state of development.

Polymers containing a metal ion bonded to an organic ligand have unusual thermal properties conferred by the metal ion. Previous workers have reported limited success in growing thermally stable, long chain complex molecules. Several examples of high thermal stability have been reported for polymers formed by joining polyfunctional ligands by chelation to a metal ion, but molecular weights have been estimated to be quite low. The low molecular weight might be attributed, in part, to the extreme insolubility of the complex which results in precipitation of the polymer before chain growth can occur. The present investigation has sought to avoid this difficulty by first producing long-chain organic molecules containing donor groups, then by coordinating these to a metal ion.

The present approach to polymer formation may be divided into the following sections:

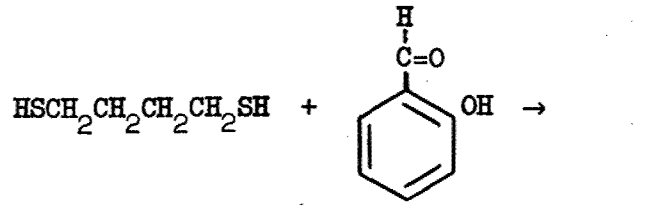
1.) Preformed organic polymers may be stabilized by inclusion of a metal ion.

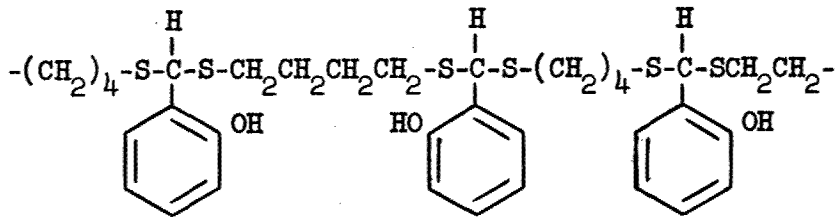
2.) Low molecular weight polyfunctional ligands may be joined by complex formation.

PREFORMED ORGANIC POLYMER STABILIZATION

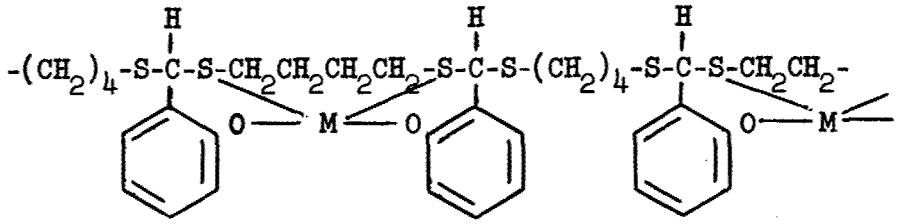
Previous attempts to prepare polymers by joining polyfunctional, low molecular weight ligands by metal ion coordination have resulted in low molecular weight materials. If, however, large polymers containing favorably placed donor groups are reacted with metal ions, it should be possible to retain the large molecular weight of the molecule. Thus, high molecular weights may be obtained by convential organic polymerization methods. Thermal properties may then be modified by coordination of a metal ion. The polymer is made non-ionic by including negative or potentially negative groups to balance the metal ion charge.

Dimercaptals The reaction of an alkyl dimercaptan with an aldehyde will produce a polymeric mercaptal. If additional coordination groups are included in the molecule, a stable linear chelate system may be formed by metal ion addition. The reaction may be illustrated by the polymerization of butylenedimercaptan with salicylaldehyde.



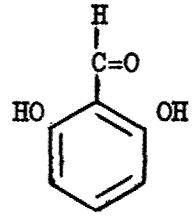


Addition of a divalent, tetracoordinate ion produces



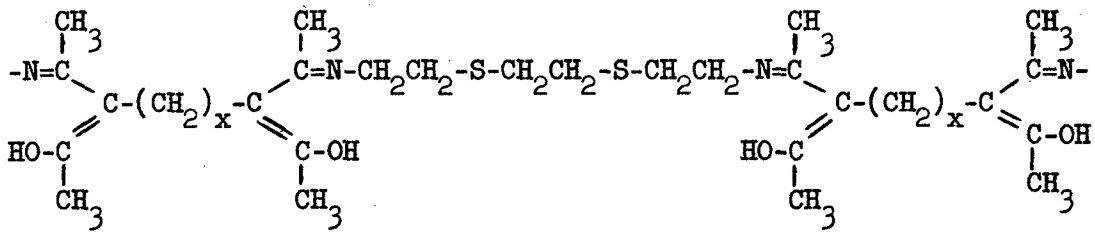
Preliminary experiments have produced gummy products with disappointingly low thermal stability (ca. 150° C) with Cu^{+2} and Ni^{+2}. Some what higher thermal stability is indicated for the Zn^{+2} chelate.

Extension of the system to the diphenol.

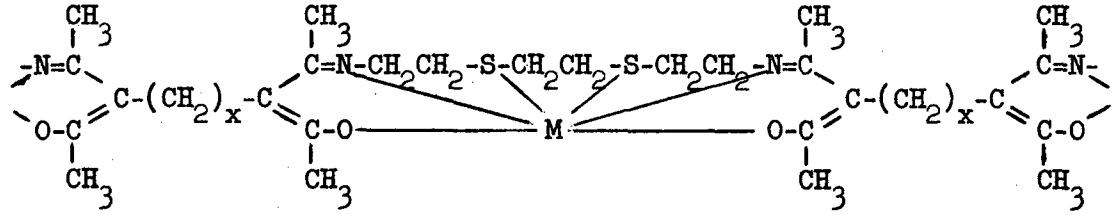


should increase thermal stability.

Schiff Base of 1,8-diamino-3,6-dithioctane with Tetraacetyl butane. Dwyer and Lions reported a high thermal stability for the metal complexes of the Schiff base of 1,8-diamino-3,6-dithioctane with acetylacetone. By substitution of a bis-betadiketone for acetylacetone an organic polymer of the following type is produced.



Addition of a divalent, hexa coordinate ion produces the following complex polymer.



COORDINATION POLYMERIZATION

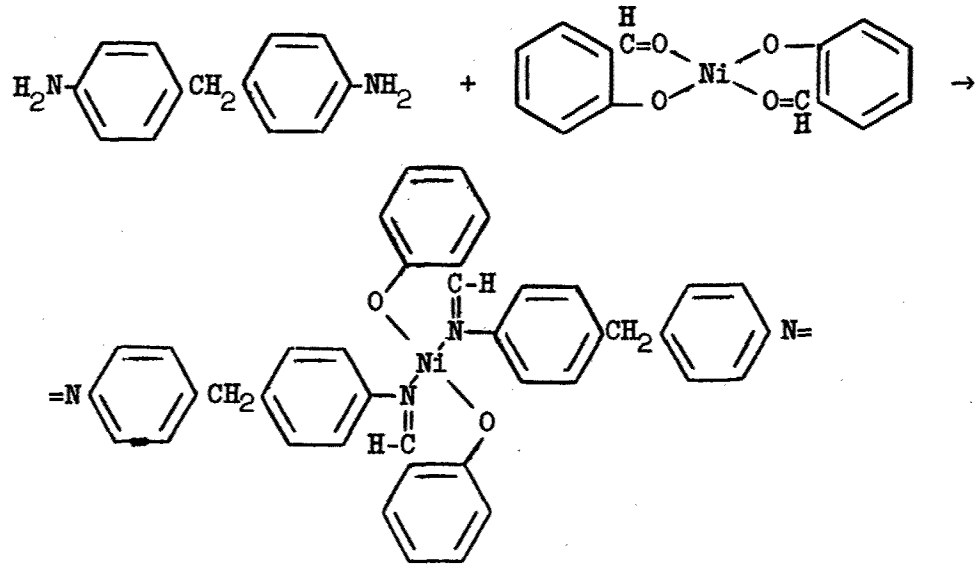
The present investigation also includes a study of polymer formation by the act of coordination. Polymerizations of this type may be achieved when steric factors prevent coordination of all donor groups of a molecule with a single metal ion. Thus, the metal acts as a bridging group between polydentate ligands. For convenience the polymerizations are classed as:

1.) Those which occur in absence of solvent (melt or solid state) and,

2.) Those which occur in solution.

Melt and Solid State Reactions. By polymerization in the molten or solid state it is felt that the difficulty of early precipitation of low molecular weight materials associated with solvent systems may be avoided. Condensation polymerization involving the loss of water is currently under investigation.

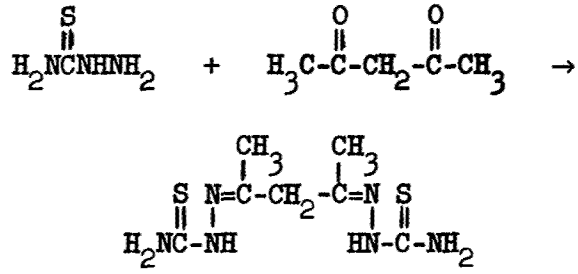
Schiff Bases of Acetylacetone and Salicyaldehyde. Schiff base formation using primary amines and aldehydes which are bound to a metal ion by a coordinate covalent bond is well known. Reaction of a diamine with the nickel salicyaldehyde complex will result in a polymeric material if steric factors prevent cyclic Schiff base formation. The following reaction between methylene- dianaline and bis-salicylaldehydo nickel(II) illustrates the principle.



When the above reaction is carried out between the finely ground solids at 80°C in vacuum over P_2O_5, a yellow, brittle solid is obtained which is stable to 300°C. The reaction is currently being extended to other amines and aldehydes and ketones.

Reactions in Solution. Precipitation of coordination polymers from a solution of the polyfunctional ligand and the metal ion is also under investigation.

Thiosemicarbazones of Dialdehydes and Diketones. Reaction of thiosemicarbazide with a diketone or dialdehyde produces a dithiosemicarbazone containing four potential donor atoms.



Reaction of this dithiosemicarbazone with Ni^{+2} in alcohol solution produces a complex stable to 180°C. The zinc chelate is only slightly more stable.

Extension of the method to other dicarbonyls is currently in progress.

DETERMINATION OF THERMAL STABILITY

Differential thermal analysis was used to determine the thermal stability of all samples reported. The samples were diluted with Al_2O_3. At a heating rate of 8°C per minute the decomposition peaks were very broad, usually extending over several minutes. Maximum stability was taken as the point of initial rise of the differential plot. Peak maxima usually occurred at a temperature which was approximately 10°C higher.

PI-BONDED INORGANIC SYSTEMS

A. F. Clifford

Purdue University

There are many indications that the search for more stable inorganic polymer systems may be more successfully pursued in the area of substances having (a) a high degree of multiple bonding using d-orbitals (i.e., "delta-bonding"), (b) high coordination number, (c) high oxidation state and (d) low bond polarity. Factors (a), (b) and (d) should contribute to hydrolytic stability. Factor (c) should enhance oxidative stability. Factor (a) should enhance thermal stability.

The contribution of multiple bonding to the stability of compounds of the transition elements with ligands containing non-metals of the third and later periods of the periodic table as well as with certain ligands containing carbon and nitrogen is now generally accepted to be of considerable importance. Pauling's original proposal[1] that the formation of double bonds

(1) L. Pauling. "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 2nd Ed., 1945, p. 254.

using $d\pi$ electrons of the transition elements could explain the strong covalent bond formation found in complex cyanides, carbonyls and nitro compounds has been extended by several workers[2]. Two different types of

(2) Y. Syrkin and M. E. Dyatkina. "The Structure of Molecules," Butterworth's, London, 1950, p. 361; M. Calvin and R. H. Bailes, J. Am. Chem. Soc., 68, 949 (1946); J. Chatt and R. G. Wilkins, J. Chem. Soc., 1952, 273; Idem., ibid., p. 4300; F. H. Burstall and R. S. Nyholm, J. Chem. Soc., 1952, 3570; G. E. Coates, J. Chem. Soc., 1951, 2003.

multiple bonding may result from the use of the d-electrons of the transition elements: the first using $p\pi$ orbitals of the ligand and the second using $d\pi$ orbitals. The first is the type which occurs in transition metal-cyanide, -carbonyl, -nitro and -nitroso complexes. This requires that the $p\pi$ orbital of the ligand be made available through resonance in the ligand group.

$$\bar{M}\text{-}C\equiv\overset{+}{O} \rightleftarrows M=C=O$$

$$\bar{M}\text{-}\overset{+}{N}\begin{matrix}\diagup O \\ \diagdown O^-\end{matrix} \rightleftarrows M=\overset{+}{N}\begin{matrix}\diagup O^- \\ \diagdown O^-\end{matrix}$$

This kind of resonance is clearly impossible if the nitrogen or carbon atom is already attached to three other atoms, as in a tertiary amine or in an alkyl group.

The second kind of multiple bonding occurs in the complexes of the transition metals with phosphines, arsines, stibines, sulfides, selenides, etc. The joined atoms approach electrical neutrality by overlap of the filled d-orbitals of the metal atom with the vacant d-orbitals of the non-metal.

$$\overset{-}{M}\text{-}\overset{+}{PR_3} \rightleftarrows M{=}PR_3$$

$$\overset{-}{M}\text{-}\overset{+}{SR_2} \rightleftarrows M{=}SR_2$$

Thus there is abundant evidence to show that although in the complexes of the non-transition elements, the order of stability is

$$(a)\quad NR_3 > PR_3 > AsR_3 > SbR_3,$$

for the transition elements, the order is generally

$$(b)\quad NR_3 \ll PR_3 > AsR_3 > SbR_3$$

This order can be interpreted in terms of a sigma bond which gradually decreases in strength as the size of the ligand atom increases and a pi bond which is nonexistent in the case of ligand atoms from the second period of the periodic table (except as noted above), is strong in the case of phosphorus and probably decreases slightly for the elements of later periods, but may make an increasing proportionate contribution to the total bond strength.

Most of the metals in the periodic table follow series (a) in their complexes. A small group of elements, centered around Pd, Ag, Ir, Pt, Au and Hg follow series (b). The boundary line between the groups is indistinct because it depends among other things upon valence. For example, copper(II) follows series (a) whereas copper(I) follows series (b). As a general rule, the higher valences follow series (a) and the lower, series (b), but this depends strongly on the ligand.

Since one of the characteristics of interest in inorganic polymers is thermal stability, data were collected from the literature to see how the thermal stabilities of oxides and sulfides compare with the concepts outlined above. The data found are given in Table 1. In general it can be seen that the agreement is very good.

Data on the nitrides and phosphides are extremely fragmentary. The only ones for which any kind of quantitative comparison is available are those of copper and iron, which in this case both show the (b)-type relationship.

Cu_3N	Cu_3P	Fe_2N	Fe_2P
d. > 470°C	m. 1005°C	d. > 560°C	m. 1365°C

Table 1

Decomposition Temperatures (°C) of Oxides and Sulfides

Series (a)		Series (b)	
AgO d. > 100	AgS d. < 20	Ag_2O d. 300	Ag_2S m. 825
Bi_2O_3 d. 1700	Bi_2S_3 d. 685	Au_2O d. 205	Au_2S d. 240
Cr_2O_3 d. >> 2500	Cr_2S_3 d. 1350	Au_2O_3 d. 160	Au_2S_3 d. 197
CuO d. 1600	CuS d. 220	CdO d. 900	CdS m. 1750 (100 atm) subl. 980
Sb_2O_5 d. 380	Sb_2S_5 d. 135	HgO d. 100	HgS (red) subl. 580
WO_2 d. >> 2500	WS_2 d. > 1200	PdO d. 600	PdS d. 950

However, Brewer[3] states "... the phosphides have a much wider range of

(3) L. Brewer, et al., Paper 4, "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," Editor, L. L. Quill, McGraw-Hill Book Company, Inc., New York, 1950.

stability throughout the periodic table than do the nitrides. Although the nitrides of iron and copper and most of the elements to the right in the periodic table (except GaN) are thermodynamically unstable, the phosphides are found far to the right. Only Tl, Bi and possibly Pb have been demonstrated not to form stable solid phosphides." Thus again the elements centered around silver and gold form phosphides which are more stable than the corresponding nitrides.

The relative coordinating ability of NF_3 and PF_3 are particularly germane to this discussion. Nitrogen trifluoride has been reported to form weak addition compounds with Lewis Acids, such as BF_3, whereas PF_3 shows no signs of being able to form such compounds[4]. This indicates that the

(4) J. W. Irvine and G. Wilkinson, Nature, 168, 514 (1951); Science, 113, 742 (1951); J. Am. Chem. Soc., 73, 5501 (1951).

availability of the unshared pair of electrons on phosphorus in PF_3 to form a sigma bond is vanishingly small. On the other hand, NF_3 apparently has no ability to displace CO from $Ni(CO)_4$, whereas PF_3, despite its inability to form sigma bonds, nevertheless gives $Ni(PF_3)_4$. It would seem that this apparent paradox must be explained in terms of the ability of the phosphorus atom to use its d-orbitals to accept electrons from the nickel atom, an ability which nitrogen necessarily lacks. The Ni-P bond in $Ni(PF_3)_4$ would appear therefore to be an almost pure pi-bond.

In view of the above, it was of interest to see whether a substance having no electron pair to form sigma bonds could form a complex with a Ni(0) atom (i.e., displace CO from $Ni(CO)_4$), utilizing only the "pi-bonding" involving the d-electrons of the nickel and the d-orbitals of the non-metal. Such a substance would be one of the pentavalent compounds of phosphorus, arsenic or antimony. In these, four of the d-orbitals are available and there is no unshared pair of electrons which can form a sigma bond. Consequently, if a pentavalent compound of this sort is found to be capable of displacing CO from $Ni(CO)_4$, it must almost necessarily be due only to interaction between the d-electrons of the nickel atom and the d-orbitals of the non-metal atom.

The Nickel Carbonyl-Pentaphenylantimony Reaction

Since most pentavalent, pentacoordinate compounds, PX_5, etc., of the nitrogen family elements are good oxidizing agents, they are unsuitable as reactants with nickel carbonyl. The pentaalkyls and pentaaryls, on the other hand, have weaker oxidizing properties and have the further advantage of not having unshared pairs in the X groups which might be donated to the nickel atom, although the possibility cannot be excluded of interaction between the nickel atom and the aromatic pi-electron systems of the

pentaaryl compounds. The pentaalkyls, although probably more desirable from this last point of view, were ruled out because of their relative instability. Of the known pentaaryls, ϕ_5P, ϕ_5As, ϕ_5Sb and ϕ_5Bi, the last was eliminated for the same reason. Of the remaining three, the antimony compound appeared to be the most appropriate not only on stability grounds but also because it seemed much more likely to be able to coordinate the nickel atom than the arsenic and phosphorus compounds with their smaller central atoms. The coordination numbers of P, As and Sb toward carbon would be predicted from radius-ratio consideration to be 4, 4 and 6, respectively, so that only antimony should be expected to coordinate a sixth atom with ease. Consequently, pentaphenylantimony was selected as the most appropriate compound for reaction with nickel carbonyl to investigate pure d-pi-d-pi interactions.

The preparation of pentaphenylantimony is not easy, but was accomplished essentially by the method of Wittig and Clauss[5]. When the

(5) G. Wittig and K. Clauss, Ann., 577, 26 (1952).

pentaphenylantimony was reacted in benzene solution with nickel carbonyl at room temperature, a yellowing of the solution occurred, followed, after a few days, by decolorization and deposition of a white solid. The solid proved to be insoluble in water and all the usual organic solvents, whereas pentaphenylantimony is soluble in solvents such as benzene and cyclohexane. The compound darkened slightly above 200°C, but showed no other reaction up to 230°C. Pentaphenylantimony, on the other hand, melts at 169-170°C. The compound was decomposed by acidic solvents such as concentrated aqueous HCl or H_2SO_4 or glacial acetic acid, as well as by aqueous NH_3, with formation of a nickel(II) salt and pentaphenylantimony, which was identified by mixed melting point. It appears certain, therefore, that pentaphenylantimony units were retained in the addition compound. The nickel-to-antimony ratio appeared, however, to be indefinite.

It seems probable that a compound of nickel and antimony has been prepared which has pure d-pi-d-pi bonds thus providing weighty evidence in favor of these interactions. The unexpected stability of the compound indicates that the interactions may indeed be much more important than has been thought. The exact nature of the compound, however, remains to be proved and work is continuing in this direction.

A similar type reaction was observed between solid $PtCl_2$ and pentaphenylantimony in a benzene solution. A white solid separated from the solution which decomposed in warm benzene or at 109°C when dry, leaving a black residue. Further work on the platinum compound was deferred in order to concentrate on the more interesting nickel compound.

Iron-Sulfur Systems. In order to obtain more information about the strength of potential bonding systems for inorganic polymers, studies are planned on a number of transition metal-sulfur systems. Preliminary work has been begun on the carbonyl mercaptides of iron, described by Hieber and coworkers[6]. The preparation of these compounds is currently

(6) W. Hieber and G. Spacu, Z. anorg. Chem., 233, 353 (1937); W. Hieber and C. Scharfenberg, Ber., 73, 1012 (1940).

underway. It is intended to employ the usual techniques to obtain as much quantitative data as possible on the stability of the iron-sulfur bond.

Since work on this contract has just gotten underway, actual experimental data are necessarily very scanty.

RESEARCH ON TRANSITION METAL-CARBON CHEMISTRY

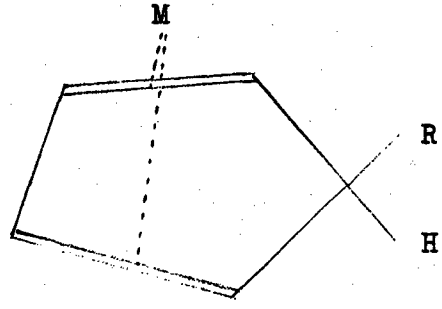
Geoffrey Wilkinson

Imperial College of Science and Technology,
London, England

The research on organometallic compounds under this Contract has only recently begun. Two lines of work are being investigated.

(a) Whilst a great number of olefin complexes of transition metals have been described in the literature, there is no reported case of perfluorinated olefins giving complexes. It is hoped to obtain perfluorobutadiene for study since, by analogy with butadiene, complexes such as $C_4F_6Fe(CO)_3$ should conceivably exist and could be thermally very stable. Until this material becomes available to us, we have studied perfluoroethylene as a model system. We have found that reactions under pressure with sodium chloroplatinite solutions give yellow salts of what is almost certainly the fluoro-olefin complex comparable to Zeise's salt. The presence of coordinated fluoro-olefins in the solutions was detected by high-resolution nuclear magnetic resonance. The complex has not been isolated yet in the pure state, but it is expected to be isolated shortly. This discovery suggests strongly that other perfluorinated olefin complexes of transition metals such as the perfluorobutadiene one can indeed be made.

(b) It has recently been shown at Imperial College that a new type of cyclopentadiene compound can be made from di-π-cyclopentadienylcobalt by the action of active halogen compounds, e.g. $2(\pi\text{-}C_5H_5)_2Co + CH_3I = \pi\text{-}C_5H_5Co(C_5H_5.CH_3) + (\pi\text{-}C_5H_5)_2CoI$. Further studies are being made with silicon and other non-metallic halides and it is hoped that new types of stable compounds can thereby be made. It has been unequivocally shown that the group added to the cyclopentadienyl ring does indeed go onto a carbon atom and in the <u>exo</u> position (see diagram).



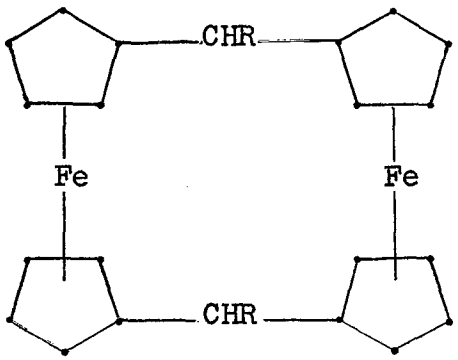
SYNTHESIS OF FERROCENE DERIVATIVES

KENNETH L. RINEHART, JR.

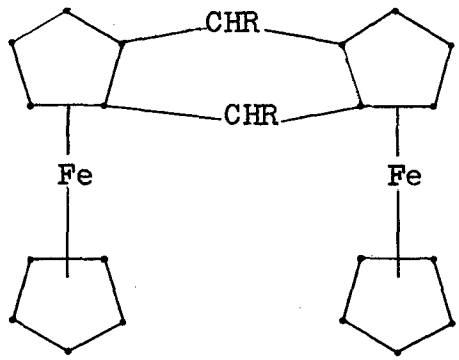
UNIVERSITY OF ILLINOIS

A. Bridged Ferrocenes. 1. Ferrocene-formaldehyde Condensation Product.

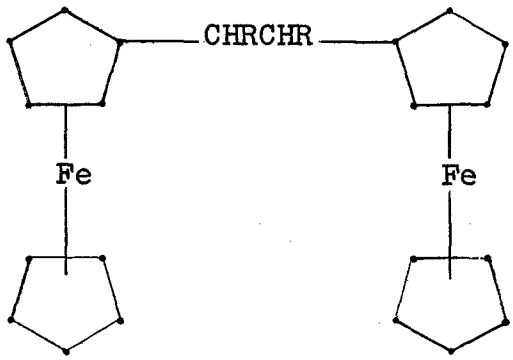
Ferrocene condenses with formaldehyde in either concentrated sulfuric acid (1) or liquid hydrofluoric acid (2) to give a compound (I) containing two ferrocene nuclei and two methylene groups (from two moles of formaldehyde). This condensation product (I) was originally assigned the structure 1,1'-bis-ferrocenylenemethane (Ia)(1,2,3). Subsequently, Nesmeyanov and co-workers (4) revised their assignment to structure Ib (1,2-bis-ferrocenylenemethane), on the basis of the presence of bands at 1110 and 1004 cm^{-1} (5) in the infrared spectrum of I, indicative of at least one unsubstituted cyclopentadienyl ring. However, the true structure of the condensation product (I) has been shown to be 1,2-diferrocenylethane (Ic).



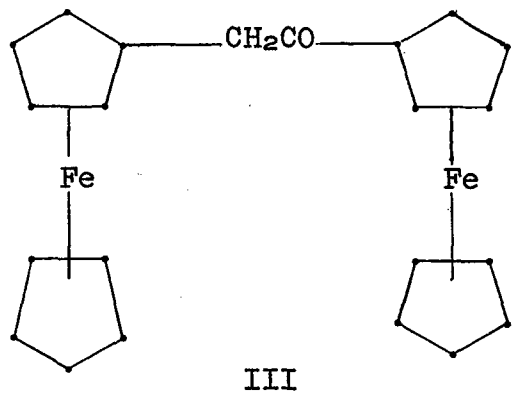
Ia, IIa



Ib, IIb



Ic, IIc



III

Ia, Ib, Ic: R = H
IIa, IIb, IIc: R = C_6H_5

Compound I, prepared by the sulfuric acid method (1), melts 190-192° in agreement with literature values (1,2). Microanalyses agree better with its formulation as Ic than as Ia or Ib and its infrared spectrum resembles closely that of ethylferrocene. A mixture melting point of I with an authentic sample of 1,2-diferrocenylethane (Ic), m.p. 193-195°, showed no depression and the infrared spectra (CS_2) of the compound (I≡Ic) from the two routes were superimposable. The latter compound was prepared by hydrogenation of ferrocenylacetylferrocene (III, desoxyferrocoin) the product of Friedel-Crafts' acylation of ferrocene with the acid chloride of ferrocenylacetic acid (6).

The structure of the similar condensation product (II) from ferrocene and benzaldehyde, first assigned structure IIa (1,2,3), later IIb (4) is, presumably, analogous, i.e., 1,2-diferrocenyl-1,2-diphenylethane (IIc) since the infrared spectrum of this compound (II) is similar to that of I.

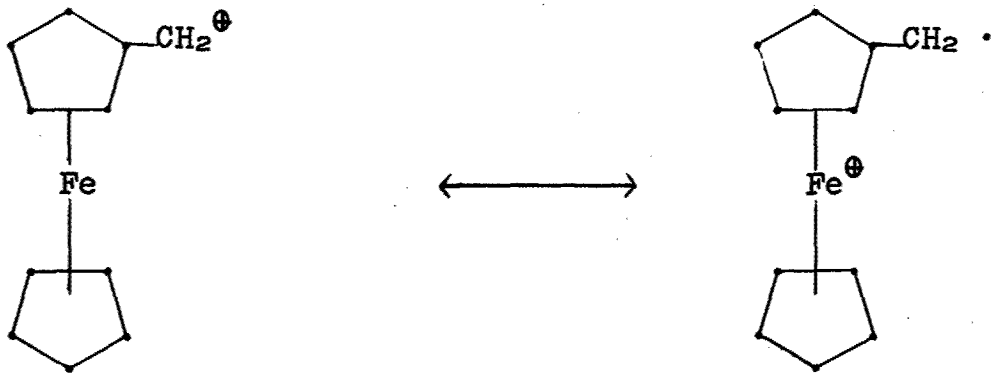
Possible mechanisms for the formation of I and II include the reaction path below, in which the key intermediate is the novel cation IV. In accord with this pathway, α-hydroxymethylferrocene (III) (7) has been converted to I under conditions identical to those employed for the conversion of ferrocene and formaldehyde to I, and the blue-green, water-soluble dication (V) of I has been isolated as its dipicrate.

$$C_{10}H_{10}Fe + CH_2O \xrightarrow{H_2SO_4} C_{10}H_9Fe\text{-}CH_2OH \longrightarrow IV$$

III

$$IV \xrightarrow[\text{ation}]{\text{dimeriz-}} (C_{10}H_9Fe\text{-}CH_2)_2^{++} \xrightarrow{SnCl_2} I$$

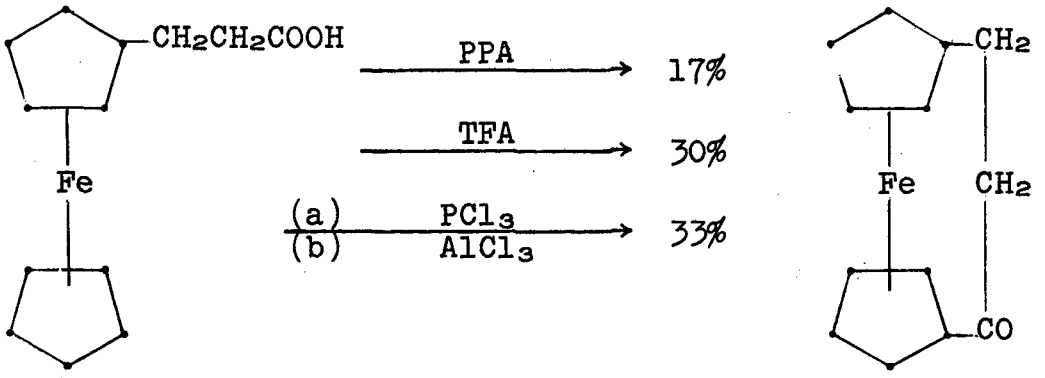
V



IV

2. 1,1'-(Trimethylene)-ferrocene Derivatives.

The bridged ketone, 1,1'-(α-ketotrimethylene)-ferrocene, VI, has been prepared previously by reaction of β-ferrocenylpropionic acid with polyphosphoric acid (8), and by reaction of the same acid with trifluoroacetic anhydride (9); in the present study the yield of VI obtained from the polyphosphoric acid procedure was found to be 17%, while that from cyclization with trifluoroacetic anhydride was 30%. In yet a third method the bridged ketone (VI) was obtained in 33% yield by conversion of β-ferrocenylpropionic acid to the acid chloride, followed by ring closure under Friedel-Crafts' conditions. The product, m.p. 145.5-146.5°, was identical from the three procedures. The ketone (VI) was further characterized by reduction to the corresponding alcohol, 1,1'-(α-hydroxytrimethylene)-ferrocene, m.p. 159°.



VI

Several attempts were made to condense ferrocene with β-chloropropionyl chloride and aluminum chloride. However, the yields of all products isolated were very low.

Acetylation of ferrocene with acetic anhydride and boron trifluoride, previously stated to give exclusively acetylferrocene (10), gave instead only 1,1'-diacetylferrocene. Attempts to di-carbethoxylate this diketone with potassium amide and diethyl carbonate (10) to diethyl 1,1'-ferrocenylene-bis-β-(β-ketopropionate) gave a complex mixture of red oils, difficult to separate.

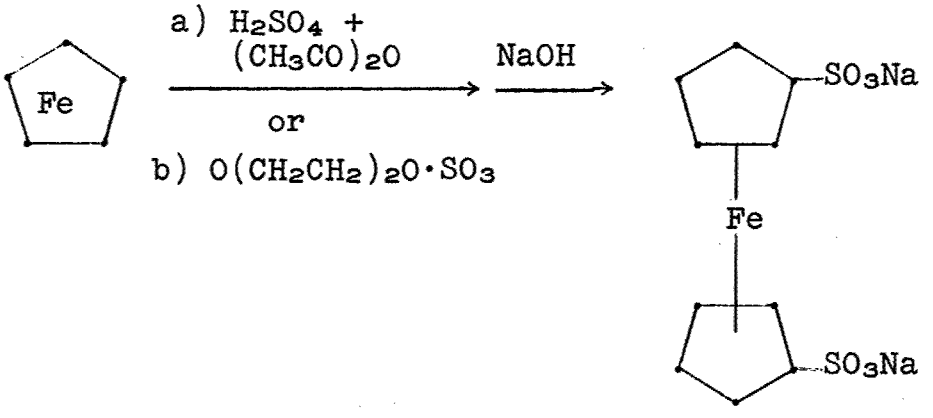
3. Attempted Acylation of Ferrocene with Maleic Anhydride.

Efforts to acylate ferrocene with maleic anhydride under various catalytic conditions were unsuccessful. Catalysts tested included aluminum chloride, stannic chloride, ferric chloride and 85% phosphoric acid, and solvents employed

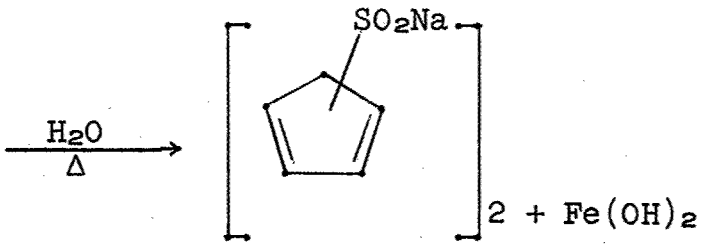
included methylene chloride, tetrachloroethane, carbon disulfide, benzene and methylcyclohexane.

B. Substituent Effects. 1. Hydrolysis of 1,1'-Ferrocenedisulfonate.

1,1'-Ferrocenedisulfonic acid was prepared from ferrocene by two routes, a) by treatment with sulfuric acid in acetic anhydride (11), and b) by treatment with a dioxane-sulfur trioxide complex (12). The dioxane-sulfur trioxide method is preferable since it gives both higher yields and purer product. The acetylating agent in the acetic anhydride-sulfuric acid method may be presumed to be acetylsulfate, CH_3COOSO_3H, since the sodium salt of this compound was obtained from the reaction mixture (13). It was identified by elemental analysis and infrared spectrum.



VII



VIII

When disodium 1,1'-ferrocenedisulfonate (VII) is heated in water a green deposit is slowly formed. This material may be identified as ferrous hydroxide by its solubility in acid and its reaction with ferricyanide ion to give a Prussian blue test. The other product of the decomposition is sodium cyclopentadienesulfonate (VIII). After destruction of the ferrocene nucleus is complete, as determined by ultraviolet

spectra, the ferrous hydroxide may be removed by filtration and the aqueous solution lyophilized to give the organic product, VIII. This compound has been identified by its elemental analysis, and that of its S-benzylthiouronium derivative, and by its infrared spectrum. The cyclopentadiene presumably exists as a dimer since its ultraviolet spectrum shows only end absorption, with no peak above 210 mμ.

Hydrolysis of the disulfonate obeys a first order rate law and is independent of hydroxide concentration over the pH range 5 to 14. The first order rate constant is also essentially constant within this range.

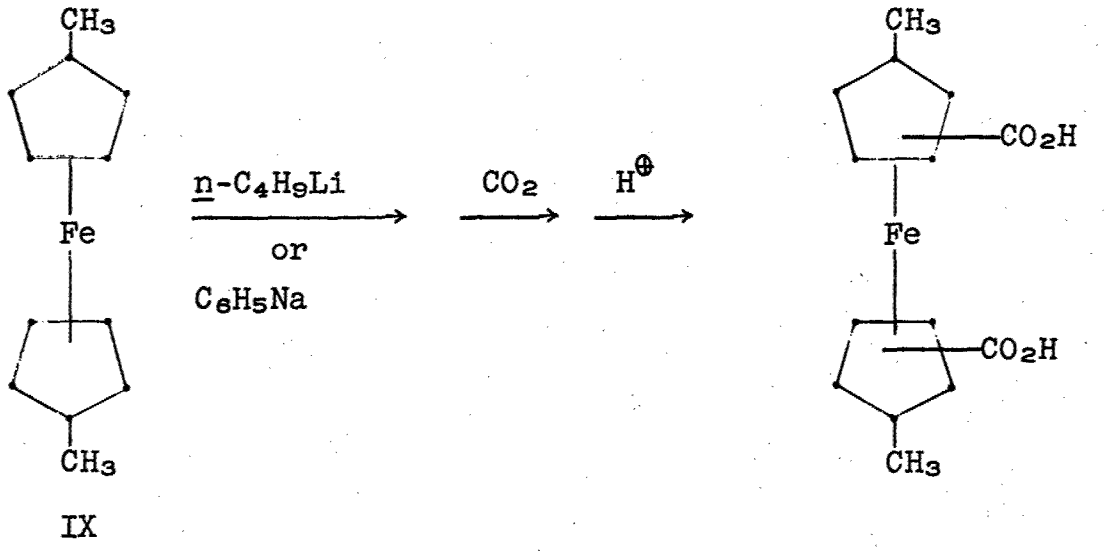
For preparative purposes it was preferable to employ more vigorous hydrolytic conditions and fused alkali was found useful in giving good yields of sodium cyclopentadienesulfonate.

2. Aminoferrocenes.

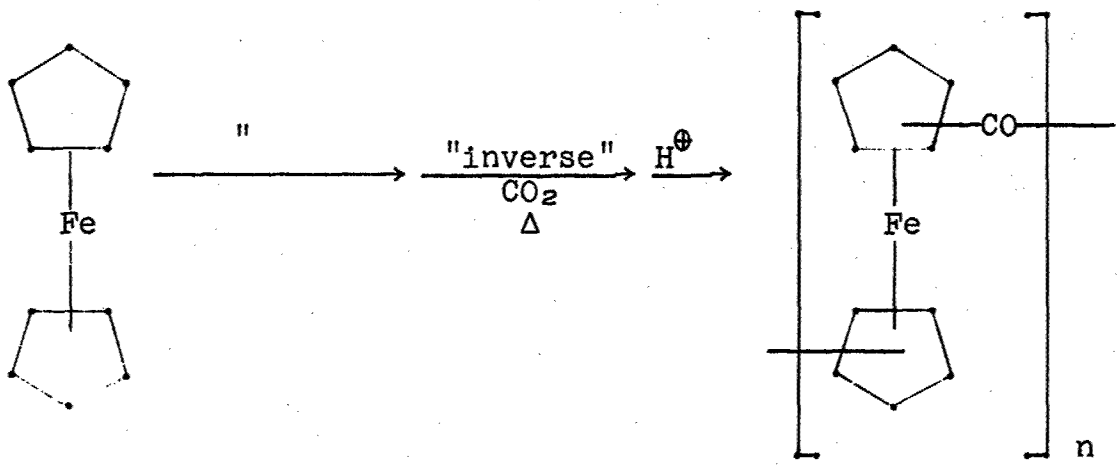
An improved method for the preparation of aminoferrocene has been developed; this involves the mono-lithiation of ferrocene with n-butyllithium (14), followed by treatment with methoxyamine. By this method aminoferrocene was obtained in 75% yield, based on recovered ferrocene. Under similar conditions, designed to give dilithioferrocene (16) and, thus, 1,1'-diaminoferrocene, no diaminoferrocene was obtained. Failure to isolate the diamino compound may be attributed to its greater oxidative instability. The procedure is a modification of that of Nesmeyanov (15), who employed O-benzylhydroxylamine to give aminoferrocene in 42% yield. The advantages of the present method are the higher yield and the commercial availability of methoxyamine.

3. Metalation of Ferrocene and 1,1'-Dimethylferrocene.

In contrast to toluene, which is metalated preferentially on the methyl group as shown by subsequent carboxylation to phenylacetic acid, dimethylferrocene (IX) is metalated exclusively (both with phenylsodium and with n-butyl lithium) on the ring in preference to the side-chain methyl groups. A similar observation was recently reported independently by Nesmeyanov and coworkers for metalation with n-amylsodium, though they failed to obtain reaction of dimethylferrocene with n-butyllithium (17).



IX



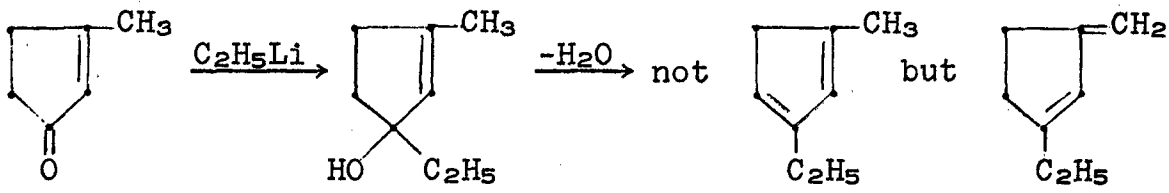
X

In an interesting extension of this reaction, inverse addition of carbon dioxide to the lithiated ferrocene has been shown to lead to polyketones. Thus, when carbon dioxide was bubbled into a warm solution of dilithio-1,1'-dimethylferrocene, a viscous, glassy liquid was obtained whose infrared spectrum shows intense aromatic ketonic absorption and whose molecular weight was determined by viscosity and neutralization equivalent measurements to be approximately 6,000. Similar treatment of dilithioferrocene resulted in a solid polymer (X) of molecular weight approximately 15,000.

C. Alkylferrocenes. 1. Attempted Preparation of 3-ethyl-1-methylcyclopentadiene.

In order to identify isomeric alkylferrocenes resulting from substitution of ferrocene, it was desirable to prepare

reference compounds from substituted cyclopentadienes. An attempt was made to prepare 3-ethyl-1-methylcyclopentadiene (XI) by treatment of 3-methyl-2-cyclopentenone with ethyllithium and dehydration of the resulting alcohol. The intermediate alcohol was obtained in good yield, but dehydration by distillation from alumina gave a compound believed to be XII rather than XI.



XI XII

2. Tetranitrofluorenone Complexes.

Attempts to characterize liquid alkylferrocenes by formation of solid complexes with tetranitrofluorenone were unsuccessful. Ferrocene and alkylferrocenes were shown by spectral changes to form the complexes in ketonic and acetic acid solvents, but the solubility properties of the adducts did not allow their isolation in pure form.

D. Spectral Correlations. 1. Infrared Spectral Independence of Ferrocene Rings.

In the course of preparation of a number of substituted ferrocenes a study has been undertaken of their infrared spectra. From analysis of over fifty spectra, the following correlation is proposed: "The infrared spectrum of a solution of a ferrocene whose rings are differently substituted, A and B, is a composite of the solution spectra of two other substituted ferrocenes, one in which both rings are substituted as A and the second in which both rings are substituted as B". This rule, which may be described as a "rule of infrared spectral independence of ferrocene rings", is illustrated by the infrared spectrum of benzoylferrocene, which contains all the bands exhibited by ferrocene and all those of 1,1'-dibenzoylferrocene, though the bands of each are reduced in intensity. This spectral correlation supports previous observations that, in solution, the rings are free to rotate with respect to one another.

2. Ultraviolet Spectra of Phenyl-substituted Ferrocenes.

The ultra-violet spectra of a number of phenyl-substitut-

ed ferrocenes have been determined. From these spectra it may be shown a) that the ferrocene nucleus is conjugated with an aromatic substituent, b) that conjugation is transmitted from one ring to another, and c) that conjugation is transmitted through each ring from substituents in a 1,3-position with respect to one another.

BIBLIOGRAPHY

1. A. N. Nesmeyanov and I. I. Kritskaya, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 253 (1956).
2. V. Weinmayr, J. Am. Chem. Soc., 77, 3009 (1955).
3. Y. T. Struchkov, Zhur. Obschei Khim., 27, 2039 (1957).
4. A. N. Nesmeyanov, L. A. Kazitsyna, B. V. Lokshin and I. I. Kritskaya, Doklady Akad. Nauk S.S.S.R., 117, 433 (1957).
5. M. Rosenblum, Ph.D. Thesis, Harvard University, August, 1953; M. Rosenblum and R. B. Woodward, J. Am. Chem. Soc., 80, 5443 (1958).
6. K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, J. Am. Chem. Soc., 79, 3420 (1957).
7. J. K. Lindsay and C. R. Hauser, J. Org. Chem., 22, 355 (1957).
8. K. L. Rinehart, Jr. and R. J. Curby, Jr., J. Am. Chem. Soc., 79, 3290 (1957).
9. R. B. Woodward and E. Csendes, personal communication.
10. C. R. Hauser and J. K. Lindsay, J. Org. Chem., 22, 482 (1957).
11. V. Weinmayr, J. Am. Chem. Soc., 77, 3009 (1955).
12. A. N. Nesmeyanov, E. G. Perevalova and S. S. Churanov, Doklady Akad. Nauk, S.S.S.R., 114, 335 (1957).
13. W. H. Richardson, unpublished observation.
14. R. A. Benkeser, D. Goggin and G. Schroll, J. Am. Chem. Soc., 76, 4025 (1954).
15. A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and L. S. Shilovtseva, Doklady Akad. Nauk, S.S.S.R., 102, 535 (1955).
16. D. W. Mayo, P. D. Shaw and M. Rausch, Chem. and Ind. (London), 1388, 1957.
17. A. N. Nesmeyanov, E. G. Perevalova, A. Z. Beinoravichute and I. L. Malygina, Doklady Akad. Nauk, S.S.S.R., 120, 1263 (1958).

POLYMERS OF GROUP III AND V ELEMENTS

by Anton B. Burg

University of Southern California

The work of this project has been directed toward the discovery of new covalent combinations of elements capable of forming strong bonds and thermally stable compounds. Enough chemical and structural understanding of such combinations should make it possible to incorporate them as useful components in thermally stable high polymers. The element phosphorus is regarded as especially promising for such purposes, for its bonds to carbon often are far harder to break than the corresponding C-N bonds; also, there are phosphine derivatives which can be included in boron-hydride polymers to form interesting transparent resins. Some of these have high thermal stability, practically limited only by a loss of medium-temperature plasticity as hydrogen (and ultimately also methane) is driven out by heating. The possible variety of such phosphorus-boron-hydride resins has been considerably widened by the recent synthesis and study of new kinds of organo-phosphines.

Related to this has been a broad study of new types of chemical bonding involving P-CF_3 bonding. The $(CF_3P)_n$ polymers themselves are not obviously useful as plastics, nor does the $(CF_3)_2P$ radical seem very promising as a polymer component in itself, but both aspects lead to a wide variety of new-type compounds. These are interesting for at least three reasons: they represent the chemical roles that phosphorus might play in fluorocarbon high-polymers; or those having both CF_3 and CH_3 groups on phosphorus may usefully be incorporated in phosphorus-boron-hydride resins; also one can see possible approaches to new polymers involving phosphorus with yet other elements, as in attempts to make $NP(CF_3)_2$ polymers analogous to $NPCl_2$ polymers but probably less likely to alter their degree of polymerization. The chemically related system of S-CF_3 bonded compounds represents the possibility of introducing non-labile electronegative groups into new phosphorus-boron resins. One result of this study was the formation of a compound purporting

to be CF_3BF_2, although not yet rigorously proved to be such. Although unstable, as any CF_3BX_2 compound might be expected to be, it could be the means of forming a phosphorus-boron resin wherein a more highly coordinated boron atom would lead to stable B-CF_3 bonding.

This program has included also a preliminary study of phosphino-aluminum compounds, the polymeric forms of which seem too reactive for great interest to the present purpose, but which might yet be included to advantage in phosphorus-boron resins. There has also been some progress in the chemistry of nitrilophosphoric halides— especially the demonstration of a splitting of trimethylamine to form $(CH_3)_2N$- substitution derivatives without breaking any of the polymer-bonding. This result discredited earlier literature on tertiary-amine adducts of the $NPCl_2$ unit.

Alkylphosphines as Resin Components

The trapping of basic units in a boron-hydride polymer was first indicated some five years ago, when the complex $(CH_3)_2NP(CH_3)_2(BH_3)_2$ was heated to form $(CH_3)_2NH$, $(CH_3)_2PH$, volatile aminoborines, the trimer and some tetramer of the $(CH_3)_2PBH_2$ unit, and a non-volatile glass wherein BH units outnumbered the sum of the $(CH_3)_2N$ and $(CH_3)_2P$ units by more than two to one and the ratio of $(CH_3)_2P$ to $(CH_3)_2N$ units varied from two to six, depending upon experimental conditions. Such resinous materials are made more directly from the pentaborane B_5H_9, the structure of which is based upon the same general principle as a boron-hydride network: a pseudo-metallic pattern with more atom-atom adjacencies than can be bonded by action of the available electrons as classical electron-pair bonds. At first it was supposed that such boron-hydride clumps were serving mostly to connect $(PB)_3$ rings; but the formation of similar resins from $(CH_3)_3P$ with B_5H_9 led to the more widely applicable idea that base units of any kind might be trapped in an extensive boron-hydride network. This idea would imply the inclusion of $(CH_3)_2P$ units, regardless of whether they were present as components in $(PB)_3$ rings, or as connectors between boron-hydride clumps, or in situations to which both of these descriptions would be applicable. These thermally stable resins adhere well to metals or to glass at elevated temperatures but they are mechanically very weak at ordinary temperatures.

Steps toward improvement of their mechanical properties have taken the form of using new types of organophosphines, the synthesis and study of which are described in the following sections.

Tetramethylbiphosphine. The slightly volatile biphosphine $P_2(CH_3)_4$ has been made more conveniently than before, by a direct reaction of the aminophosphine $(CH_3)_2NP(CH_3)_2$ with dimethylphosphine. Equilibrium at a 65% yield of $P_2(CH_3)_4$ can be established fairly quickly by heating the mixture to 100° C., and after the product has been isolated, the remaining mixture can be equilibrated again, and the process repeated. After removal of nearly 90% of the theoretical yield of $P_2(CH_3)_4$, the action of just enough HCl removes all of the $(CH_3)_2N$ groups as the amine hydrochloride, and the yield of the biphosphine approaches 100%.

A resin made from tetramethylbiphosphine and pentaborane-9, and having the approximate empirical formula $[B_{10}H_9(Me_2P)_4]_x$, was submitted to WADC for tests of its dielectric properties. Its thermoplastic range was around 300°C., above which test-samples lost some hydrogen (and methane above 400°C.), with conversion to a cindery brown product at 440°C. Another resin sample was made by the earlier $(CH_3)_2NP(CH_3)_2$-B_5H_9 process, and also submitted for tests of dielectric properties. This sample had a glue-like consistency at 326°C. Its empirical formula was roughly $(B_3H_2Base)_x$, where the base unit was mostly $(CH_3)_2P$.

An Ethylene-Connected Diphosphine. The new compound $(CH_3)_2PC_2H_4P(CH_3)_2$ (m.p. 0°C.; b.p. est. 188°C.) was made by addition of tetramethylbiphosphine to ethylene. The reaction was fairly slow even at 300°C.; but in the presence of a trace of iodine, it approached completion during 120 hours at 267°C. The diphosphine was converted to the double-borine adduct $(CH_3)_2PC_2H_4P(CH_3)_2(BH_3)_2$ quantitatively by reaction with diborane. This adduct was sublimable under high vacuum at 150°C. Attempts to remove a BH_3 group from it, by heating it to higher temperatures with trimethylamine, were only slightly successful, indicating the great strength with which phosphorus in this diphosphine bonds to boron.

A Diphosphine-Cross-Linked Resin. The previously-reported

resins made from trimethylphosphine and pentaborane-9 (ratio of B to P near 5; B:H ratio increasing from 1.4 to 4 between 250 and 490°C.) had shown interesting thermoplastic character but also extreme mechanical weakness. Hence it seemed well to form more internal connections by using the new double tertiary phosphine with pentaborane-9. In order to avoid too much cross linking, the experiment was tried with equimolar proportions of trimethylphosphine and the diphosphine, along with the same molar quantity of pentaborane-9. However, the final resin contained very little trimethylphosphine, the main function of which was the removal of BH_3 groups in the form of $(CH_3)_3PBH_3$. The empirical formula of the resin, after heating to 320°C. in vacuo to remove volatile components, was $[B_{81}H_{36}diph_{13}(Me_2P)_2]_x$, representing a far lower ratio of boron to phosphorus than had been observed when the resin was made only from trimethylphosphine and pentaborane-9. It is reasonable to suppose that much of the diphosphine had BH_3 attached to one P atom, leaving the other P atom to behave uni-functionally in regard to bonding with the boron-hydride polymer network. However, the self-adhesiveness and mechanical strength of the resin had been noticeably improved, so that we are encouraged to try further experimental work along this line.

The Use of a Bis-Phosphino-Amine. The very strong bonding which accounts for the stability of boron nitride made it seem useful to try the inclusion of nitrogen atoms in the phosphino-polyborane type of resin. For this purpose it was convenient to bring pentaborane-9 into reaction with a bis-phosphino-amine which had been discovered some years ago by Wagner and Burg, namely $(CH_3)_2P(NH)P(CH_3)_2$. This was made by the more recent Burg-Slota method: the ammonolysis of $(CH_3)_2NP(CH_3)_2$, from which one obtains also some of the tris-phosphino-amine $[(CH_3)_3P]_3N$ and the biphosphine $P_2(CH_3)_4$.

This bis-phosphino-amine reacted with pentaborane-9 (present in excess) in a molar ratio of 9:7, and the heated reaction-product gave off hydrogen, some dimethylphosphine, and very little else. In reactions of this type, it is safe to assume that all N-P bonds are broken, forming either N-H and P-B bonds or P-H and N-B bonds; then the N-H and P-H bonds react with more B-H bonds to make hydrogen and P-B or N-B bonds. After heating to 356°C., the strictly white non-volatile solid

product had the empirical formula $[B_{15}H_9N_4(Me_2P)_7]_x$. It had plastic character at elevated temperatures, as shown by its tendency to form large, collapsing bubbles in vacuo at 350°C., but it was very fragile and brittle at room temperature. It appeared as a mixture of transparent glass and opaque white lumps, suggesting that some boron nitride might have formed separately, so that few borazine rings were included in the structure of the resin.

The Amino-Cyclic-Phosphine. The compound $(CH_3)_2NPC_4H_8$ was made some time ago and used to make a resin by reaction with pentaborane-9, the main purpose being to include the C_4H_8P ring in a phosphino-polyborane resin. The actual resin from this source was nearly as stable as those derived from $(CH_3)_2NP(CH_3)_2$, the chief difference being that it liberated short-chain hydrocarbons at temperatures at which the simpler resins would give off methane. The accompanying black color apparently did not imply loss of mechanical properties, for the resin seemed to be a little tougher than those not involving any C_4H_8P rings. However, the assumption that the initial aminophosphine had the phosphorus atom in such a ring had not been proved beyond doubt.

This doubt has been corrected in recent studies, wherein the aminophosphine was converted to its mono-BH_3 complex and heated to form the ring phosphine C_4H_8PH and the phosphinoborine $(C_4H_8PBH_2)_3$. The ring phosphine C_4H_8PH was proved to be such by the character of its infra-red spectrum, which was compared with those of pyrrolidine (C_4H_8NH) and tetrahydrofuran (C_4H_8O). It was also used with diborane to make the paddle-wheel trimer $(C_4H_8PBH_2)_3$, which was identified (by its 169°C. melting point) with previously analyzed samples arising as by-product material from the resin-forming reaction or from the aminophosphine-diborane reaction. The formation of the trimer $(C_4H_8PBH_2)_3$ from C_4H_8PH demonstrated that this could not have been an open-chain primary phosphine, which could only have formed more highly polymeric phosphinoborines. The phosphine C_4H_8PH melted at -88°, had an estimated b.p. of 105°, and showed the correct molecular weight. It appears to be the first cyclic P-H compound ever made.

Phosphines Containing the $(CF_3)_2P$ Unit

New Chemistry of $P_2(CF_3)_4$. It has become possible to make the biphosphine without resort to the somewhat tedious reaction of $(CF_3)_2PI$ with mercury, for the reasonably fast reaction $2(CF_3)_2PCl + (CH_3)_3Sb \longrightarrow (CH_3)_3SbCl_2 + P_2(CF_3)_4$ occurs in a fairly clean manner at room temperature. Although the reagent trimethylstibine is not widely and cheaply available, this reaction suggests that there may be other dehalogenating agents which would serve as well.

The activation of this biphosphine for various possible reactions is important because it could become a source of a wide variety of useful new phosphines. Hence it is interesting that $P_2(CF_3)_4$ combines with trimethylphosphine, thereby acquiring chemical properties such as to suggest the interpretive formula $(CH_3)_3PP(CF_3)_2^+ P(CF_3)_2^-$. For example, this complex reacts with HCl to give a high yield of $(CF_3)_2PH$, although $P_2(CF_3)_4$ itself is inert toward HCl and other strong acids.

Another interesting reaction found in our recent work on $P_2(CF_3)_4$ was its addition across the double bond of ethylene, cleanly forming the new diphosphine $(CF_3)_2PC_2H_4P(CF_3)_2$ (m.p. -51°C.; volatility 1.8 mm. at 0°C.) even at room temperature. this result may be understood by regarding $P_2(CF_3)_4$ as a pseudohalogen, wherein the highly electronegative CF_3 groups make the P-P bond especially similar to the Cl-Cl bond. Thus the reaction occurs far more easily than the analogous addition of $P_2(CH_3)_4$ to ethylene. However, it is a curious fact that $P_2(CF_3)_4$ did not add to acetylene in our initial experiments to that purpose; nor was there any better success when we tried activation of the $P_2(CF_3)_4$ with trimethylphosphine. It was also not possible at first to add $P_2(CF_3)_4$ to C_2F_4, although the reaction does succeed when a little iodine is used as a catalyst.

A Hybrid Biphosphine. It has been reported before that tetramethylbiphosphine acts as a strong bifunctional base, which forms either a single or double BH_3 complex— both convertible by heat to phosphinoborine polymers— whereas $P_2(CF_3)_4$ is quite inert toward diborane and has not yet been

converted directly to any phosphinoborine polymers. Hence it seems reasonable that a hybrid biphosphine such as $(CH_3)_2PP(CF_3)_2$ might react with diborane under suitable conditions, eventually to form a phosphinoborine polymer wherein some H on B is replaced by $(CF_3)_2P$ groups. Accordingly this hybrid biphosphine has been synthesized and studied. The method of synthesis was the action of $(CH_3)_2PH$ upon $(CF_3)_2PCl$ in the presence of trimethylamine, leading to 90% yields of the desired $(CH_3)_2PP(CF_3)_2$ (m.p. -79°C.; b.p. est. 120°).

The ultra-violet absorption spectrum of this hybrid biphosphine was compared with those of $P_2(CF_3)_4$ and $P_2(CH_3)_4$, showing a strong maximum at 2330 Å., between those for the two symmetrical biphosphines, but nearer to $P_2(CH_3)_4$ than to $P_2(CF_3)_4$ in both wave-length and intensity. Chemically, however, the hybrid biphosphine differs in many ways from either of its symmetrical analogues.

One of its simplest reactions is a very clean splitting by HCl at room temperature, forming $(CH_3)_2PCl$ and $(CF_3)_2PH$ solely. This demonstrates another new way to make $(CF_3)_2PH$, beyond the new reaction of PH_3 with $(CF_3)_2PI$, recently reported by G.S. Harris (J. Chem. Soc. 1958, 512); but especially interesting is the preferential formation of this phosphine even though no such reaction occurs between HCl and $(CF_3)_2PP(CF_3)_2$. If the HCl added first to the phosphorus atom expected to have the stronger base-action, or if chloride were to go directly to the phosphorus atom which ought to be the better electron-acceptor, the expected phosphines would be $(CF_3)_2PCl$ and $(CH_3)_2PH$; and the formation of the latter would be energetically favored by the formation of a stable hydrochloride. However, it could be argued that the oxidation-reduction potentials would favor the observed result, and somehow the best reaction mechanism leads directly to this.

The hydrolytic splitting of $(CH_3)_2PP(CF_3)_2$ also agrees with the expected oxidation-reduction equilibria— and again opposite to the idea that the proton goes to the more strongly basic phosphorus atom— for the main products are $(CF_3)_2PH$ and the typical disproportionation products of $(CH_3)_2POH$: some $(CH_3)_2PH$ but more of a solid probably consisting of dimethyl-phosphinic acid and its phosphonium salt $(CH_3)_2PH_2^+(CH_3)_2PO O^-$.

Opposite to these tendencies, the reaction of diborane with $(CH_3)_2PP(CF_3)_2$ agreed with the idea that the more strongly basic phosphorus atom attaches the electron acceptor, for the first observable step was the formation of the mono-BH_3 complex $(CH_3)_2PP(CF_3)_2 \cdot BH_3$ (m.p. -30°C.). On heating for 22 hours at 90°C., this was split at the P-P bond, presumably forming the $(CH_3)_2PBH_2$ unit and transferring hydride to the $(CF_3)_2P^+$ unit to make $(CF_3)_2PH$. However, the yield of $(CF_3)_2PH$ was only 46%. The rest of the $(CF_3)_2P$ units remained in the non-volatile rust-orange colored phosphinoborine polymer. These $(CF_3)_2P$ units may not have replaced H on B in the phosphinoborine polymer, for no hydrogen came off at any stage of the process.

In regard to stability, the hybrid biphosphine contrasts poorly with either tetramethylbiphosphine or its perfluoro-analogue, both of which decompose only slowly at 300°C. The point of incipient decomposition of the hybrid biphosphine is around 75°C. At 110°C., one sample was 87% decomposed during seven days, forming a non-volatile brown viscous liquid and volatile products which seemed to be mostly $CH_3P(CF_3)_2$ and $(CH_3)_2PCH_3$. If so, the brown liquid would represent a very interesting copolymerization of CH_3P and CF_3P units.

The behavior of the hybrid biphosphine toward methyl iodide is quite unlike that of either $P_2(CF_3)_4$, which is inert, or $P_2(CH_3)_4$, which rapidly forms a very stable 1:1 adduct. When $(CH_3)_2PP(CF_3)_2$ reacted with CH_3I (45 hours at 50°C. or 10 days at room temperature) the main result was a redistribution of phosphine units to form $P_2(CF_3)_4$ and $P_2(CH_3)_4 \cdot CH_3I$. There was a small yield of $(CF_3)_3P$, indicating some transfer of CF_3 groups from one phosphorus atom to another, but the major course of events seems to have been determined by the high stability of the methiodide of tetramethylbiphosphine. It is not difficult to suggest a mechanism consistent with other knowledge: let the first step be the formation of a methiodide, $(CH_3)_3PP(CF_3)_2^+I^-$; then the positive ion of this would be like that of the complex which we formulated as $(CH_3)_3PP(CF_3)_2^+P(CF_3)_2^-$. Since this is decidedly unstable, reverting easily to $(CH_3)_3P$ and $P_2(CF_3)_4$, we should expect the positive ion of the methiodide to dissociate into $(CH_3)_3P$ and $P(CF_3)_2^+$ for the attack upon $(CH_3)_2PP(CF_3)_2$ to make $(CH_3)_2PP(CH_3)_3I$ and $P_2(CF_3)_4$.

It is worthy of mention that the hybrid biphosphine reacts with trimethylamine to form a 1:1 adduct. This would be most naturally formulated as $(CH_3)_3NP(CF_3)_2^+P(CH_3)_2^-$; however, its reaction with HCl gives a 67% yield of $(CF_3)_2PH$ rather than much of any $(CH_3)_2PH_2Cl$; and this result is more like the HCl cleavage of the hybrid biphosphine itself, than the expected attachment of a proton to the anion of the complex.

In its reaction with ethylene, the hybrid biphosphine differs again from both of the symmetrical biphosphines, for the main result is decomposition to form a brown oil, at temperatures noticeably lower than are required for ordinary thermal decomposition. The ethylene apparently acts as a catalyst, for one mole of it can cause the destruction of three moles of the hybrid biphosphine.

The P-O-P Compound. A study of the consequences of the P-O-P linkage at the phosphine stage of oxidation has begun with the synthesis $2(CF_3)_2PI + Ag_2CO_3 \rightarrow (CF_3)_2POP(CF_3)_2 + 2AgI + CO_2$. The new phosphoxane (m.p. -64°C.; b.p. est. 79°C.) seems to be stable against rearrangement to the biphosphine monoxide form— a type of reaction which may account for the failure of attempts to make $(CH_3)_2POP(CH_3)_2$ from silver carbonate and dimethyl-chlorophosphine. It also proved to be inert toward boron trifluoride, unlike the disiloxanes, which react to make fluorosilanes.

The diphosphoxane reacts with ethylene even at room temperature, forming as a major product a new compound which seems to be $(CF_3)_2PC_2H_4OP(CF_3)_2$ (m.p. 5.0°; b.p. est. 201.7°C.). A more volatile by-product— evidently another new compound— is also under further investigation. The PC_2H_4OP linkage is believed to occur in the polymer derived from the rearrangement of the ring compound $C_2H_4O_2PCF_3$ (q.v.); and the product here offers the opportunity to study the character of this linkage without complications due to polymerization.

A preliminary study of the infra-red spectrum of the diphoxane showed intense absorption at 925 $cm.^{-1}$, corresponding to the P-O-P linkage. There was no evidence of any P=O stretching vibration (range 1310 to 1250 $cm.^{-1}$). However, it has not been decided whether the P-O-P linkage approaches

linearity, as in disiloxane, or only has a wide angle on oxygen as in the silicone polymers. The fact that $(CF_3)_2POP(CF_3)_2$ is slightly more volatile than $P_2(CF_3)_4$ is parallel to the comparison of $H_3SiOSiH_3$ with Si_2H_6.

Phosphines Containing the CF_3P Unit

The CF_3P unit offers a wide variety of chemistry related to polymers. In particular, its bivalent character makes it a possible unit in copolymers, and it is highly eligible for use as a cross-link. Also, it can be used to make alkylphosphines and polyphosphines for trial as components of P-B-H resins; and oxidation of the phosphorus to the pentavalent state (either directly or by rearrangements like the Michaelis and Arbuzov reactions) offers opportunities for formation or modification of polymers. Finally, any new dimensions of variety, such as a full study would demonstrate, should apply to $C_nF_{2n+1}P$ units just as well as to CF_3P. There has been some progress along the lines here indicated, but the subject has only just begun, relative to its large potentiality.

Further Knowledge of the $(CF_3P)_n$ Polymers. A most convenient source of the CF_3P unit is the group of $(CF_3P)_n$ polymers, of which the volatile tetramer and pentamer are made quantitatively by the action of mercury upon CF_3PI_2 at room temperature. They are formed also in good yields by the pyrolysis of $P_2(CF_3)_4$; and we have found recently that the 400°C. thermal conversion of $(CF_3)_2PH$ can be managed in such a way as to yield exclusively HCF_3, $(CF_3P)_4$, $(CF_3P)_5$, and higher CF_3P polymers (not volatile at room temperature) in goodly proportions. Thus the whole system of CF_3P polymers can be got from $(CF_3)_2PH$ by a quantitative process; and has become more accessible as a result of the new PH_3-$(CF_3)_2PI$ method of making $(CF_3)_2PH$ in high yields (G.S. Harris, J. Chem. Soc. 1958 p. 512).

A considerable part of our knowledge of the $(CF_3P)_n$ polymers and their consequences came to publication within the past year: J. Am. Chem.Soc. 80, 6161 (1958). This paper includes much that was not known at the time of the October, 1957 Contractors' Conference: the demonstration of the formula of the biphosphine $(CF_3PH)_2$ (a hydrolysis product of the CF_3P

tetramer); the discovery of the triphosphine $H_2(CF_3P)_3$ as a hydrolysis product of $(CF_3P)_5$ and the demonstration of its formula by a quantitative nickel-catalyzed conversion to CF_3PH_2 and $(CF_3P)_n$; new evidences of directive effects in the basic hydrolysis of P-P bonded chains and rings; and the O_2-oxidation of $(CF_3P)_4$ to the thermally stable but easily hydrolyzable $(CF_3PO_2)_x$ polymers, with no evidence of any true intermediates except unstable peroxides.

Another recent publication, J. Am. Chem. Soc. 80, 2334 (1958), describes CF_3-P-Ni-CO compounds, including polymers based upon the reaction of more than one P atom in $(CF_3P)_4$ and displacement of more than one CO from each nickel atom. The details of these subjects are left to the Journal publications, since there is much later-knowledge to be described here.

Basic Depolymerization of CF_3P Polymers. Quite important to further progress on this subject is the recent discovery that the $(CF_3P)_n$ ring compounds can be depolymerized by bases at room temperature, to form complexes which behave as reactive sources of the CF_3P unit or of open $(CF_3P)_n$ chains. Thus molecular weight studies of $(CF_3P)_4$ with trimethylphosphine as the solvent showed major conversion to $(CH_3)_3PPCF_3$; but high values of the molecular weight, relative to the monomer, made it reasonable to suppose that there were also entities such as $(CH_3)_3P(CF_3P)_n$ in the yellow-brown solutions. Trimethylamine also formed such complexes; and in either case the tertiary base could be removed by high-vacuum distillation at room temperature. After such dissociations, the less-volatile remainder was the equilibrium mixture of about 83% $(CF_3P)_4$ and 17% $(CF_3P)_5$. Thus a catalytic effect was expected and found: a small mixing-in of trimethylphosphine to either $(CF_3P)_4$ or $(CF_3P)_5$ caused a fairly rapid conversion to the equilibrium mixture.

A complex such as $(CH_3)_3PPCF_3$ would be expected to act as a base, through employment of a lone-pair of electrons on P as an agent for bonding to Lewis acids; or if the trimethylphosphine were in course of being removed, the free CF_3P unit could act as a Lewis acid (electron-acceptor) itself. Hence it became interesting to try the action of HCl upon $(CH_3)_3PPCF_3$. The main result of the room-temperature reaction was the removal of the trimethylphosphine as the hydrochloride, leaving the CF_3P

units to form what seems to have been mostly the $(CF_3P)_x$ high polymer. Some CF_3PH_2 and CF_3PCl_2 also were formed; and the possibility of some CF_3PHCl was not eliminated. Perhaps of greater interest was the action of methyl chloride upon the complex $(CH_3)_3PPCF_3$ and its chain congeners. This slower process seems to have produced some methylated polyphosphines, the nature of which is still under investigation.

Alcohol Reactions of the Tetramer. The reaction of $(CF_3P)_4$ with either methanol or ethylene-glycol leads to yields of the triphosphine $H_2(CF_3P)_3$ as high as 50%. In the methanol case (reaction below room temperature) it was possible to show that the P-P bond had been broken in a fairly random manner, after the initial formation of the open-chain $CH_3O(CF_3P)_4H$. Thus there were noticeable yields of CF_3PH_2 and $(CF_3PH)_2$ as well as the triphosphine; and the methoxy-PCF_3 compounds included CH_3OPHCF_3, $(CH_3O)_2PCF_3$, $CH_3O(CF_3P)_2H$, and less volatile material which might well involve doubly methoxylated P_2 and P_3 chains. The ethylene-glycol reaction was far slower, requiring extensive heating at 100°C. for a reasonable degree of completion. This experiment, involving equimolar proportions of $(CF_3P)_4$ and $C_2H_4(OH)_2$, was done in tetralin as the solvent, with the hope that the initially-formed $HOC_2H_4O(CF_3P)_4H$ would undergo internal self-alcoholysis more than intermolecular alcoholysis. Thus the favored formation of the stable five-membered-ring compound $C_2H_4O_2PCF_3$ would enhance the yield of the triphosphine by leaving only hydrogen for the ends of the P_3 chain. Actually, the yield of the volatile fraction corresponding to $C_2H_4O_2PCF_3$ (13 mm. at 0°C.) represented 75% of the ethylene-glycol and was mole-for mole equivalent to the unrecovered $(CF_3P)_4$. The other volatile products, expressed in moles per mole of used-up $(CF_3P)_4$, were $0.50H_2(CF_3P)_3$, $0.07CF_3PH_2$, $0.02(CF_3PH)_2$, and $0.013HCF_3$. Analogues of the methoxy-polyphosphines doubtless were present among the non-volatile products.

Character of the Triphosphine. The triphosphine $H_2(CF_3P)_3$ showed vapor-tension values implying a normal boiling point of 124°C. Its melting point is below the temperature range in which it is appreciably volatile. Its decomposition into $(CF_3P)_n$ and $(CF_3PH)_2$ is mildly catalyzed by mercury, but far more strongly by even such a trace of a tertiary phosphine as

may be absorbed into the grease of a stop-cock. An 8% portion of trimethylphosphine added to a sample of $H_2(CF_3P)_3$ acted in a few minutes at room temperature to give an 87% yield of $(CF_3PH)_2$ and 91% of the calculated CF_3P tetramer-pentamer mixture. This appears to be the best way to get good yields of the biphosphine $(CF_3PH)_2$. The catalysis seems to be related to the formation of the complex $(CH_3)_3PPCF_3$.

Polymerization of the Glycol-Ring Phosphine. The volatile material which seemed to be the ring compound $C_2H_4O_2PCF_3$ was stored for some weeks with some slight access of air and water-vapor, and changed almost entirely to a glassy-gummy non-volatile material, from which scarcely any volatile components could be recovered. It seems most probable, although not finally proved, that the change was due to the typical rearrangement of an alkyl phosphine to the phosphine-oxide form. This would mean a polymer based upon the unit $-OC_2H_4\overset{O}{\overset{\|}{P}}CF_3$ which would be a new type related to the phosphinic acids. The possible utility of such a type is interesting to consider, but much is yet to be done toward testing its reality.

Some Consequences of the CF_3S Chemistry

For some time work has been going on, concerning the possible application of CF_3-S compounds to polymer chemistry. The compound CF_3SSCF_3 was converted by ammonia to CF_3SNH_2, which reacted with HCl to make CF_3SCl. Very recently the new volatile $CF_3SN(CH_3)_2$ (m.p. -99°C.; b.p. est. 52°) was made in a similar manner. The reaction of CF_3SCl with diborane was shown to produce small yields of a new volatile material having all the properties expected of CF_3BF_2, a substance which would be highly desirable for possible use in making B-CF_3 derivatives of phosphinoborine polymers. The substance is a stronger electron-acceptor than BF_3, as expected on account of the failure of the CF_3 group to participate in back-coordination to boron as the F atom does. Its tendency to decompose into boron trifluoride and a white polymer would correspond to expectations which we argued in our earliest Air Force Reports. Sulfur has been proved to be absent from the purified $(CH_3)_2O$ complex of this substance. The infra-red spectrum clearly showed the CF_3 group, which was prominent also in the mass spectrogram. The mass spectrogram also gave an indication of $CF_3BF_2^+$ particles with the proper ratio of boron isotopes. As

yet, however, a dependable elementary analysis has not been obtained.

Chemistry of Phosphorus Aluminum Bonding

The promising character of phosphorus-boron compounds, in relation to the search for thermally stable polymers, led to the question whether phosphorus-aluminum bonding would support similarly attractive polymer systems. It was expected that the higher coordination number of aluminum would make the P-Al-H compounds easier to hydrolyze than the corresponding P-B-H materials; and indeed this was true of the $[(CH_3)_2PAl(CH_3)_2]_3$ which was described by Davidson and Brown, J. Am. Chem. Soc. 64, 316 (1942). However, the chance of finding some strongly-bonded situations made the subject worthy of fuller scrutiny.

For the synthesis of phosphino-aluminum hydrides it was necessary to work in liquid dimethylphosphine as the solvent, for the ether solutions of aluminum hydride were not reactive enough toward dimethylphosphine. In fact, it was considerably easier to get a precipitate of aluminum hydride with a small inclusion of P-Al bonded material, than to attach AlH_3 to $(CH_3)_2PH$ for the usual first stage of a phosphinolysis. On the other hand, when $LiAlH_4$ and Al_2Cl_6 were mixed in liquid $(CH_3)_2PH$, the phosphinolysis went beyond the first stage, represented by the formula $(CH_3)_2PAlH_2$. This composition was obtained more cleanly by the reaction $(CH_3)_2PCl + LiAlH_4 \longrightarrow (CH_3)_2PAlH_2 + H_2 + LiCl$, again in liquid dimethylphosphine. The degree of polymerization of this phosphino-aluminum hydride was not determined. It proved to be easily hydrolyzable and not very resistant to heat, on account of the weakness of Al-H bonding. The phosphinolysis of $LiAlH_4$ itself could be pushed as far as the stage represented by the formula $LiHAl(PMe_2)_3$. This product also was easily hydrolyzable, but may prove to be useful as a source of the prospective compound $Al(PMe_2)_3$.

Compositions corresponding to $HAlCl_2$ and H_2AlCl were formed in liquid dimethylphosphine, with which they reacted to form materials analyzing as $(CH_3)_2PAlCl_2$ and $[(CH_3)_2P]_2AlCl$. These slowly precipitated from the dimethylphosphine solution, but were soluble in benzene. Dependable molecular weights could not be obtained. On heating in vacuo, these materials

gave sublimates (near 300°C.) richer in chloride and residues having higher P:Al ratios. Again, such materials were easily hydrolyzed, and accordingly not difficult to analyze. On the whole, it appears that the P-Al compounds are not very useful as polymers themselves, but the presence of P-Al bonds in other polymers might have beneficial effects yet to be determined.

Chemistry of Nitrilophosphoric Halides

Our studies on the chemistry of the $NPCl_2$ and NPF_2 ring polymers have been published: J. Am. Chem. Soc. 81, 836 (1959). It was shown that $(NPCl_2)_3$ splits $(CH_3)_3N$ even at room temperature, placing $(CH_3)_2N$ groups on P and forming $(CH_3)_4NCl$ without disturbing the $(NP)_3$ ring. This result contradicted the dissertation by Schäpperkötter (Münster, 1925), who claimed to have formed complexes of monomeric $NPCl_2$ with many tertiary amines. We found that triethylamine and pyridine do not appreciably attack $(NPCl_2)_3$, nor are the NPF_2 trimer or tetramer much affected even by trimethylamine. The $(CH_3)_3N$-$(NPCl_2)_n$ reactions seem unique, and offer a fairly clean way to insert $(CH_3)_2N$ groups in place of chlorine on phosphorus.

Substitution of alkyl groups for halide on phosphorus has been a long-standing problem in this field, for the usual organo-metallic reagents are inert toward $(NPCl_2)_3$ except under conditions so violent as to destroy the desired product. Very recently the trimer and tetramer of $(CH_3)_2PN$ were made by the reaction between $(CH_3)_2PCl_3$ and NH_4Cl: H.T. Searle, Proc. Chem. Soc. 1959, p. 7. A somewhat similar ammonolysis to form some higher alkyl derivatives was done under Haber at the Naval Ordnance Laboratory in Corona, California. Our own work has shown that $(NPCl_2)_3$ reacts well enough with sodium acetylide (NaC_2H), forming polymeric material in which it appears that the $(NP)_3$ rings are connected by C-C units. The first sample of this polymer was not unusually stable toward heat, but there are yet some possibilities for modifications leading to stabler material. In particular, the C-C bonding probably is to some extent unsaturated, and would become less reactive on treatment with appropriate reagents.

PHOSPHINOBORINE POLYMERS

Ross I. Wagner

American Potash & Chemical Corporation
Whittier, California

I. Introduction

The primary objective of our research program in the field of phosphinoborine compounds is to develop the syntheses and chemistry of candidate materials for use as elastomers, adhesives and/or fluids at elevated temperatures. The phosphinoborines offer a promising field of study since as a class these compounds show unusual resistance to thermal decomposition and to oxidative and hydrolytic attack.

Initial work led mainly to cyclic phosphinoborine trimers and tetramers which were used as model compounds to study the effects of a variety of substituents on physical and chemical properties. The only P-substituent found to effect preparation of higher polymers was hydrogen but these polymers were markedly unstable to oxygen. Among the trimeric compounds aryl substituents on phosphorus enhance oxidative stability over aliphatic substituted derivatives. B-Halogen substituents resulted in decreased hydrolytic stability compared with analogous B-H compounds. Of the cyclic phosphinoborines the trimers, which appear more stable thermally than tetramers, are all of comparable thermal stability.

II. Discussion

A. Phosphinoborines

1. Linear Phosphinoborine Polymers

a. Dimethylphosphinoborine Polymer

A series of pyrolyses of dimethylphosphine borine according to the equation:

$$n(CH_3)_2PHBH_3 + R_3N \xrightarrow{\Delta} \left[(CH_3)_2PBH_2\right]_n NR_3 + nH_2 \qquad (1)$$

was performed on a 7-15 mmole scale to determine the feasibility of preparing linear phosphinoborine polymers as well as the effects of some of the reaction variables. The addition of a basic chain-end blocking group to the reaction mixture presumably causes the formation of a coordinate link between the basic group and the boron atom of dimethylphosphinoborine monomer, thereby suppressing the facile formation of cyclic trimeric and tetrameric dimethylphosphinoborine, which are formed exclusively in the absence of a blocking group, and thus allowing a linear polymer to grow. At present the assumption that the polymers are linear is not supported

by any direct experimental evidence but indirect evidence (vide infra) favors this configuration. Alternate structures are hard to visualize except possibly macro rings which then would contain no chain-end blocking groups.

The preliminary results of experiments designed to test the effect of temperature, heating time, nature of chain-end blocking groups, presence of stainless steel, a large glass surface, and added linear polymer on the yield of linear polymer are presented in Table I. Variations of time and temperature in both the preparation and the work-up of the product tend to render the yield and molecular weight data qualitative at best. Inspection of Table I reveals that reaction temperature and nature of the chain-end blocking group appear to influence most the yield of linear polymer. The startling decrease of linear polymer yield at 238-48°C. (experiments 5-7) relative to that obtained at 200°C. indicates that trimeric and tetrameric products are thermodynamically more stable than linear polymer. Thermal stability studies confirm the greater stability of the cyclic configurations. The equally startling decrease in yield when triethylenediamine was used as a blocking group (experiments 30-31) suggests that the rate of depolymerization is equal or greater than the rate of polymerization.

The addition of polymer in experiments 2 and 8 was to supply preformed chains throughout the reaction in the hope that longer chains might be formed; the low yields of polymer suggest that too few chain ends were present to allow significant chain growth. The addition of stainless steel filings in experiment 24 was to determine whether stainless steel vessels could be used for the preparation of large amounts of polymer without undue lowering of the yield. The effect of a large glass surface was tested in experiment 23 by packing the reaction tube with Pyrex glass wool. It would appear that a large surface area is somewhat detrimental to the yield of polymer. Experiment 11 with dimethylamine as a blocking group was only moderately successful; the possibility existed here that a small amount of dimethylaminoborine might serve as a chain-end but it is not certain whether any dimethylaminoborine actually formed.

A large scale preparation of dimethylphosphinoborine linear polymer was successfully carried out in 53.3% yield using a high pressure stainless steel bomb (experiment 17). The isopiestically determined molecular weight of the polymer was 6014 corresponding to a degree of polymerization of 80. The slightly higher yield obtained in this large run when compared with the yield of corresponding vacuum line experiments can be ascribed to the higher concentration of reactants under the conditions of the large run. Another large scale preparation (experiment 18) produced only a 1% yield of polymer probably because most of the triethylamine in the reaction mixture was complexed with excess diborane.

In an attempt to prepare dimethylphosphinoborine linear polymer at atmospheric pressure, two pyrolyses of dimethylphosphine borine were done; one in the presence of triethylamine and the other in the presence of tri-n-butylamine. In both cases only dimethylphosphinoborine trimer and tetramer formed presumably either because of the loss of

TABLE I

Results of Preliminary Dimethylphosphine Borine Pyrolysis
Experiments with Chain-End Blocking Agents

Expt.	Chain-End Blocking Group	Blocking Group: $(CH_3)_2PHBH_3$ Mole Ratio	Reaction Time, hrs.	Reaction Temp.,[a] °C.	Per Cent Yield Products			Polymer	
					H_2	Trimer and Tetramer	Polymer	m.p. (corr), °C.	D.P.
1	$(CH_3)_2PH$	1.1	63	150					
			35	180	100.9	67.5	33.3	159-61	43
2[b]	$(CH_3)_2PH$	1	17	180	-	79.7	ca 0.1[d]	161-71	43
3	$(CH_3)_2PH$	2	17.5	200	106.0	78.0	20.4	176-80	-
4	$(CH_3)_2PH$	0.1	16	200	98.7	69.9	31.6	164-65	-
5	$(CH_3)_2PH$	0.9	16.5	248	99.5	97.6	2.4[e]	-	-
6	$(CH_3)_2PH$	0.1	16.5	237	99.2	96.6	3.4[e]	-	-
7	none	0	16.5	238	98.0	98.8	1.2[e]	-	-
8[c]	none	0	17	180	96.4	87.4	8.3	163-66	43
9	$(CH_3)_2PH$ $(CH_3)_3N$	0.8	20	200	99.2	71.9	25.4	167-68	-
10	$(CH_3)_3P$	0.34	35	200	102.4	88.5	9.2	148-55	-
11	$(CH_3)_2NH$	0.04	21	200	-	74.9	21.4	164-65	-
12	$(CH_3)_3N$	1	40	200	96.5	72.9	22.8	164-67	-
13	$(CH_3)_3N$	0.5	36	200	-	60.6	35.7	167-68	-
14	$(CH_3)_3N$	0.1	21	200	96.1	63.4	33.4	163-66	-
15	$(C_2H_5)_3N$	1.05	19	200	100.6	-	55.5	160-66	-
16	$(C_2H_5)_3N$	1	44	200	99.6	57.9	39.0	156-61	-
17	$(C_2H_5)_3N$	0.43	29	200	91.5	34.6	53.3	170-72	80
18	$(C_2H_5)_3N$	0.04	48	185	94.6	95.5	1.3	168-70	-
19	$(C_2H_5)_3N$	0.15	23	200	96.3	56.0	42.8	164-66	-
20	$(C_2H_5)_3N$	0.13	17	200	96.1	58.1	38.6	156-59	-
21	$(C_2H_5)_3N$	0.12	14	200	95.8	67.5	30.8	155-60	-
22	$(C_2H_5)_3N$	0.1	17	200	96.8	50.2	44.5	164-68	-

TABLE I (Cont'd.)

Expt.	Chain-End Blocking Group	Blocking Group: $(CH_3)_2PHBH_3$ Mole Ratio	Reaction Time, hrs.	Reaction Temp., (a) °C.	Per Cent Yield Products			Polymer	
					H_2	Trimer and Tetramer	Polymer	m.p. (corr), °C.	D.P.
23 (g)	$(C_2H_5)_3N$	0.1	23	200	97.0	65.5	27.7	160-63	-
24 (h)	$(C_2H_5)_3N$	0.08	20	200	-	54.6	39.8	155-67	-
25	$(C_2H_5)_3N$	0.02	22	200	95.7	50.2	47.0	160-65	-
26	$(C_4H_9)_3N$	0.18	20	200	101.3	-	44.6	164-68	-
27	$[(C_2H_5)_2NCH_2]_2$	0.24	19	200	97.6	-	57.7	169-72	183
28	$[(CH_3)_2NCH_2]_2$	0.35	21	200	101.3	-	41.9	159-61	-
29	$CH_3\underline{NCH_2CH_2NHCH_2CH_2}$	0.55	20	200	129.7	-	38.1	166	-
30	$N(CH_2CH_2)_3N$	0.44	20	200	70.5	-	-	-	-
31	$N(CH_2CH_2)_3N$	0.39	55	200	92.5	-	1.1	175-83	-

(a) Temperatures varied ±15°C.
(b) 4.7 cc. of polymer from expt. 1 added.
(c) 6.9 cc. of polymer from expt. 1 added.
(d) Reaction not carried to completion.
(e) By difference, polymer not isolated.
(f) Volume in liters at STP; expt. run in stainless steel bomb.
(g) Reaction tube packed with glass wool.
(h) 280 mg. of stainless steel filings added to reaction tube.

dimethylphosphine from the reaction zone by a displacement reaction forming triethylamine borine or simple volatilization of the tertiary amine from the reaction zone. In an experiment in a sealed tube (experiment 26) tri-n-butylamine was as effective in promoting the formation of linear polymer as triethylamine.

N,N,N',N'-Tetraethylethylenediamine as the chain-end blocking group has led thus far to the best yields of linear polymer although triethylamine is almost as effective. In general, the yield of polymer is better when tertiary amines are used as chain-end blocking groups rather than phosphines. A series of quantitative experiments will be required before the effects of base strength and steric requirements of the end-group on the yield and degree of polymerization of the polymers may be defined.

The degree of polymerization (D.P.) of the combined linear polymers formed in experiments 1, 2, and 8 was determined by Rast micro and isopiestic methods. The former method gave D.P. 11.3 and the latter D.P. 43. The large discrepancy between D.P. values for the two methods can be rationalized since the Rast method is known to be notoriously inaccurate with phosphorus compounds and high molecular weight compounds while the isopiestic method is considered to be accurate within about 5%. All other linear polymer molecular weight data were determined isopiestically.

b. Other P,P-Disubstituted Phosphinoborine Polymers

The pyrolysis of methylethylphosphine borine in the presence of triethylamine produced a linear polymer in 43% yield having plastic-like properties. The polymer is a translucent colorless plastic material of m.p. 118-26°C. having an isopiestically determined molecular weight of 1836 which corresponds to a degree of polymerization of 20. The polymer is quite soluble in benzene, unlike dimethylphosphinoborine linear polymer, and its solubility can be ascribed to its relatively low molecular weight and low crystal lattice energy. The lower degree of polymerization of this methylethylphosphinoborine linear polymer relative to that of dimethylphosphinoborine linear polymers obtained under similar conditions possibly may be ascribed to a slower rate of chain growth caused by the larger bulk of the ethyl group relative to a methyl group.

Diethylphosphinoborine linear polymer, prepared in 16.7% yield, is a brittle, translucent white solid, m.p. 263-67°C., sufficiently insoluble in benzene to prevent determination of the molecular weight. The poor yield may be a result of the use of too high a sublimation temperature during the separation of the volatile material under high vacuum.

Methyl-n-propylphosphinoborine linear polymer of molecular weight 1062 (D.P. 10.4) was prepared in 55.4% yield; it is an extremely viscous, colorless liquid. Methyl-i-propyl-, cyclotetramethylene-, and methylphenylphosphinoborine linear polymers have been prepared, the first two in 2.7% and 8.2% yield, respectively. The yield of the latter polymer could not be measured directly since trimeric and tetrameric by-products

could not be removed from the polymer. However, the molecular weight of the product mixture, 787 (D.P. 5.8), indicated the presence of higher molecular weight species than trimer and tetramer in a yield comparable to that of dimethylphosphinoborine polymer. All of the above products are extremely viscous liquids soluble in most common organic solvents and therefore probably have relatively low molecular weights. Insufficient material was obtained to permit molecular weight determinations on the methyl-i-propyl- and cyclotetramethylenephosphinoborine polymers.

Attempts to form linear polymers by pyrolysis of methyldodecyl-, diphenyl-, and dicyclohexylphosphine borines in the presence of triethylamine appears to have produced mainly trimeric and tetrameric products. With the diphenyl- and dicyclohexyl- derivatives, pure trimers were isolated and characterized. The residue obtained on evaporation of the mother liquor from the diphenylphosphinoborine trimer crystallization had a molecular weight suggesting it to be either linear dimer or cyclic trimer with a low molecular weight contaminant. With the methyldodecyl-derivative a very small amount of linear polymer may have formed, but could not be isolated because the very low volatilities of trimer and tetramer do not permit fractional distillation of the mixture. The molecular weight of the methyldodecyl- product mixture prepared under linear conditions was 870 (D.P. 3.8) and that of the reference trimer-tetramer mixture (vide infra) was 829 (D.P. 3.6) which is somewhat tenuous evidence for the presence of some higher molecular weight species. Also, the refractive index of the reference trimer-tetramer mixture is slightly lower than that of the material of molecular weight 870. The reasons for inhibition of linear polymer formation in these cases are at present unknown but may well be related to the steric bulk of the substituents on phosphorus and their effect on the relative rates of formation of cyclic and straight chain species.

An attempt to prepare methylallylphosphinoborine linear polymer resulted in isolation in 78.8% yield of a foamy, clear, extremely brittle benzene-soluble solid, m.p. 76-78°C., which showed no residual unsaturation in an infrared spectrum. The data are insufficient to indicate whether the material obtained resulted from addition of a P-H or B-H bond to the olefinic linkage or from addition polymerization of the carbon unsaturation. The polymer is doubtless a somewhat cross-linked phosphinoborine of low molecular weight.

c. Attempt to Prepare Linear Dimethylphosphinodimethylborine Polymer

The dehydrohalogenation of dimethylphosphine dimethylbromoborine in the presence of a 20% excess of triethylamine produced a 63.8% yield of dimethylphosphinodimethylborine trimer but no linear polymer. The bulk of the non-trimeric material was more volatile than the trimer. Pyrolysis of a portion of this fraction yielded hydrogen, methane, dimethylphosphine, an unidentified volatile, dimethylphosphinodimethylborine trimer and an uncharacterized tacky liquid residue.

Another experiment using conventional equipment in a hydrocarbon solvent yielded no identifiable products.

d. Copyrolysis of the Binary Phosphine Borine Systems Dimethyl- Methyldodecyl- and Methylethyl- Methylallyl- in the Presence of Triethylamine

Pyrolyses of dimethyl- with methyldodecylphosphine borine and methylethyl- with methylallylphosphine borine in the presence of triethylamine led in both systems to waxy polymers of m.p. 122-25°C. and m.p. 77-85°C., respectively. In the former system the polymer exhibits properties expected of a plasticised dimethylphosphinoborine polymer. The question whether the methyldodecylphosphinoborine units are incorporated in the polymer or in trimers which act as plasticizers cannot be answered without additional data. The structure of the polymer formed in the latter system is unknown at the present time. An attempt to prepare methylallylphosphinoborine trimer for reference purposes resulted in a mixture of benzene-soluble liquid and insoluble solid (m.p. 145-57°C.) materials. Neither material showed the presence of unsaturation in infrared spectra, a result consistent with the previously mentioned attempt to prepare linear methylallylphosphinoborine polymer. This information suggests that the products consist of phosphinoborine rings cross-linked by saturated carbon chains.

e. Dimethylphosphinoborine--Methylphosphinoborine and Methylethylphosphinoborine--Methylphosphinoborine Copolymers

In two separate experiments methylethylphosphine borine and dimethylphosphine borine mixed with methylphosphine borine in ratios of 4:1 and 9:1 were pyrolyzed in the presence of triethylamine and gave 13.1% and 27.6% yields, respectively, of products which were not volatile at 200°C. in high vacuum. The 13.1% product was a tacky, cloudy semisolid and the 27.6% product was a brittle, translucent glass. The structures of the two products are unknown but may correspond to multi-ring B-P copolymers, branched linear polymers or linear polymers which have been cross-linked by the CH_3P- group.

f. Reactions of Linear Dimethylphosphinoborine Polymer

Chlorination of dimethylphosphinoborine linear polymer was accomplished with methyl chloride in the presence of aluminum chloride. A 78.6% yield of colorless, powdery chlorinated polymer was obtained which did not melt below 360°C. and was insoluble in common organic solvents and dilute acid.

A number of polymer growth experiments have been done in which dimethylphosphinoborine linear polymer was treated with various acids in an effort to remove some of the basic end groups and thus allow the new free chain-ends to combine with other polymer chain-ends. Treatment of polymer at 180°C. with a deficiency of hydrogen chloride gave a

product slightly more flexible than starting material. A molecular weight determination showed the D.P. to have increased from 80 to 167. Partial thermal degradation of another sample of polymer (D.P. 80) by gentle flaming at about the melting point (172°C.) in high vacuum left about 85% of the starting material as nonvolatile residue which had D.P. 87 as determined by the isopiestic method. Tentatively it appears that chain-lengthening may be thermally induced but is enhanced in the presence of hydrogen chloride. Several more definitive experiments are required. In a similar experiment the polymer was treated with a deficiency of boron trifluoride and was mostly converted to trimer. Several experiments conducted in refluxing solvents containing deficiencies of p-toluenesulfonic acid, boron trifluoride etherate, or aqueous hydrochloric acid appeared to have no effect on the polymer.

2. Cyclic Phosphinoborine Polymers

a. Syntheses of Cyclic Phosphinoborines

The syntheses of methyldodecyl-, cyclotetramethylene-, dicyclohexyl-, and diphenylphosphinoborine trimers by pyrolysis of the corresponding phosphine borines were without complication and served to provide in several instances practical experience in handling relatively large amounts of material.

Similarly, copyrolysis of a 3:1 mixture of dimethyl- and methylphosphine borines produced a nonvolatile copolymer glass and by-product dimethylphosphinoborine trimer, the latter in an amount predicted from previous experiments using different reactant ratios. In addition, diphenylphosphinoborine trimer has been prepared by pyrolysis of the reduction product of diphenylphosphinic chloride and sodium borohydride thus extending the scope of this reaction from aliphatic to aromatic derivatives. Attempts to prepare trimeric phosphinoborines carrying unsaturated substituents on phosphorus appeared to yield products without residual carbon-carbon unsaturation. The double bonds survive the preparation of the phosphine borine adducts but react on standing.

A series of phosphine haloborines was treated with triethylamine to affect dehydrohalogenation. Although dimethylphosphinodimethylborine trimer was prepared on a large scale without difficulty using high vacuum techniques, the synthesis failed when done in conventional bench equipment. Trace amounts of oxygen and water introduced with the nitrogen atmosphere may have caused the failure. Phenylmethylphosphine dimethylbromoborine, diphenylphosphine dimethylbromoborine, phenylmethylphosphine diethylchloroborine, and cyclotetramethylenephosphinodiethylchloroborine, each produced a good yield of by-product triethylammonium halide on dehydrohalogenation with triethylamine but only from the first of these compounds could any trimeric phosphinoborine be isolated and characterized. Apparently the trimerization is dependent on both the steric requirements and the base and acid strengths of the phosphorus and boron moieties, with the monomers formed from weaker bases and acids being internally compensated to a greater degree.

b. Kinetics of Dimethylphosphine Borine Pyrolysis

Second-order plots shown in Figure 1 were made for the vapor phase pyrolyses of dimethylphosphine borine carried out at each temperature. In each case, a straight line was obtained, indicating that the reaction remained second-order throughout the temperature range studied. An Arrhenius plot of the rate data is shown in Figure 2, from which the activation energy was determined as 36.7 kcal. $mole^{-1}$ and the preexponential term as 6.8×10^{19} cc. $mole^{-1}$ $sec.^{-1}$.

Kinetic studies of dimethylphosphine borine in the liquid phase required a knowledge of density values of the adduct at 140°C. and higher. Due to rapid decomposition, it was not considered practicable to determine densities at these temperatures and thus density determinations made at lower temperatures were extrapolated to higher temperatures. The volume of 0.2746 g. dimethylphosphine borine was measured at a series of temperatures between 0°C. and 86°C. to determine the equation $d = 0.7785 - 0.000750t$ for the density (g./cc.) of dimethylphosphine borine as a function of temperature (°C.).

Three pyrolyses of dimethylphosphine borine liquid-vapor systems were carried out at 140.0°C. such that approximately three-fourths of the adduct would be present initially as the liquid phase under reaction conditions. The kinetic results for one run are plotted in Figure 3. Different order plots of the data of this run were made to attempt to obtain a gross over-all order for the pyrolysis. A plot of $n^{-1.5}$ vs. time gave a straight line, indicating a gross order of 2.5. However, in view of the heterogeneous nature of the system, this value is not considered mechanistically significant. Further analysis of the data will require time-consuming approximation methods and will be pursued as time permits.

c. Reactions of Cyclic Phosphinoborines

In two separate attempts to find a means of B-chlorinating phosphinoborines without using pressure vessels, n-butyl chloride and carbon tetrachloride were used as a solvent and chlorinating agent in the reaction:

$$[(CH_3)_2PBH_2]_3 + 6RCl \xrightarrow{AlCl_3} [(CH_3)_2PBCl_2]_3 + 6RH \qquad (2)$$

The aluminum chloride catalyzed reaction using carbon tetrachloride appears to be a much more satisfactory method because of the absence of by-product oils formed as a result of solvent decomposition.

All six hydridic hydrogens in methylethylphosphinoborine trimer on treatment with methyl chloride--aluminum chloride were replaced by chlorine rather than just five as found when carbon tetrachloride alone was used as a chlorinating agent. Evidently steric hindrance is not as important in the aluminum chloride catalyzed reaction. This same reasoning apparently does not apply in the case of the bicyclic dimethylphosphinoborine--

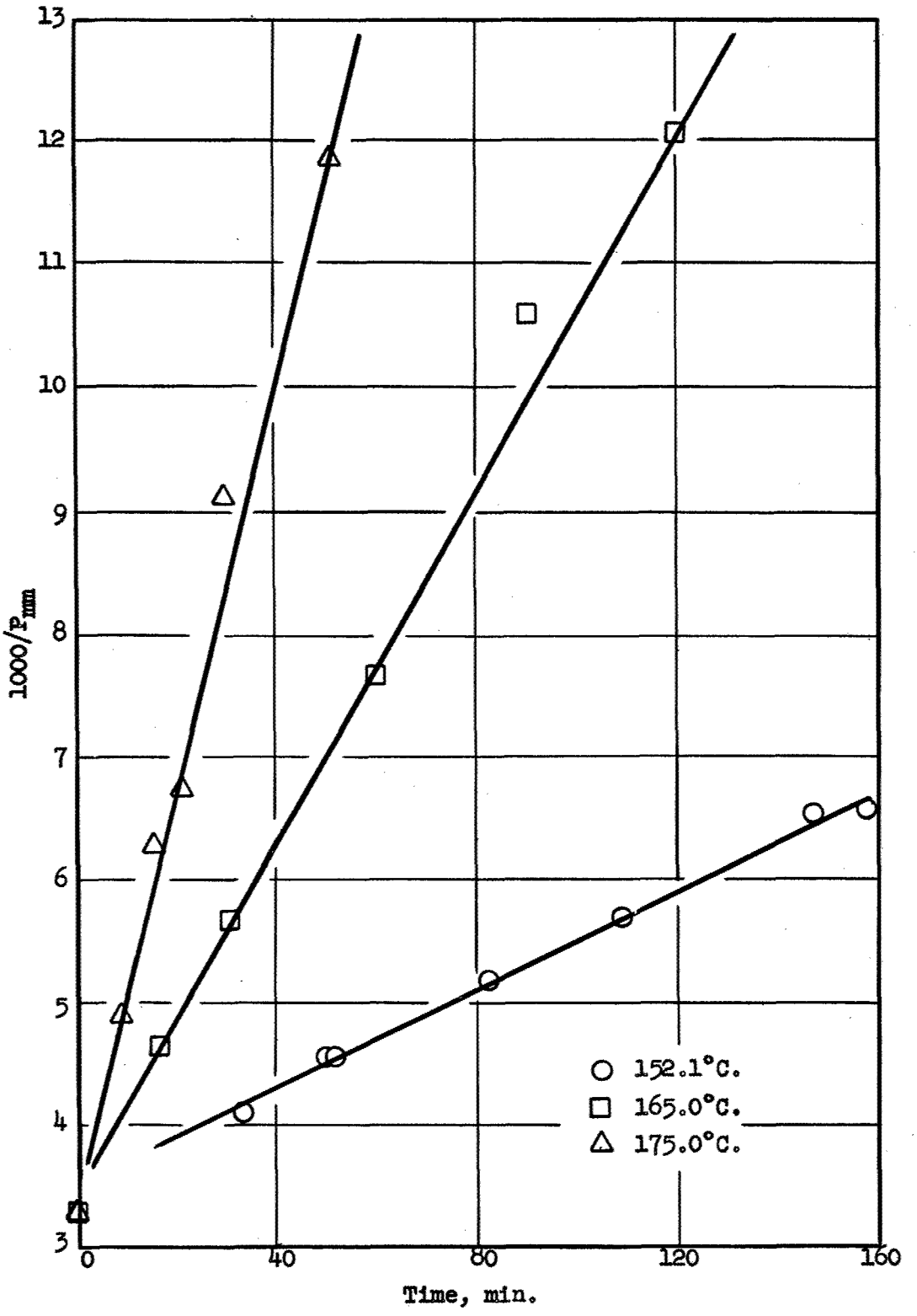


Figure 1. Second Order Plot for the Pyrolysis of Dimethylphosphine Borine

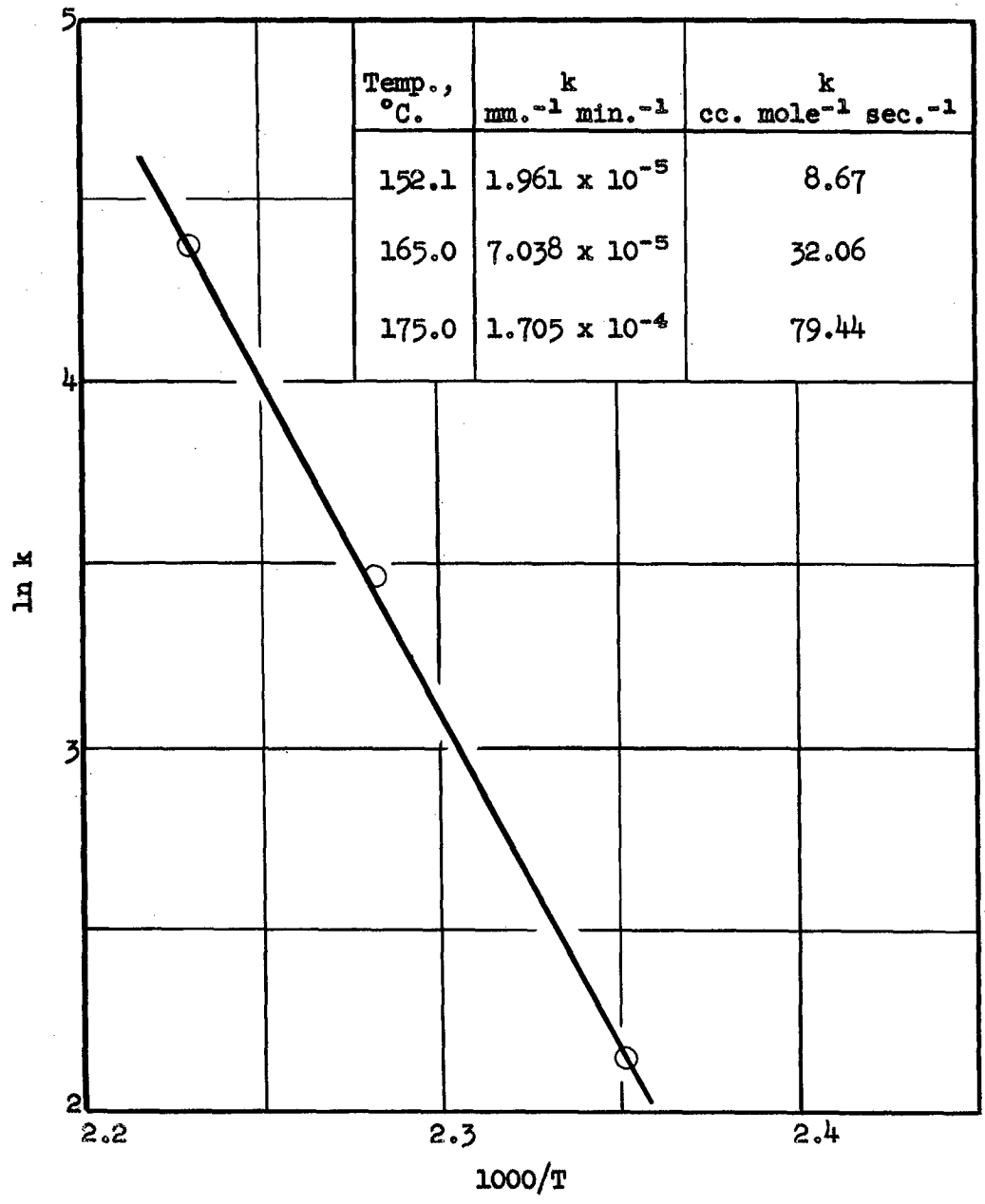


Figure 2. Arrhenius Plot for Pyrolysis of Dimethylphosphine Borine

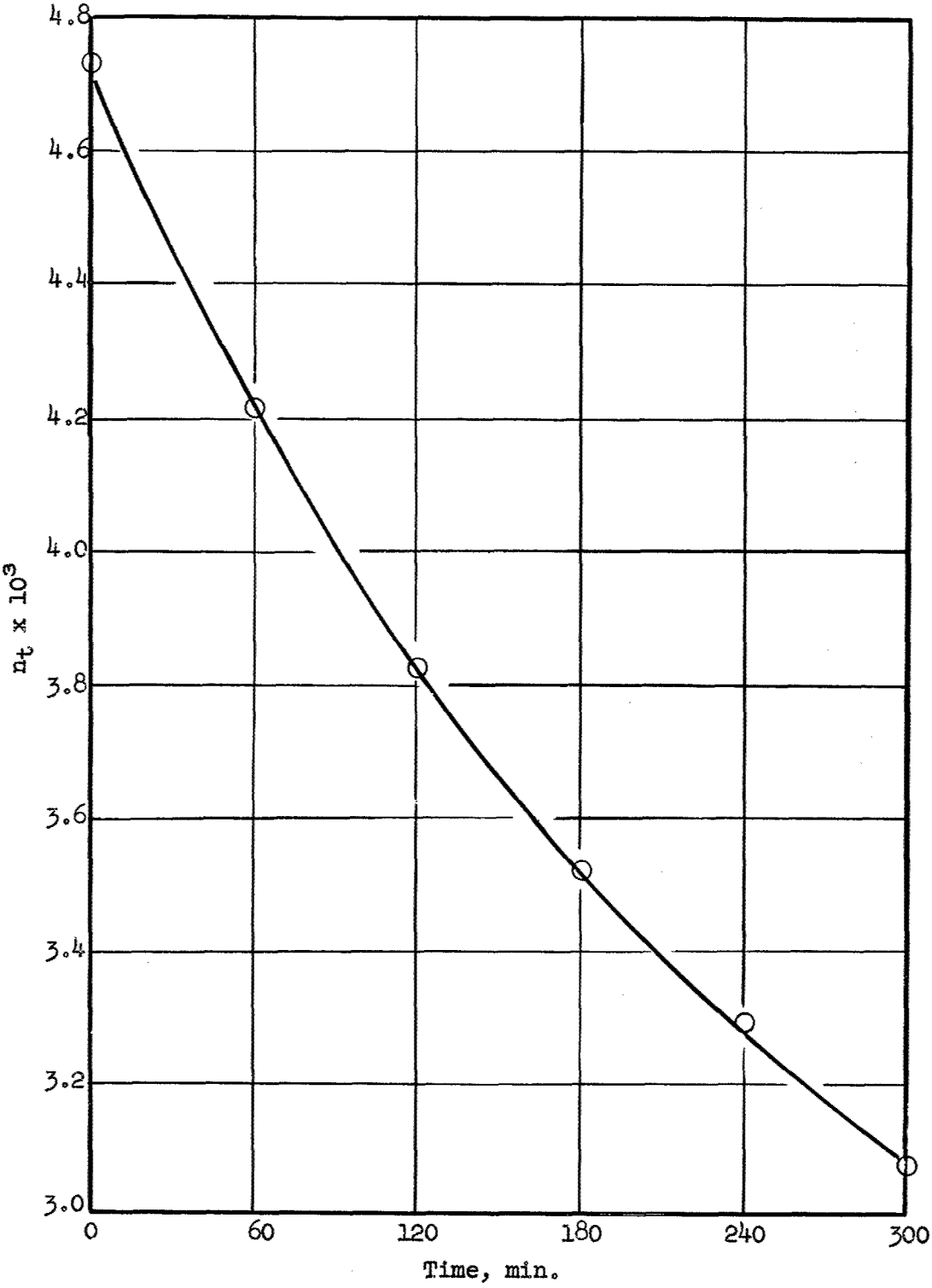


Figure 3. Vapor-Liquid Pyrolysis of Dimethylphosphine Borine

methylphosphinoborine pentamer since with either of the above mentioned chlorinating agents only eight of the nine hydridic hydrogens were replaced.

The bromination of dimethylphosphinoborine trimer with bromine in glacial acetic acid yielded what appears to be a mixture of isomeric tribromides. The stoichiometric amount of bromine required to replace all six of the hydridic hydrogens introduced only 3.93 bromine atoms per $[(CH_3)_2PBH_2]_3$. Treatment of diphenylphosphinoborine trimer with excess elemental chlorine resulted in reaction beyond replacement of the six hydridic hydrogens by chlorine.

A 14.2% yield of benzaldehyde 2,4-dinitrophenylhydrazone was obtained from the interaction of dimethylphosphinoborine trimer, benzoyl chloride and aluminum chloride in carbon disulfide solution. It would appear from the lack of reaction between trimer and benzoyl chloride alone and the destruction of trimer by aluminum chloride in benzene, that possibly removal of chlorine from organic chlorides by trimer first involves complex formation between trimer and aluminum chloride rather than between the organic halide and aluminum chloride as might be presumed by analogy with the accepted mechanism of Friedel-Crafts type reactions.

In an effort to substitute hydrogen in dimethylphosphinoborine trimer with other groups, the reactions of the trimer with sulfuric acid and cyanogen bromide were tested in two experiments. Trimer did not react to any great extent with concentrated sulfuric acid at 0°C. but did react with cyanogen bromide at 90°C. to give some charring and a very high melting substance containing boron, nitrogen, and bromine.

Dimethylphosphinoborine trimer was treated with methyllithium at room temperature and -70°C. in sealed tube reactions, and in refluxing ether employing aluminum chloride as a catalyst without observable alkylation.

B. Evaluation of Phosphinoborines

1. Oxidative Stability

Spontaneous ignition temperatures in air (S.I.T.) of a number of phosphinoborine linear and cyclic polymers have been determined by heating in an open cup and are listed in Table II. Of all the compounds tested, dicyclohexylphosphinoborine trimer has shown the highest S.I.T., 484°C. There appears to be no correlation between S.I.T. and the nature of the end group in dimethylphosphinoborine linear polymer. These results suggest that the bond which is first broken or oxidized is not associated with the end group but is a bond common to all the polymers such as the B-H, P-B, P-C or C-H bond. An increase in the size of the groups attached to phosphorus appears to increase S.I.T. very slightly in linear polymers but the substitution of chlorine for hydrogen on boron appears to have no effect. The latter observation indicates that the B-H and B-Cl bonds are probably not the first broken under conditions of the tests.

TABLE II

Spontaneous Ignition Temperatures of Phosphinoborines

Compound	S.I.T., °C.	Remarks
$[(CH_3)_2PBH_2]_x \cdot (CH_3)_2PH$	274	M.W. 3276; m.p. 163-65°C.
$[(CH_3)_2PBH_2]_x \cdot (CH_3)_2PH$	275	m.p. 176-80°C.
$[(CH_3)_2PBH_2]_x \cdot (CH_3)_3N$	283	m.p. 164-67°C.
$[(CH_3)_2PBH_2]_x \cdot (CH_3)_2NH$	282	m.p. 164-65°C.
$[(CH_3)_2PBH_2]_x \cdot (CH_3)_3P$	278	m.p. 148-55°C.
$[(CH_3)_2PBH_2]_x \cdot (C_2H_5)_3N$	267	M.W. 6014; m.p. 170-72°C.
$[(CH_3)_2PBH_2]_x \cdot (n\text{-}C_4H_9)_3N$	288	m.p. 164-68°C.
$[(CH_3)_2PBH_2]_x \cdot (C_2H_5)_3N$	287	M.W. 12,426; m.p. 171-73°C.
$[(CH_3)_2PBH_2]_x \cdot [(C_2H_5)_2NCH_2]_2$	286	M.W. 13,632; m.p. 169-72°C.
$[(CH_3)_2PBH_2]_x [(CH_3)_2NCH_2]_2$	280	m.p. 159-61°C.
$[CH_3(C_2H_5)PBH_2]_x \cdot (C_2H_5)_3N$	293	M.W. 1836; m.p. 118-26°C.
$[CH_3(CH\text{-}CHCH_2)PBH_2]_x \cdot (C_2H_5)_3N$	340	structure unknown; evolved gas ignites at 291°C. as sample melts, solid ignites at 340°C.
$[(C_2H_5)_2PBH_2]_x \cdot (C_2H_5)_3N$	290	-
$[(CH_3)_2PBCl_2]_x \cdot (C_2H_5)_3N$	280	-
$[CH_3(C_2H_5)PBCl_2]_3$	364	-
$[(CH_3)_2PBHBr]_3$	294	-
$[(CH_2)_4PBH_2]_3$	233	-
$[(C_6H_{11})_2PBH_2]_3$	484	-
$[CH_3(C_6H_5)PB(CH_3)_2]_3$	304	-

2. Hydrolytic Stability

The extent of hydrolysis of a number of phosphinoborines during 24 hours at 202°C. has been determined and the results are reported in Table III. Cyclic phosphinoborines having only hydrogen on boron are far more resistant to hydrolysis than linear polymers or B-halogen substituted compounds. In this screening test, no clear correlation between end group and hydrolytic stability of the variously prepared dimethylphosphinoborine linear polymers is evident.

3. Thermal Stability

The preliminary experiments fail to define clearly the temperature at which linear dimethylphosphinoborine polymer begins to decompose. Some decomposition was observed at 170°C. but more exacting temperature control will be required before decomposition rates can be determined.

Heating dimethylphosphinoborine polymer in vacuum at about 170°C. for half an hour was found to result in formation of 22.1% of trimer-tetramer mixture and further heating for one hour at 245°C. gave 80.2% trimer-tetramer mixture. In one hour at 203°C. in high vacuum dimethylphosphinodichloroborine linear polymer lost 26.3% of its weight and after one hour at 250°C. essentially all of the polymer had volatilized. The volatile products were not conclusively identified but had infrared spectra very similar to dimethylphosphinodichloroborine trimer. The stability of the chlorinated polymer does not appear to be markedly different from dimethylphosphinoborine linear polymer.

C. Organophosphines

Three synthetic approaches to organophosphines have been used to prepare a variety of phosphine derivatives including five hitherto unreported.

First, alkylation of phosphinide or organophosphinide ion in liquid ammonia was used to prepare phenylmethylphosphine and p-bis(methylphosphino)benzene from the respective aromatic phosphines in good yield. Alkylation of methylphosphine with n-dodecyl chloride and allyl chloride using the same process produced the respective methylalkylphosphines although the isolated yields were low. An attempt to prepare 1,2-bis(methylphosphino)ethane from methylphosphinide ion and ethylene dichloride resulted instead in a spectrum of products including a volatile phosphine tentatively characterized as methylvinylphosphine.

The second synthetic method, used to prepare methylphosphine from phosphorus and sodium in liquid ammonia, was analyzed statistically to establish the equation $\hat{y} = 51.8+2.85X_1-2.45X_2-1.85X_3$, which on interpretation indicates that 51.8% yield will be improved on increasing the sodium concentration (X_1) above 2.25M, decreasing the Na:P ratio (X_2) below 3.5, and decreasing the reaction time (X_3) to less than 3.5 hours.

TABLE III

Phosphinoborine Hydrolysis Studies

cc. Used	Compound	Hydrolysis Products Found						Remarks
		H_3BO_3		HX		H_2		
		cc.	%	cc.	%	cc.	%	
31.6*	$[(CH_3)_2PBH_2]_x \cdot (C_2H_5)_3N$	12.4	38.4-38.8	-	-	29.0	22.9	M.W. 12,426; m.p. 171-73°C.
30.1*	$[(CH_3)_2PBH_2]_x \cdot (C_2H_5)_3N$	7.52	24.1-24.5	-	-	23.8	19.6	M.W. 6014; m.p. 170-72°C.
33.1*	$[(CH_3)_2PBH_2]_x \cdot (CH_3)_2PH$	21.0	62.9-63.2	-	-	-	-	M.W. 3276; m.p. 163-65°C.; H_2 lost
29.4*	$[(CH_3)_2PBH_2]_x \cdot (CH_3)_2PH$	17.5	61.3-61.6	-	-	-	-	m.p. 176-80°C.; H_2 lost
16.8*	$[(CH_3)_2PBH_2]_x \cdot (CH_3)_2NH$	8.46	48.9-49.5	-	-	22.3	33.2	m.p. 164-65°C.
38.1*	$[(CH_3)_2PBH_2]_x[(C_2H_5)_2NCH_2]_2$	18.7	48.3-48.7	-	-	-	-	M.W. 13,632; m.p. 169-72°C.; H_2 lost
8.47*	$[(CH_3)_2PBCl_2]_x \cdot (C_2H_5)_3N$	7.30	83.2-84.3	10.3	61.1	5.02	28.0	-
6.63*	$[(C_2H_5)_2PBH_2]_x \cdot (C_2H_5)_3N$	5.68	81.9-83.3	-	-	10.7	40.3	-
16.4*	$[(CH_3)(C_2H_5)PBH_2]_x \cdot (C_2H_5)_3N$	14.9	89.4-90.0	-	-	29.8	45.4	M.W. 1836
3.71	$[(C_6H_{11})_2PBH_2]_3$	0.38	1.2-2.0	-	-	0.032	0.22	-
8.56	$[(CH_2)_4PBH_2]_3$	0.90	2.5-2.9	-	-	-	-	H_2 lost
5.37	$[(CH_3)_2PBHBr]_3$	16.6	101.7-102.3	15.9	98.7	29.0	60.6	-
5.63	$[C_6H_5(CH_3)PB(CH_3)_2]_3$	-	-	9.8	29.0	3.7	11.0	-

* Calculations based on monomer.

An attempt to use methylamine in place of ammonia as the reaction solvent for the alkali metal-phosphorus synthesis of primary alkyl phosphines was unsuccessful.

The third process, based on the conversion of organic halides to the corresponding phosphines via intermediate organoaminophosphines and organochlorophosphines, has been used in whole or in part to prepare a number of phosphine derivatives including phenyl-, diphenyl- and dicyclohexylphosphines in addition to the new primary difunctional aromatic phosphine, p-diphosphinobenzene.

An ethereal solution of dimethylaminophenylmethylphosphine was refluxed with lithium aluminum hydride and aluminum trichloride to investigate the direct reduction of the P-N bond. The phenylmethylphosphine isolated appeared to be a disproportionation product of phenylmethylphosphine oxide formed on hydrolysis of the starting material rather than a primary product of reduction reaction.

III. Summary and Conclusions

Although conditions for preparing high molecular weight polymers in high yield have not been optimized, the preparation of linear dimethylphosphinoborine polymer has been accomplished and constitutes a major breakthrough in this field. Preliminary experiments have indicated that reaction temperature and base strength of the end group are two of the more important factors influencing polymer yield. The decreased yields of polymer formed when a variety of organic radicals were substituted for methyl radicals suggests a steric requirement as well is involved in polymer formation. The predicted further polymerization of dimethylphosphinoborine polymer on treatment with hydrogen chloride was observed but the unexpected depolymerization observed on treatment with boron trifluoride remains unexplained.

Several new cyclic phosphinoborine derivatives have been prepared and certain of their properties were observed. Attempts to prepare trimeric phosphinoborine derivatives by the dehydrohalogenation procedure show this synthetic method to have serious limitations presumably of a steric nature. The order, Arrhenius activation energy and preexponential factor have been determined for the vapor-phase pyrolysis of dimethylphosphine borine.

On screening for oxidative, hydrolytic and thermal stabilities linear polymers show reasonable resistance to degradation although with the exception of oxidative stability the polymers appear more labile than their cyclic counterparts. Dicyclohexylphosphinoborine trimer showed the highest oxidative stability (stable in air up to 484°C.) of all phosphinoborine derivatives yet prepared suggesting perhaps that the phosphorus atom is the site of attack by oxygen. Data are yet insufficient to attempt correlation of hydrolytic stability with molecular weight.

A synthetic method of potentially wide scope has been developed and used to prepare primary and secondary aryl and cycloaliphatic phosphines.

Secondary phosphines containing unsaturated radicals have been prepared but proved to be unstable either on standing alone or on reaction with diborane. The nature of products formed on reaction of the centers of unsaturation is not yet known.

BORON POLYMERS

Allen L. McCloskey

U. S. Borax Research Corporation
Anaheim, California

I. INTRODUCTION

The objective of this research program is to investigate the chemistry of new inorganic or semi-inorganic polymer systems showing promise of a high degree of thermal stability at 1000°F. Emphasis on inorganic systems results from the fact that polymers with carbon-carbon bonds predominating in the skeletal structure, and even the most favorably substituted silicone polymers, fail to show the thermal stability at 1000°F which is needed to meet projected Air Force operating requirements. Considerations of bond energy and bonding type, as well as analogy with known inorganic structures such as boron, boric oxide, boron monoxide and boron nitride have indicated that certain other types of boron polymers may be useful at the temperatures noted above. The major effort in this program has been the study of B-N and B-B bonded systems. The synthesis and evaluation of prototype and monomer compounds and the search for and study of polymerization reactions in these two bonding systems are described below.

II. B-N BONDING SYSTEM

A. INTRODUCTION

1. The B-N bonding system presents a combination of factors which indicate that it should be suitable for the preparation of thermally stable polymers. The thermal dissociation energy for the B-N bond is ~105 Kcal./mole. While boron nitride is extremely stable thermally, its other properties render it unsuitable for use in most systems. However, by proper selection of substituents on boron and nitrogen it should be possible to form linear $\{B\text{-}N\}_n$ and $\{B\text{-}N\text{-}C_x\}_n$ structures with useful thermal stability. In this connection the bond dissociation energies of some types of bonds which might be present in such polymers are tabulated below.

Bond	Dissociation Energy, Kcal./mole	Bond	Dissociation Energy, Kcal./mole
B-N	105	C_{al}-N	82
B_{ar}-N_{ar}	115	C_{al}-C_{al}	74
B-C_{al}	89	C_{ar}-C_{ar}	98
B-C_{ar}	(~100 probably)	C_{al}-H	101
B-OR	113	C_{ar}-H	102
C_{ar}-N_{ar}	110	C_{al}-O	93
N-H	102	C_{ar}-O	107

It has been suggested (Reference 1) that bond dissociation energies in the neighborhood of 100 Kcal./mole are necessary for thermal stability at 1000°F, thus the C_{al}-C_{al}, C_{al}-O, C_{al}-B, and C_{al}-N bonds should probably be avoided.

2. The investigation of syntheses of prototype molecules and potential monomers such as borazoles and alkylaminoboranes has seen emphasized in the present work, although the preparation of polymeric species and the thermal stability of various systems have also been studied.

B. DISCUSSION

1. Monomers and Prototypes

a. Borazoles

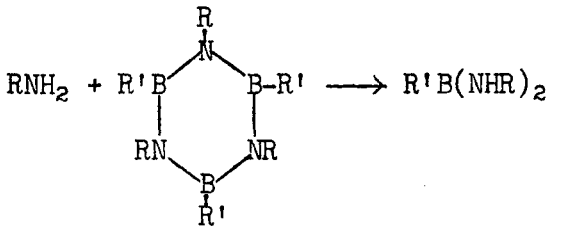
The synthesis of symmetrically substituted borazoles on a molar-to-kilogram scale in good yields has been accomplished. The Brown-Laubengayer technique (Reference 2) has been used to prepare the following B-trichloroborazoles with various substituents on the nitrogen atoms: B-trichloroborazole, B-trichloro-N-trimethylborazole and B-trichloro-N-triphenylborazole. The Schaeffer-Anderson method (Reference 3) was used to prepare N-trimethylborazole, substituting sodium borohydride for the lithium salt previously reported. A series of B-alkylated borazoles were prepared by Grignard alkylation of the appropriate B-trichloroborazoles (References 4, 5, 6, 7). These included hexaphenylborazole, hexamethylborazole, B-triphenylborazole, B-triphenyl-N-trimethylborazole, B-trimethyl-N-triphenylborazole, B-trimethylborazole, B-triethyl-N-trimethylborazole, B-tributyl-N-trimethylborazole, and B-tributyl-N-triphenylborazole. In the preparations of the various B- or N-aromatic substituted borazoles by organo-metallic reagents, the formation of a borazole-magnesium halide complex made separation of the products in pure form difficult, and low yields resulted. Treatment of the reaction mixture with water or with triethylamine decomposed the complex and allowed recovery of the products in good yields. One "unsymmetrical" borazole, B-chloro-B-dibutyl-N-trimethylborazole, was prepared by Sisler's method (Reference 7). A new route to the formation of borazoles was discovered: treatment of a tris(alkylamino)borane with an amine hydrochloride at elevated temperature results in condensation of the aminoborane to B-tris(alkylamino)-N-trialkyl-borazole. B-tris(isopropylamino)-N-triisopropylborazole and an X-triisopropyl-X-trimethyl-B-triaminoborazole were prepared in this manner.

b. Aminoboranes

The recently discovered transamination of boron-nitrogen compounds has provided a convenient method of synthesis of alkylaminoboranes:

$$R_2NH + \rangle B\text{-}NR'_2 \longrightarrow R'_2NH + \rangle B\text{-}NR_2$$

Since no hydrogen chloride nor amine hydrochloride is formed as a by-product, alkylaminoboranes sensitive to protonic acids can be prepared successfully. The transamination reaction will also take place using B-trialkylborazoles as one of the reagents:

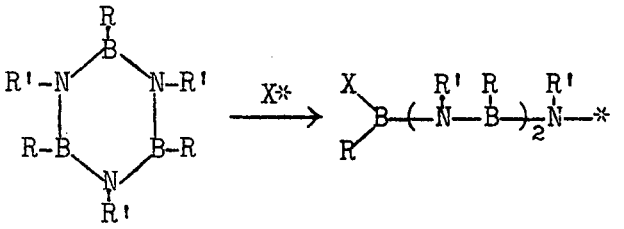


This provides a route to alkyl-bis-(alkylamino)boranes without involving the preparation and isolation of alkylboron dichlorides. The following compounds were prepared by transamination from the material in brackets: tris(anilino)borane [tris(isopropylamino)borane], tris(N-methylanilino)-borane [tris(isopropylamino)borane], tris(diphenylamino)borane [tris-(diethylamino)borane], tris(pyrrolidino)borane [tris(isopropylamino)borane], tris(2-pyridylamino)borane [tris(diethylamino)borane], bis(n-butylamino)methylborane [hexamethylborazole]. The reaction has also been used to prepare polymeric materials as discussed below.

2. Polymerization Reactions

a. Linearization of Borazoles

The research in this part of the program has been designed to find catalysts and reaction conditions that will open one of the bonds in the borazole ring:

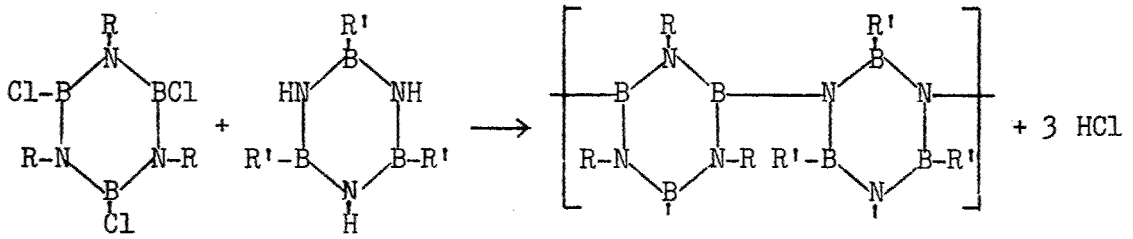


The resulting activated linear fragment could then attack another borazole ring, etc., in a propagation reaction. The series of reactions will probably be in equilibria and it remains to be seen whether small ring structures or high polymers will be the most favored. The research has involved attempted linearization of hexamethyl, N-trimethyl-, B-triphenyl- and B-triphenyl-N-trimethyl borazoles at temperatures ranging from -35° to 365°C, alone and in the presence of the following catalysts: sodium amide, ammonia, sodium, tris(t-butylamino)borane, triethylamine, methyl-magnesium bromide alone or in ether, azo-bis-isobutyronitrile, magnesium chloride, t-butyl peroxide, methylamine hydrochloride, water plus

ether, trifluoroacetic acid plus ether, phenylmagnesium bromide plus ether, t-butylamine, phosphorus trichloride plus ether, u.v. irradiation, potassium oxide, zinc bromide, n-butylamine and dimethylamine. In practically all experiments, 70-100% of the borazole was recovered, and the residue was not polymeric. However, the reaction of hexamethylborazole with n-butylamine at 310°C and the reactions at 365°C of B-triphenyl-N-trimethylborazole with n-butylamine, dimethylamine, potassium oxide or zinc bromide gave resinous materials. The constitutions of these thermoplastic resins have not yet been determined, but their formation is considered significant. Attempts to prepare a linear B-N polymer directly following the procedure of Hough and Schaeffer (Reference 8) yielded only borazole.

b. Condensation of Borazoles

The investigation of condensation reactions of borazoles is based on the fact that the products would be polymeric materials in which the borazole ring is retained intact as shown in the following example:



In this type of polymer, the resonance energy of the psuedo-aromatic borazole ring is retained, thus increasing thermal stability. Polymers of this general type have been described by Lappert (Reference 9) and the discovery of the loss of amine from tris(methylamino)borane to give polymeric residues was previously discussed (Reference 10). Resinous materials have been obtained from the reaction of B-trichloroborazoles with B-tris(alkylamino)-borazoles when heated, surprisingly without evolution of hydrogen chloride. These are probably polyborazolylamines, in which the rings are joined together by R-N groups. The reactants were trifunctional, so the resins are probably three-dimensional networks.

c. Polymerization by Transamination

Until the discovery of the transamination reaction in these laboratories, attempts to synthesize polymers containing B-N and R in the backbone of the polymer chain involved the reaction of amines with boron halides. The concomittant formation of hydrogen halide interfered with the polymerization reaction by tying up amine end groups as amine hydrohalides which could not react and which contaminated the reaction products. The transamination reaction, however, has made it possible to prepare similar polymers in systems where the only by-product is a volatile amine. Thus treatment of B-triphenyl-borazole with 2-methyl-4,6-bis(methylamino)-3-

triazine at 250°C in quinoline solution resulted in the formation of a material which softened at 230°C and was stable at 500°C in the absence of air. Treatment of hexamethylborazole with N,N-diallylmelamine in dioxane yielded methylamine and a light brown resin. When the resin was heated on a hot stage, it melted in the range 80-95°C to a cloudy liquid which clarified at about 110°C. At about 200°C a gas was suddenly evolved, the liquid foamed and set to a solid resin which was then stable to 300°C. It is possible that the foaming was due to a condensation that took place by attack of amine hydrogen on the diallylamine groups, eliminating the amine and cross-linking the product to a three-dimensional network.

III. $(B\text{-}B)_n$ POLYMERS

A. INTRODUCTION

No systematic approach to the preparation of pure boron-boron chains or to the incorporation of heterogeneous atoms in predominantly boron-boron chains has previously been made. The absence of knowledge in this field makes it imperative to include a study of boron-boron systems in any comprehensive search for thermally stable boron-containing polymers. Theoretical considerations such as the bond energy of the B-B bond (about 80 Kcal./mole) and bonding types possible for B-B systems suggest that these systems would be stable. The study of prototypes and polymerization mechanisms in B-B bonded systems is dependent either on materials known to have B-B bonds in their structure or reactions capable of producing B-B bonds. Known source materials which contain B-B bonds are boron hydride structures such as decaborane and the pentaboranes, derivatives of diboron tetrachloride (Reference 11), B_4Cl_4 (Reference 12), polymeric haloboron compounds such as

(References 13, 14), boron monoxide (References 15, 16), and elemental boron. Reactions known to produce B-B bonds are the thermal decomposition of boron hydrides, the arc discharge (References 11, 17) and microwave excitation (Reference 18) preparations of B_2Cl_4, the thermal decomposition and electrodelese discharge reactions of BI_3 (Reference 14), the electric discharge treatment of BBr_3 (Reference 13), the synthesis of boron monoxide by the high temperature reduction of B_2O_3 with boron (Reference 15), various methods of producing elemental boron, and the questionable reduction of chlorodimethoxyborane with sodium amalgam (Reference 19). Most of the diboron compounds described in the literature were obtained from diboron tetrachloride which has only been prepared in small quantities and at present does not appear to be a practical starting material for the preparation of the desired diboron compounds in macro amounts. Another possible starting material for simple boron-boron compounds is "boron suboxide", $(BO)_n$, which has been prepared by heating B_2O_3 with boron (Reference 15). However, the general method chosen for synthetic studies at the inception of the present program was the reaction of monohaloboron

compounds with active metals. This reaction is energetically and mechan-

$$2\ R_2BX + 2\ M \longrightarrow R_2B\text{-}BR_2 + 2\ MX$$

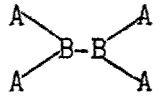
istically favorable and examples in which this type of reaction did occur have been reported by Schlesinger (References 11b, 20, 21) and Wiberg (Reference 22). However, no boron-boron bonded products were isolated from any of these reactions. Bromodiphenylborane (Reference 23), 2-chloro-1,3,2-dioxaborolane (Reference 21), and trichloroborazole (Reference 24) did not react with sodium, perhaps because bulk sodium was used in these cases.

B. DISCUSSION

1. Prototypes and Monomers

a. Choice of Monomer Systems

The choice of the most suitable types of compounds for initial preparation and study was made on theoretical considerations as well as the characteristics of known diboron compounds. The B-B and B-A bond strengths in a molecule such as



would be greatly influenced by the electron-donating properties of A. Since trivalent boron is an electron deficient species, any adjacent electron-rich atom A will strengthen the B-A bond (and also the B-B bond) by participation of its unshared electron pairs in the B-A bond, giving it more double bond character and greater bond strength. On this basis tetraalkoxy diboron and tetraamino diboron compounds which have oxygen and nitrogen (both with unshared electron pairs) atoms attached to boron should be comparatively stable. Of the two, the amino compounds should be more stable, since the electrons on nitrogen usually enter into the type of bonding described more readily than do those on oxygen. It would also be predicted that the B-A bond in tetraalkyl derivatives would be weaker by comparison, and that the B-X bond in the boron tetrahalides would become weaker going down the periodic table (i.e., B-F > B-Cl, etc.). The available information on these compounds supports these conclusions, and on this basis it was decided first to attempt the preparation of tetraalkoxy and tetraamino derivatives. These conclusions, which were based on a simple consideration of the B-A bond, are also supported by consideration of the more or less unique nature of boron. There is a strong tendency for trivalent boron to fill the fourth orbital and assume a tetravalent state. This behavior would be undesirable in the production of boron-boron chain polymers. For example, the cage structure, B_4Cl_4 (rather than boron-boron chains) is formed as a by-product in the preparation of B_2Cl_4 from BCl_3. The same behavior is common in the boron hydride field. The formation of cage type structures by filling of the fourth orbital on boron should be reduced in compounds containing oxygen or nitrogen atoms (rather than chlorine or hydrogen)bonded to boron. The

available electrons on these atoms can essentially fill the fourth orbital of adjacent boron and will make the formation of boron-boron chains more likely than with hydrogen, halogen (except possibly fluorine) or saturated substituents attached to boron.

b. Reduction of Halodialkoxyboranes

Attempts to prepare tetraethoxydiboron by Wiberg's reported (Reference 19) reaction of chlorodiethoxyborane with sodium amalgam were unsuccessful. The use of highly dispersed sodium as the reducing agent also failed to give any of the tetraethoxy compound in toluene solution. However, reactions definitely occurred in both cases and significant yields of sodium chloride were obtained. The only additional product identified was ethyl borate. It appeared that chlorodiethoxyborane did react with sodium dispersion but that the products were unstable at the temperatures necessary for reaction. When refluxing diethyl ether was used as a solvent no reaction occurred and chlorodiethoxyborane was found to react with the solvents when tetrahydrofuran or diglyme were used.

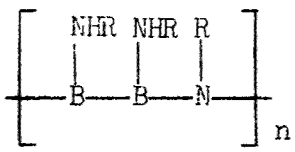
c. Preparation of Tetra(dimethylamino)diboron

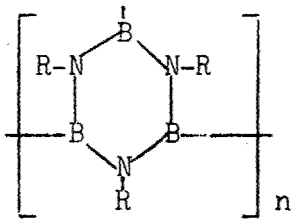
Since the tetraalkoxydiboron products from chlorodiethoxyborane and active metals appeared to be unstable under the conditions necessary for reaction, the reduction of halo-bis(dialkylamino)boranes was studied. These reactions would lead to tetra(dialkylamino)diborons which were believed to be more stable than tetraalkoxydiborons on the basis of Schlesinger's (Reference 11b) work on tetra(dimethylamino)-diboron. Reactions of bromo- and chloro-bis(dimethylamino)boranes with sodium dispersion, potassium dispersion and sodium-potassium alloys were investigated as possible methods for the preparation of tetra(dimethylamino)diboron. The most satisfactory results have been obtained by adding bromo-bis(dimethylamino)borane to an excess of sodium dispersion in refluxing toluene which gave over 80% yields of pure tetra(dimethylamino)-diboron. Preliminary studies have shown this material to be stable up to about 200°C at atmospheric pressure in a nitrogen atmosphere. Reaction is significantly slower with the chlorodiaminoborane, and potassium or sodium-potassium alloy led to incomplete conversions even though the reactions of haloboranes with these materials were initiated at lower temperatures than with sodium dispersion. It is possible that potassium is more susceptible than sodium to surface deactivation by resulting metal halides even though reactions were conducted under conditions of high speed stirring with the metals in their molten states. The preparation of tetra(dimethylamino)diboron represents the first preparation, other than the questionable work of Wiberg (Reference 19), of an isolable boron-boron bonded compound by the reactions between a haloboron and a reducing metal. This facile synthesis of a boron-boron compound provided entry into a class of materials hitherto available only by tedious methods.

d. Reactions of Tetra(dimethylamino)diboron

(1) Transamination

Transamination reactions of tetra(dimethylamino)-diboron with representative primary and secondary amines gave the expected four moles of dimethylamine and tetraaminodiboron derivatives. When a primary amine derivative, tetra(n-hexylamino)diboron, was heated, n-hexylamine was evolved leaving a residue which had a significantly higher molecular weight and boron content than the original diboron material. This molecular weight increase by amine evolution can be explained by the formation of linear and/or cyclic systems as shown and is related to the previously discussed reactions of tris(methylamino)borane (Reference 10).





(2) Alcoholysis

Wiberg first described the preparation of tetraethoxydiboron from chlorodiethoxyborane and sodium amalgam (Reference 19). The vapor pressure was not given because spontaneous decomposition was reported to give ethyl borate and elemental boron. Schlesinger has prepared (Reference 11b) tetraethoxydiboron from diboron tetrachloride and ethanol and found it to be "reasonably stable" with a vapor pressure of 1 mm. at 25.9°C. Thermal decomposition gave ethyl borate but no elemental boron (Reference 25). The preparation of tetraethoxydiboron from tetra(dimethylamino)diboron and ethanol by simple stripping of dimethylamine proved to be unsatisfactory, because the last traces of dimethylamine were difficult to remove and because ethyl borate was always produced as a by-product. The most satisfactory method developed involved reaction of tetra(dimethylamino)diboron with four moles of ethanol in the presence of an ether solution of four moles of hydrogen chloride. The resulting dimethylamine hydrochloride was filtered to give a nitrogen-free product containing a 56% yield of tetraethoxydiboron contaminated with 10% ethyl borate. Separation of this mixture by fractionation at 10^{-6} mm. gave pure tetraethoxydiboron, vapor pressure 1 mm. at 24°C (Schlesinger reported v.p. 1 mm. at 25.9°C). This material appeared to be stable at or below room temperature but disproportionated to ethyl borate and higher boron-containing materials at higher temperatures (vide infra). Only approximately 70% of the theoretical dimethylamine could be displaced from tetra(dimethylamino)-diboron by methanol. The products were not identified and appeared to be mixtures of various salts and mixed methoxy-dimethylamino diborons. Reactions of tetra(dimethylamino)diboron with isopropyl alcohol resulted

in the theoretical amounts of displaced dimethylamine, and distillation gave nitrogen-free products which were mostly isopropyl borate and contained about 25% of the theoretical tetraisopropoxydiboron. Isopropyl borate was probably formed by thermal disproportionation during the distillation, since tetraisopropoxydiboron is less volatile than tetraethoxydiboron, and pot temperatures in the distillation reached 100°C. The reaction of tetra(dimethylamino)diboron with phenol gave the theoretical four moles of dimethylamine and a brown oil. Treatment of this oil with petroleum ether (b.p. 20-40°C) gave a residual solid material with a high boron content, and concentration of the solvent yielded a fraction containing significant amounts of phenyl borate. There was some evidence for the presence of small quantities of tetraphenoxydiboron. Tetra(dimethylamino)diboron reacted with 8-hydroxyquinoline to give four moles of dimethylamine and crude tetra(quinolin-8-oxy)diboron. This material did not show unusual thermal stability, but this may have been due to the fact that complete purification was not attained. It is believed that most of the tetraalkoxy preparations above as well as any additional ones will be greatly facilitated by the use of the hydrogen chloride technique described for tetraethoxydiboron.

(3) Hydrolysis

Tetrahydroxydiboron (sub-boric acid) has been prepared by the hydrolysis of diboron tetrachloride (Reference 16) and reportedly by the hydrolysis of tetramethoxydiboron (Reference 19). This material is important to the present program because it is an intermediate in the preparation of $(BO)_n$ (Reference 16) which is a potential starting material for the synthesis of other B-B compounds. Hydrolysis of tetra(dimethylamino)diboron with four moles of water did not give the tetrahydroxy acid as expected but an intermediate compound which has the approximate formula, $B_2(OH)_3NMe_2$ based on elemental analyses. This material retained essentially all of its dimethylamine when dissolved in water and the water evaporated. This behavior suggests the possibility of some type of salt formation. Reaction of tetra(dimethylamino)diboron with two moles of water was also investigated as a direct route to $(BO)_n$, but comparable results were obtained: significant amounts of dimethylamine were retained even when the product was heated at 250°C at 1 mm. Tetrahydroxydiboron has now been obtained alternatively by hydrolysis of tetraethoxydiboron. Dehydration of the tetra hydroxy compound led to $(BO)_n$ as described in the literature (Reference 16).

(4) Reaction with Hydrogen Halides and Boron Halides

The preparations of various diboron tetrahalides have been reported (References 11, 14) and their high reactivity has been demonstrated. Because of their reactivity they would be valuable intermediates in the preparation of other B-B materials. Since the known preparative methods for these materials are tedious, reactions of tetra(dimethylamino)diboron with hydrogen halides and boron halides were

investigated as possible methods for the preparation of partially or completely substituted diboron materials. Reaction of tetra(dimethylamino)-diboron with excess hydrogen chloride at 80°C showed absorption of 5.74 moles of hydrogen chloride per mole of diboron compound. Unidentified products which showed characteristic B-Cl absorption in the infrared were obtained. When excess boron fluoride was added to tetra(dimethylamino)-diboron and the mixture warmed to 120°C, 2.56 moles of boron fluoride was retained per mole of diboron compound and 2.97 moles of difluoro(dimethylamino)borane was isolated. The residual product was formulated as $B_2F_{2.56}(NMe_2)_{1.44}$ based on the assumption that the reaction involved simple displacement of the dimethylamino group by fluoride. Excess boron chloride reacted exothermically with tetra(dimethylamino)diboron at 30°C with the retention of 2.63 moles of boron chloride per mole of diboron compound. The products were 3.8-4.0 moles of dichloro(dimethylamino)-borane and a polymeric orange liquid. These results suggested the initial formation of diboron tetrachloride followed by disproportionation to BCl_3 and $(BCl)_x$ polymers as shown. The disproportionation of diboron

$$B_2(NMe_2)_4 + 4\ BCl_3 \longrightarrow 4\ Me_2NBCl_2 + B_2Cl_4$$

$$x\ B_2Cl_4 \longrightarrow (BCl)_x + xBCl_3$$

tetrachloride to boron chloride and colored BCl polymers has been demonstrated (Reference 11b) although the rate at 30°C is rather slow. It is possible that the disproportionation occurred at an intermediate stage of chlorine substitution or that the disproportionation is catalyzed by some of the amino substituted compounds present in the reaction mixture.

2. Polymerization Reactions

a. Disproportionation Reactions

Alkyl or aryl orthoborates were obtained whenever attempts were made to prepare tetraalkoxy- or tetraaryloxydiborons. In cases where hydroxylic solvents were present, one possible route for orthoborate production is B-B cleavage followed by reaction of the resulting BH compound with additional ROH as follows. However, materials of

$$(RO)_2B\text{-}B(OR)_2 + ROH \longrightarrow (RO)_3B + HB(OR)_2$$

$$HB(OR)_2 + ROH \longrightarrow (RO)_3B + H_2$$

high boron content were produced concurrently with orthoborates in all cases including those when excess ROH was present. This information suggested that orthoborates are also formed by a thermal disproportionation reaction of the following type. Preliminary experiments have shown that

$$n(RO)_2B\text{-}B(OR)_2 \xrightarrow{\Delta} n(RO)_3B + (ROB)_n$$

tetraethoxydiboron gave 40.9 and 53.5% yields of ethyl borate based on the equation above after heating for six hours at 50 and 100°C respectively. The residual products from these thermal studies contained 15-17% boron and represent (ROB) polymers of 5-10 boron atoms.

b. Polymers from Boron Hydrides

(1) Background

The formation of boron hydride polymers from the pyrolysis of volatile boron hydrides has been known for many years. Although these materials contain boron-boron bonds, the structures are complicated by extensive hydrogen-bridge bonding and the occurrence of uncharacterized structural units derived from the pentaboranes, decaborane and other higher boranes. The production of borane polymers by more readily controllable chemical methods was desirable, and the studies described below were directed toward the chemical removal of BH_3 units from boron hydrides leaving reactive boron hydride fragments capable of forming polymers. Burg (Reference 26) reported the reaction of pentaborane-9 with trimethylamine to give two moles of trimethylamine-borine (BH_3NMe_3) and a polymeric solid presumably consisting of repeating B_3H_3 units. Similar reactions of pentaborane-9 and amines had been observed in this laboratory, and the polymeric products obtained showed unusual thermal stability.

(2) Discussion of Results

The reaction of pentaborane-9 with trimethylamine gave trimethylamine borine and a polymeric material as described by Burg (Reference 26). However, in all experiments less than two moles (the maximum was 1.68 moles) of trimethylamine-borine were obtained per mole of pentaborane-9, and the polymeric product was always contaminated with trimethylamine. In a typical case where the reaction mixture was warmed to 150°C, the products included 1.17 mole of BH_3NMe_3 per mole of pentaborane-9 and a polymeric material corresponding to $B_{1.00}H_{1.23}(NMe_3)_{0.22}$. The trimethylamine proved to be unexpectedly difficult to remove. Chemical treatment with boron fluoride at 150°C for four days gave a minimum N/B ratio of 0.204, and treatment with boron fluoride in solution also had little effect. The fact that the N/B ratio approached 1/5 suggested the possibility of discrete "$B_5H_xNMe_3$" units in the polymeric structure. The value of x was 5.0 and 6.8 for polymers heated to maximum temperatures of 150 and 100°C respectively and 7.0 for materials not heated above 80-90°C. A proposed reaction sequence for the 80-90°C case is given below. The obvious relationship

$$4\ B_5H_9 + 8\ Me_3N \longrightarrow 5\ Me_3N{\cdot}BH_3 + 3\ [B_5H_7NMe_3]$$

between the formula of the yellow resinous "$B_5H_7NMe_3$" derivative obtained and a trimethylamine complex of decaborane is believed to be coincidental

since "$B_5H_7NMe_3$" loses hydrogen above 120°C, and does not give decaborane on treatment with BF_3. The product obtained originally at 150°C was heated for one hour in a closed tube at 275°C to give methane, a small amount of trimethylamine, and a residual product, $B_{1.00}H_{0.86}N_{0.19}M_{0.44}$ (or alternatively $B_{1.00}H_{0.86}(NMe_2)_{0.13}(NMe_3)_{0.06}$). When the 150°C product was heated for four hours at 300-310°C, a material similar to that obtained at 275°C was recovered. Both products approached the general formula $(BX)_n$ where x = H or Me_2N, but the material produced at 300-310°C was a polymer of higher molecular weight. It was insoluble in acetone and gave a diffuse X-ray diffraction pattern, whereas the 275°C product was acetone-soluble and its X-ray pattern contained two distinct rings. The product from thermal treatment at 275°C was pyrolyzed at 550 ± 10°C both in a closed system and under vacuum. Less decomposition was noted in the closed system pyrolysis which gave non-condensable gases and a brittle tan product which contained BH bonds and corresponded to $B_5H_2NMe_3$. Decomposition in vacuo gave significantly more non-condensable gases and a black solid residue which contained no BH bonds and corresponded to $B_{1.00}H_{0.73}C_{0.26}N_{0.18}$. The ratios of hydrogen to methane in the non-condensable products were 0.70 in a closed system and 1.92 under vacuum. These polymeric products from pentaborane-9 and trimethylamine showed remarkable hydrolytic stability when treated with water, boiling methanol, dilute hydrochloric acid or methanolic hydrochloric acid. For example, when the polymer corresponding to the formula $B_{1.00}H_{1.01}(NMe_3)_{0.22}$ was heated under pressure at 150°C for 5.5 days with dilute hydrochloric acid, a total of only 8.2% of the calculated hydrogen was liberated. When the product $[B_{1.00}H_{0.86}N_{0.19}Me_{0.44}]$ from treatment at 275°C was heated at 150°C with dilute hydrochloric acid for five days, only 1.3% of the calculated hydrogen was obtained. Treatment of the 275°C material with methanol for 5.5 days at 70°C gave essentially no hydrogen. Since polymers derived from pentaborane-9 and trimethylamine are not pure boron hydride polymers, and since they have been shown to decompose extensively when heated to temperatures above 450°C, further work on these systems has been postponed.

IV. CONCLUSIONS

A. The most favorable reactions for achievement of high molecular weight B-N polymers appear to be ring-opening of borazoles, transamination, and the related reaction which involves loss of amine from suitably substituted B-NHR compounds.

B. The facile preparation of tetra(dimethylamino)diboron and its conversion to many other B-B bonded monomers represent a significant contribution to the general field of boron chemistry.

C. The disproportionation of diboron compounds offers a possible route to high molecular weight B-B polymers.

V. ACKNOWLEDGMENT

A. This work was supported by the Materials Laboratory, Wright Air Development Center, under Contract AF 33(616)-5931.

B. It is a pleasure to acknowledge the contributions of the following scientists in the work described herein:

Dr. R. J. Brotherton
Dr. G. W. Campbell
Dr. W. D. English
Mr. P. D. Faurote
Mr. H. Goldsmith
Miss I. E. Leidner
Mr. L. L. Petterson

C. Special acknowledgment is due to Dr. H. Steinberg who made major contributions to the inception of the B-B program at U. S. Borax Research Corporation.

VI. REFERENCES

1. J. O. Smith, et al., Monsanto Chemical Co., Contract No. AF 33(616)-5553, Task No. 73313 - First Quarterly Report, June 6 (1958).

2. C. A. Brown and A. W. Laubengayer, J. Am. Chem. Soc., 77, 3699 (1955).

3. G. W. Schaeffer and E. R. Anderson, ibid, 71, 2143 (1949).

4. H. J. Becher and S. Frick, Z. Anorg. Chem., 295, 83 (1958).

5. S. J. Groszos and S. F. Stafiej, J. Am. Chem. Soc., 80, 1357 (1958).

6. L. B. Scott and R. C. Morris, U. S. Pat. 2,821,463, June 28, 1958.

7. G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, J. Am. Chem. Soc., 80, 4515 (1958).

8. W. V. Hough and G. W. Schaeffer, U. S. Pat. 2,809,171, Oct. 8, 1957.

9. M. F. Lappert, Proc. Chem. Soc., 59 (1959).

10. A. L. McCloskey and H. Goldsmith, Paper presented at the 132nd National ACS Meeting, New York, N. Y., Sept. 8-13, 1957, Abstracts p. 54-P.

11. (a) T. Wartik, R. E. Moore, and H. I. Schlesinger, J. Am. Chem. Soc., 71, 3265 (1949); (b) G. Urry, T. Wartik, R. E. Moore, and H. I. Schlesinger, J. Am. Chem. Soc., 76, 5293 (1954); (c) A. Finch and H. I. Schlesinger, J. Am. Chem. Soc., 80, 3573 (1958).

12. G. Urry, T. Wartik, and H. I. Schlesinger, J. Am. Chem. Soc., 74 5809, (1952).

13. A. Pflugmacher and W. Diener,Angew. Chem., 69, 777 (1957).

14. W. C. Schumb, E. L. Gamble and M. D. Banus, J. Am. Chem. Soc., 71, 3225 (1949).

15. F. A. Kanda et al., J. Am. Chem. Soc., 78, 1509 (1956); M. D. Scheer, J. Phys. Chem., 62, 490 (1958).

16. T. Wartik and E. F. Apple, J. Am. Chem. Soc., 77, 6400 (1955); T. Wartik and E. F. Apple, J. Am. Chem. Soc., 80, 6155 (1958).

17. A. K. Holiday and A. G. Massey, J. Am. Chem. Soc., 80, 4744 (1958).

18. J. W. Frazer and R. T. Holzmann, J. Am. Chem. Soc., 80, 2907 (1958).

19. E. Wiberg and W. Ruschmann, Ber., 70B, 1393 (1937).

20. H. I. Schlesinger and G. Urry, Contract N6-ori-20, T.O. Ten, August 1, 1954.

21. H. I. Schlesinger and G. Urry, Contract N6-ori-20, T.O. Ten, August 1, 1955.

22. E. Wiberg and W. Ruschmann, Ber., 70, 1583 (1937).

23. W. Abel, W. Gerrard and M. F. Lappert, J. Chem. Soc., 5051 (1957).

24. F. B. Hutto, Masters Thesis, Cornell University, 1950.

25. H. I. Schlesinger, G. W. Schaeffer, and T. Wartik, Contract N6-ori-20, T.O. X., July 1, 1948-June 30, 1949.

26. A. B. Burg, J. Am. Chem. Soc., 79, 2129 (1957).

INORGANIC POLYMER FLUIDS

John A. Parkins

E. I. du Pont de Nemours and Co., Inc.
Explosives Department
EASTERN LABORATORY
Gibbstown, New Jersey

Introduction

The objective of this investigation is the preparation of base-stock fluids useful at 1000°F. as lubricants, greases, and hydraulic fluids. The study included inorganic polymers, modified glasses, and low-melting eutectic mixtures of inorganic compounds.

Inorganic Polymers

In this study, the criterion for polymers is that the skeletal structure be inorganic with attached modifying groups to attain the requisite physical properties. The ultimate goal is a polymer containing no carbon to carbon bonds. The systems studied have been confined to those polymers containing certain elements of Group V b, with attention being directed to derivatives of nitrilic halides of these elements, antimony oxide derivatives similar in structure to the siloxanes, and other polymers derived from substituted stibines.

Phosphorus Nitrilic Chloride

Phosphorus nitrilic chloride $(PNCl_2)_n$ was studied primarily as a model inorganic polymer to provide an insight into means to control the molecular weight of the polymer and provide additional information on the effect of changes in constitution on physical and chemical properties, namely liquid range, thermal stability, and hydrolytic stability.

Essentially all of the work recorded in the literature on the preparation of derivatives of phosphorus nitrilic chloride has been concerned with work on the crystalline trimer and tetramer fractions, which comprise the greater part of the product obtained in the usual method of preparation (Ref. 1). Stabilization of the liquid polymer fractions, which usually are obtained in very small quantities, to polymerization and depolymerization at elevated temperatures would, in part, solve the problem. The extrapolated atmospheric-pressure boiling point of the heptamer ($(PNCl_2)_7$, b.p. = ca. 550°C.) indicates that the heptamer would be a liquid in the temperature range desired.

In order to provide a workable quantity of the liquid, high-polymer phosphorus nitrilic chloride was depolymerized by chlorine. The crystalline fractions, which were isolated from the product of the usual method of preparation in sym-tetrachloroethane (Ref. 1), were heated in air at 260°C. for one hour. This treatment converted the system to a rubbery mass. This rubber was suspended in refluxing carbon tetrachloride through which chlorine was passed for 24 hours. From this system was isolated an amber, viscous polymer, equivalent to 15% of the starting crystalline material, a small quantity of crystalline polymer, and a larger quantity of unconverted elastomer. The average molecular weight of the liquid was 1000. Similarly, experiments in which the rubber was suspended in water saturated with chlorine and through which chlorine was passed for 6 hours resulted in recovery of liquid polymer, equivalent to 20% of the starting crystalline material and having a molecular weight ranging from 512 to 700 in several preparations (mol. wt. $(PNCl_2)_7$ = 812). Thus, a means of obtaining workable quantities of liquid phosphorus nitrilic chloride has been provided, and depolymerization by means of chlorine provides additional insight into the polymerization-depolymerization behavior.

The study of the effect of changes in constitution on stability involved work with liquid phosphorus nitrilic chloride. The phosphorus-fluorine bond is inherently more stable, so the fluoride of the liquid polymer was prepared. The liquid polymer was dissolved in acetonitrile to which sodium fluoride was added, and the system was refluxed for 24 hours. The resulting product had only about 50% of the chlorine replaced with fluorine. A similar system, in which a small quantity of chlorine was passed during reflux, resulted in essentially complete replacement of chlorine with fluorine:

Analysis of PNF_2	% P	% N	% F	% Cl
Calculated	37.30	16.90	45.80	0
Found	25.53	13.34	47.90	1.37

The discrepancy in the analysis is attributed to the lack of homogeneity of the liquid (a sludge-like material). This liquid boiled at ca. 120°C.; therefore, its utility as a high-temperature fluid is precluded.

Similar experiments in an effort to prepare phosphorus nitrilic cyanate with potassium cyanate in acetonitrile were unsuccessful. A large fraction of the liquid phosphorus nitrilic chloride and a small quantity of tar were recovered.

The reaction between phosphorus nitrilic chloride and benzene occurs in ultraviolet light with the formation of the phenyl derivative (Ref. 2). Radiation of a benzene solution of liquid phosphorus nitrilic

chloride (n = 6 to 7) with ultraviolet light (λ = 3660 A.) for 24 hours resulted in no substitution of chlorine with phenyl groups. Radiation intensity was somewhat less than that used by Dishon and Hirshberg (Ref. 2). Further work with a more intense radiation source of shorter wave length is under way in an attempt to effect substitution to a greater extent than attained by Dishon and Hirshberg with the trimer.

Antimony and Arsenic Nitrilic Chloride

In accord with the statement in the literature that the sealed-tube reaction between antimony pentachloride and ammonium chloride does not produce antimony nitrilic chloride ($SbNCl_2$) (Ref. 3), the solution method of Schenk and Römer for the preparation of phosphorus nitrilic chloride was ineffectual for the preparation of antimony nitrilic chloride. Likewise, arsenic trichloride, ammonium chloride, and chlorine in refluxing sym-tetrachloroethane did not produce the arsenic analog ($AsNCl_2$). Further, a solution of antimony trichloride in carbon tetrachloride caused a vigorous decomposition of nitrogen trichloride in carbon tetrachloride, but the only product was a moisture-sensitive, amorphous material presumed to be a mixture of antimony chlorides.

There was hope that somewhat higher temperatures might establish the antimony-nitrogen structure, which could be chlorinated to obtain the desired nitrilic chloride. Antimony pentachloride and ammonia were contacted by passing the reactants through a hot tube at 300°C. A gray to black amorphous solid was formed in the tube, and large quantities of ammonium chloride emanated from the moisture trap on the heated tube. Elemental analysis of the amorphous solid was inconclusive as to its identity. The solid, suspended in refluxing carbon tetrachloride, was treated with chlorine for 24 hours. Most of the solid was recovered unchanged, but a very small quantity of a brown, tacky and elastic material was obtained from the supernatant carbon tetrachloride. This material, in contrast with the antimony chlorides, was not sensitive to moisture. In spite of this encouraging result, repeated efforts never produced more than trace quantities of this tacky material. The infrared spectrum of this material was compared with the spectra of phosphorus nitrilic chloride and several authentic antimony compounds. The unidentified tacky material had two intense overlapping, moderately broad bands at 12.7 microns and 13.1 microns; phosphorus nitrilic chloride had a broad general absorption, apparently composed of several overlapping bands from 7.3 microns to 8.4 microns. Antimony oxide is characterized by absorption at 13.60 microns and 14.40 microns, which has been attributed to antimony-oxygen bonds. On the basis of comparative spectra, the region of absorption of the tacky material is about that which could be expected for the antimony-nitrogen structure of antimony nitrilic chloride. A search of standard

literature sources of infrared spectra, however, revealed nothing pertinent (Ref. 4).

Antimony in the Phosphorus Nitrilic Chloride System

The possibility that antimony could be incorporated in the polymerization system of phosphorus nitrilic chloride was investigated. The effect of varying the molar ratio of phosphorus pentachloride to antimony pentachloride was investigated in standard preparative reactions for phosphorus nitrilic chloride. Table I shows that the presence of larger quantities of antimony pentachloride prevents polymer formation. At a molar ratio of 10:1 (PCl_5:$SbCl_5$), however, the polymer yield was increased over the control which contained no antimony pentachloride.

TABLE I

The Effect of $SbCl_5$ on Polymer Yield in $PNCl_2$ Preparations

Ratio of PCl_5:$SbCl_5$	Polymer Yield	Yield Based on PCl_5
No $SbCl_5$ (Control)	20.4 g.	93%
1:1	None	0
3:1	None	0
5:1	None	0
10:1	22.5 g.	102%

Work is under way to compare the product of the system containing antimony pentachloride with phosphorus nitrilic chloride (from control, Table I). The general appearance of the two products is similar, except that the antimony-containing polymer is very dark brown. The phosphorus nitrilic chloride from the control preparation is soluble in benzene (5 g. in 25 cc.), while an appreciable fraction (ca. 35%) of the polymer containing antimony is not. Detailed fractionation and study of the properties of the latter material are incomplete.

Antimony Oxide Modification: "Stiboxanes"

Modification of antimony oxide has included the attempted preparation of polymer having alternating antimony and oxygen atoms in the chain and having attached modifying groups, i.e., a "stiboxane" similar to the siloxanes. The direct approach employed valentinite which is orthorhombic antimony trioxide (Sb_2O_3) having "infinite" chains of antimony-oxygen atoms bound laterally by bridge oxygen atoms. It has been shown that valentinite is more reactive than senarmontite (cubic Sb_2O_3) (Ref. 5) and that the bridge antimony-oxygen bonds are of lower energy than the corresponding chain bonds (Ref. 6). This

should, by use of a controlled quantity of thionyl chloride under mild conditions, permit replacement of the bridge oxygen with chlorine, leaving the chains intact according to the stoichiometric equation

$$Sb_2O_3 + SOCl_2 \longrightarrow 2\ SbOCl + SO_2.$$

The chlorine atoms would provide reactive sites for attachment of modifying groups.

Senarmontite was sublimed at a temperature above 650°C. to produce glistening needles; X-ray diffraction analysis revealed that this sublimed material contained about equal parts of valentinite and senarmontite. The infrared spectrum of senarmontite had a broad absorption band at 13.60 microns which is attributed to the antimony-oxygen bond. The spectrum of valentinite (carefully selected, well-defined needles) showed this same band at 13.60 microns and an additional broad band, partially overlapping the former at 14.40 microns, which was assigned to a lower energy antimony-oxygen bond (Table II).

TABLE II

Infrared Spectra of Antimony Compounds

Compound	Absorption Bands (microns)	Assignments and Remarks
1. Sb_2O_3 (senarmontite)	13.60 (broad)	Sb-O cubic
2. Sb_2O_3 (valentinite)	13.60 (broad)	Sb-O cubic
	14.40 (broad)	Sb-O bridge of lower energy
3. $(C_6H_5)_3Sb$	13.70 (sharp)	Phenyl group on Sb
	14.86 (sharp)	
4. $(C_6H_5)_3SbBr_2$	13.70 (sharp)	Phenyl on Sb
	14.65 (sharp)	Perturbed by Br
5. $(C_6H_5)_3SbF_2$	13.50 (sharp)	Phenyl on Sb
	14.45 (sharp)	Perturbed by F
6. $((C_6H_5)_3SbBr)_2O$	12.85 (sharp)	Sb-O, higher energy than cubic Sb_2O_3
	13.60 (sharp)	Phenyl groups on Sb
	14.50 (sharp)	
7. Phenyl "stiboxane" bromide	13.60 (sharp with shoulder)	Phenyl on Sb
	14.75 (sharp)	No Sb-O
8. Phenyl "stiboxane"	12.85 (sharp)	Sb-O as in 5.
	13.60 (sharp)	Phenyl on Sb
	14.52 (sharp with irregular shoulder)	

Valentinite was allowed to react with thionyl chloride vapor in a closed vessel at room temperature and a pressure of about 1/2 atmosphere for 24 hours. The needles which were swollen by this treatment were reacted with bromobenzene (Wurtz Reaction). The purified product had a melting range of from 245° to 250°C. Part of the product was reacted with bromine in an effort to obtain the pentavalent compound:

$$\left(\begin{matrix}-\mathrm{SbO}- \\ | \\ \mathrm{R}\end{matrix}\right) + \mathrm{Br_2} \longrightarrow \left(\begin{matrix}\mathrm{Br_2} \\ | \\ -\mathrm{SbO} \\ | \\ \mathrm{R}\end{matrix}\right)$$

The melting range of this compound was from 142° to 155°C. The infrared spectra of these compounds were compared with those of the oxides and pertinent stibine derivatives (see Table II). The "stiboxane" which was not brominated had a band at 12.65 microns, which was assigned to the oxygen bonds of the authentic anhydro(triphenyl stibine oxybromide) $((C_6H_5)_3SbBr)_2O$. This absorption represents higher bonding energy than the bonding energy of the oxide linkage of the two antimony oxides studied and suggests that the antimony oxide skeletal structure of this compound might have the required thermal stability. The brominated "stiboxane" did not exhibit the infrared absorption attributed to the oxide bond; however, a small shoulder appeared on one of the nearby phenyl bands which might be due to a slight oxide absorption.

Stibine Derivatives

Stibines (R_3Sb) were considered as a route to "stiboxanes" and as an intermediate to other antimony polymers. Triphenyl stibine ($(C_6H_5)_3Sb$) was prepared by a standard method (Ref. 7) and was allowed to react with bromine to obtain the dibromide ($(C_6H_5)_3SbBr_2$). Triphenyl stibine dibromide was allowed to react with silver oxide (Ref. 8) to obtain anhydro(triphenyl stibine oxybromide):

$$(C_6H_5)_3\underset{\mathrm{Br}}{\overset{|}{\mathrm{Sb}}}\text{-O-}\underset{\mathrm{Br}}{\overset{|}{\mathrm{Sb}}}(C_6H_5)_3.$$

This compound was allowed to react in benzene solution with more silver oxide in an effort to obtain the repeating antimony oxide chain structure. Reaction of silver oxide with the antimony compound in dilute benzene solution resulted in triphenyl antimony oxide ($(C_6H_5)_3Sb{=}O$). Reactions in more concentrated systems are under way in an effort to effect the end-to-end coupling of a linear polymer.

Triphenyl stibine dibromide was allowed to react with sodium fluoride in acetonitrile. The resulting difluoride, which was obtained in good yield, had a melting range of from 110° to 116°C. (Residual bromine was 1.67%; no test for fluoride ion was obtained from a suspension of the compound in boiling water.)

Several antimony compounds, as shown in Table III, were heated at 275°C. in an oven for 16 hours.

TABLE III

The Effect of Heating Antimony Compounds in Air at 275°C. for 16 Hours

Compound	Initial m.p. °C.	% Wt. Loss	Final m.p., °C., and Appearance
$(C_6H_5)_3Sb$	47 to 50	31.2	Some melted at 200, not all by 300; dark brown color
$(C_6H_5)_3SbBr_2$	224 to 227	65.3	Trace melted below 300. Dark brown to black
$(C_6H_5)_3SbF_2$	110 to 116	37.5	72 to 84; only slight discoloration
$((C_6H_5)_3SbBr)_2O$	260 to 266	57.6	Did not melt below 300. Dark brown to black
Phenyl "stiboxane"	245 to 250	43.5	150 to 160; slight discoloration, dark tan
$(C_6H_5)_3Sb{=}O$	195 to 217	47.5	Did not melt below 300. Light brown

At 275°C., all of the compounds lost considerable weight, and decomposition occurred as indicated by changes in melting point and color of all compounds (all were white or nearly so initially). This test provides preliminary screening of thermal stability of candidate structures and also suggests that treatment at elevated temperatures might be employed to obtain thermally stable materials from some of these compounds. Two of the compounds tested at 275°C., triphenyl stibine difluoride and phenyl "stiboxane", showed little discoloration and a decrease in melting point. Larger samples are being prepared to determine the composition and physical properties of the products of pyrolysis of these two materials.

Low-Melting Eutectics

To facilitate the search for compositions of metal salts and oxides which might melt at temperatures low enough to provide a fluid

of interest, the kinetics of the melting and freezing process were studied (Ref. 9), and general relationships were formulated as a guide. Briefly, desirable compositions are ones which would undergo an increase in the number of components upon melting, but which would revert to the lower number of components upon freezing:

$$2MX(s) + 2NX(s) \rightleftarrows MNX_2(liq.) + MX(liq.) + NX(liq.), \text{ or}$$

$$2MX_a(s) + 2NX_b(s) \rightleftarrows MX_{a-y}(liq.) + NX_b + y(liq.) + MX_a(liq.) + NX_b(liq.)$$

Further, to provide a more rapid means of screening compositions in the laboratory, the zone-melting technique was adapted to eutectic isolation. The equipment employed consisted of an electric resistance-heated zone, driven downward over an ingot which was contained in a small-diameter glass tube. Since the lowest melting composition travels with the heated zone, the eutectic ultimately collects near the bottom.

Testing of the zone-melting equipment was accomplished with a silver nitrate-potassium nitrate mixture of a noneutectic composition. After eight passes at 6 inches per hour of the heated zone, nearly pure eutectic, m.p. 130°C., collected at the lower end of the ingot; the portion at the upper end melted at 225°C. A trial of the system

$$SbI_3 + SnI_4 \rightleftarrows SbI_5 + SnI_2$$

revealed that decomposition to liberate iodine occurs, and no uniform low-melting eutectic could be isolated. The search for candidate systems is continuing.

Glass Modification

Molten glasses represent systems of macromolecules in which the freedom of flow is inhibited by oxygen bridges which crosslink the macromolecular chains. If these bridges could be selectively blocked without destruction of the chains, the chains could move with appreciable fluidity at greatly reduced temperatures. In laminar flow the bridge bonds are constantly being broken, and under this condition blocking atoms or groups could be added to block re-establishment of bridge bonds.

An effort was made, therefore, to add lithium oxide to molten boric oxide glass during shear in the annulus of a platinum-clad cup

and bob assembly. Mechanical difficulties have prevented complete evaluation of this approach; however, slight lowering of the softening temperature of the glass was accomplished. In view of the mechanical difficulties of this approach to glass modification, further efforts with this approach have been deferred and experimentation directed to the chemical approach, the preparation of a "stiboxane".

BIBLIOGRAPHY

1. Schenk, R. and Römer, G., Ber. 57, 1343 (1924).

2. Dishon, B. R. and Hirshberg, Y., J. Polymer Sci. 4, 75 (1949).

3. Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. VIII, p. 724, London, Longmans, Green & Co. (1929).

4. An I.B.M. search was run on IR spectra compiled by Subcommittee 3, on Standard Data of ASTM Committee E 13, on Absorption Spectroscopy. Compendium complete to 1958.

5. Mellor, J. W., op. cit. Vol. IX, p. 425.

6. Dainton, F. S., Trans. Faraday Soc. 43, 244 (1947).

7. Hiers, G. S., Organic Syntheses. Collective Vol. I, p. 550, New York, Wiley (1941).

8. Hantzsch, A. and Hibbert, H., Ber. 40, 1512 (1907).

9. Hinshelwood, C. N., The Structure of Physical Chemistry. p. 88, Oxford, The Clarendon Press (1951).

SOME REACTIONS OF THE PHOSPHONITRILIC HALIDES

L. F. Audrieth

University of Illinois

It is doubtful if much interest would have been manifested in the phosphonitrilic compounds had it not been for the discovery by an American Chemist, Dr. H. N. Stokes (1), that the phosphonitrilic chlorides, when heated to temperatures above 300°, undergo polymerization to rubber-like materials. Unfortunately, however, the phosphonitrilic chloride rubbers suffer two serious disadvantages. First, they seem to represent a metastable physical state and, like elastomeric sulfur, revert on standing to the lower molecular weight and more stable crystalline polyhomologs. Secondly, the attached chlorine atoms even in the polymer are susceptible to solvolytic attack and undergo hydrolysis on contact with atmospheric moisture. Many attempts have therefore been made to replace the chlorine atoms in the lower molecular weight polyhomologs and in the polymeric products by other groups or atoms in order to develop better stability characteristics.

Our research efforts under the sponsorship of the Polymer Division of the Materials Laboratory of WADC and of the National Science Foundation (NSF-G2743) have covered investigations along several lines. First, we have carried out synthetic work entailing reactions of the trimeric and tetrameric phosphonitrilic chlorides with various primary and secondary aliphatic amines, with aromatic amines and with a selected number of polyamines in order to prepare partially or completely N-substituted phosphonitrilamides. We have also examined the properties of a hexa-hydrazide obtained by reaction with hydrazine. Secondly, we have given some consideration to the preparation of the dithiophosphonitrilic acids with the empirical formula $PN(SH)_2$. Thirdly, we have been interested in replacing halogens by halogenoid groups and to this end have effected the preparation of the phosphonitrilic isothiocyanates. Fourth, we have developed a method for the determination of halogen in the phosphonitrilic halides and their partial solvolysis products entailing reaction with metal-ammonia solutions. These studies were initially carried out in an attempt to prepare a phosphonitrilic hydride. Fifth, we have studied the preparation, properties and reactions of the phosphonitrilamides.

N-Substituted Phosphonitrilamides.-

Since the phosphonitrilic chlorides are the

nitrogen analogs of the metaphosphoryl chlorides, solvolytic reactions take place quite readily. Dr. G. Tesi has prepared di- and hexa- substituted derivatives by the action of di-n-butylamine upon trimeric phosphonitrilic chloride. Qualitatively, formation of the di-substituted derivative, $P_3N_3Cl_4[N(C_4H_9)_2]_2$ takes place quite readily. Replacement of the remaining four chlorine atoms to give the hexa-substituted derivative requires more time and higher temperatures. The hexa-substituted compound, $P_3N_3[N(C_4H_9)_2]_6$, when heated at 300°, undergoes a decomposition reaction which entails, at least in part, attack on the carbon chain in the di-n-butylamido groups, as indicated by mass spectrographic analysis of the gaseous decomposition products. The corresponding hexanilide appears to be much more stable thermally.

During the course of his doctoral studies on the phosphonitrilic halides, Dr. William E. Bull (2) isolated a tris-diethylamidotrichlorotriphosphonitrile, $P_3N_3Cl_3(NEt_2)_3$. He also found that ethylenediamine does not react under the given experimental conditions as a polyfunctional amine to bring about cross-linkage, but that reaction occurs with the replacement of two of the chlorine atoms by β-aminoethylamide groups. Even with an excess of ethylenediamine, the product isolated from the reaction mixture was found to be the di-hydrochloride of a bis-β-aminoethylamidotetrachlorotriphosphonitrile, $P_3N_3Cl_4(NHC_2H_4NH_2.HCl)_2$. Orthophenylenediamine gives a product corresponding to substitution of two chlorine atoms.

Reaction of an ether solution of trimeric phosphonitrilic chloride with a slurry of anhydrous hydrazine and ether, results in the formation of the hexahydrazide, $P_3N_3(N_2H_3)_6$ (3). This substance is relatively unstable, decomposes when heated above 300°, but does react as a typical hydrazide with formation of the corresponding hydrazones when treated with aldehydes.

Attempted Preparation of the Phosphonitrilic Hydrosulfides (dithio Phosphonitrilic Acids, or dithiometaphosphimic acids).-

Even though the preparation of some phosphonitrilic mercpatides, $[PN(SR)_2]$, has been reported, it is significant that the simple phosphonitrilic hydrosulfides have never been described. The low molecular weight compounds $[PN(SH)_2]_{3,4}$ should represent interesting starting materials for preparation of polymeric products. These substances might be expected to react with aldehydes, with oxidizing agents to form products containing S-S linkages, or to undergo desolvation with the elimination of hydrogen sulfide to form eventually a highly polymeric phosphonitrilic sulfide,

$(PNS)_n$. The latter substance has not been investigated further since its preparation was reported by Stock (4). Its structure is still unknown. Stock allowed P_4S_{10} to react with liquid ammonia and isolated two compounds from the reaction mixture: a) a compound whose composition can be represented by the empirical formula $PN_3S_2H_8$ corresponding to the diammonium salt of a nitridodithiophosphoric acid, $[NP(SH)_2 \cdot 2NH_3]$ of unknown molecular complexity and, b) the triammonium salt of imidotrithiophosphoric acid. The parent acids of these two substances are related to each other as desolvation products, the first being formed by the elimination of hydrogen sulfide from the second. Stock found that thermal decomposition

$$HNP(SH)_3 \xrightarrow{-H_2S} [NP(SH)_2] \xrightarrow{-H_2S} [PNS]_x$$

of either of these or of the original P_4S_{10}-ammonia reaction mixture led to formation of a substance whose composition corresponded to a phosphonitrilic sulfide. It is obvious, however, that a simple molecular formula cannot be ascribed to either the phosphonitrilic sulfide, or the so-called nitridodithiophosphoric acid. It is our opinion that Stock did have in hand salts of the products which we have attempted to prepare by other methods, although unsuccessfully.

We have attempted to affect thiosolvolysis of the trimeric chloride with liquid hydrogen sulfide, both at low temperatures and under pressure. Although the trimeric phosphonitrilic chloride is soluble in liquid H_2S, no reaction takes place even after standing for long periods of time at room temperature. Liquid hydrogen sulfide would appear to be a rather exotic solvent from which to effect recrystallization of the $PNCl_2$ trimer! Reaction of the trimeric chloride with solutions of hydrogen sulfide in liquid ammonia, with ammonium sulfide in methanol, with triethylamine in liquid hydrogen sulfide, and hydrogen sulfide in triethylamine did not lead to the formation of the desired product.

The Phosphonitrilic Isothiocyanates.-

Except for the reported replacement of chlorine atoms by azide groups (5), no successful attempts have been made to attach other halogenoid groups on the inorganic, but aromatic-like, phosphonitrilic ring systems. We have found (6) that the interaction of potassium thiocyanate with the trimeric and tetrameric phosphonitrilic chlorides in an appropriate solvent, such as acetone, results in the formation of the corresponding isothiocyanates. Rapid reaction takes place with the precipitation of potassium chloride; in the case of the trimer the corresponding isothiocyanate is recovered from the acetone solution; in the case of the tetramer a considerable amount of the less soluble phosphonitrilic isothiocyanate is also precipitated along with

potassium chloride. Some of the physical properties and solubility relationships of the trimeric and tetrameric isothiocyanates are given in Table I.

Infra-red studies indicate retention of the trimeric and the tetrameric ring systems. Strong absorptions at 1016 cm.$^{-1}$ and 1960 cm.$^{-1}$ suggest that the products contain the isothiocyanate grouping (7). Molecular weights also confirm these structures.

From a chemical point of view, the isothiocyanates are extraordinarily interesting substances. They undergo polymerization to elastomeric products at relatively low temperatures (150°) in contra-distinction to the behavior of the corresponding fluorides, chlorides, and bromides which require much higher temperatures. But more interesting even than these polymerization processes, is the fact that a polyfunctional isothiocyanate is available for reaction with a wide variety of active hydrogen compounds, such as ammonia, amines, alcohols, hydrazines, substituted hydrazines, polyhydroxy compounds, as well as polyamines. Work on this subject has been carried out in our laboratories by Dr. R. J. A. Otto, Dr. G. Tesi, and Dr. F. Sherif.

Reaction of Phosphonitrilic Halogen Compounds with Metal-Ammonia Solutions.-

This investigation was originally carried out in the hope that the phosphonitrilic halides would behave like aromatic halogen compounds on treatment with metal-ammonia solutions, that is, lead to the formation of the phosphonitrilic hydrides, or the corresponding amides. Dr. Bull (2) determined the reaction ratio by titrating a solution of sodium in liquid ammonia with a toluene solution of trimeric phosphonitrilic chloride. The reaction ratio consistently approximated eight moles of sodium per mole of trimer. An attempt to work up this reaction mixture indicated that disruption of the trimeric ring system had occurred, and that some reduction of phosphorus had taken place as indicated by the evolution of phosphine on treatment of the product with water.

We have, however, used this reaction as the first step in the quantitative determination of chlorine in the phosphonitrilic chlorides and their partial substitution products. The reaction with metal-ammonia solution effects quantitative conversion of covalent chlorine into ionic chloride. After reaction with metal-ammonia solution, excess of the latter is destroyed by the addition of ammonium nitrate; the solution is evaporated, then acidified with nitric acid and halogen determined by any one of a number of conventional procedures.

Table I

THE PHOSPHONITRILIC ISOTHIOCYANATES

$$(PNCl_2)_{3,4} + 6(g)KSCN \xrightarrow[\text{acetone}]{} [PN(NCS)_2]_{3,4} + 6(g)KCl\downarrow$$

		$[PN(NCS)_2]_3$	$[PN(NCS)_2]_4$
1.	Melting points	42°	90°
2.	Solys. g/100g. solvent at 0°		
	water	insol.	insol.
	acetone	5.14	0.1
	n-heptane	5.23	0.26
	ether	20.9	0.7
	CCl_4	v.s.	11.2

The Phosphonitrilamides.-

Reaction of phosphorus pentachloride with excess liquid ammonia presumably leads to the formation of a mixture of polyhomologous phosphonitrilamides. With the objective in mind of characterizing this PCl_5-NH_3 product mixture Dr. Sowerby has prepared the pure trimeric and tetrameric phosphonitrilamides by the reaction of the corresponding chlorides with liquid ammonia under pressure. Each has been characterized by x-ray diffraction and infra-red study. Chemical properties have also been studied. Aqueous solutions react with varying quantities of formaldehyde to give, initially, water-soluble products which upon evaporation are converted into glassy, water-insoluble products. Both phosphonitrilamides dissolve in 100% acetic acid. From such solutions, compounds corresponding in composition to a 3-HOAc and a 4-HOAc solvate can be precipitated by addition of organic solvents. Deammonation studies at 125°C., further indicate that there is a marked difference in thermal stabilities of the two phosphonitrilamides, but that both decompose at 200°C. eventually with the elimination of one mole of ammonia per mole of monomeric phosphonitrilamide. The resulting phosphams possess the proper analytical composition but are both amorphous materials. Thermogravimetric deammonations carried out by Dr. Saul Gordon of Picatinny Arsenal indicate that deammonation is continuous, over a range of temperatures, after products corresponding to "phospham" have been formed. The deammonation phenomena are quite different from those experienced when phosphorus oxytriamide is subjected to thermogravimetric analysis. Ammonia losses corresponding to the successive formation of polymeric phosphorus oxyimide amide and a highly polymeric phosphorus oxynitride occur at temperatures around 150° and 750°, respectively. We have been particularly interested in this deammonation process because there is a possibility that the intermediate phosphorus oxyimide amide, $PO(NH)(NH_2)$,

of unknown molecular complexity, could very well be represented formula-wise as a monomeric hydroxoamido-phosphonitrile, $[(NP)(OH)(NH_2)]$.

ACKNOWLEDGEMENTS

The assistance of personnel associated with the Victor Chemical Works Research Laboratories, Chicago Heights, Illinois is acknowledged with gratitude. The author also takes this opportunity to express his deep personal appreciation to a loyal and enthusiastic group of co-workers, without whose efforts these researches could not possibly have been carried out, comprising Dr. D. B. Sowerby, Dr. R. J. A. Otto, Dr. G. Tesi, Dr. F. G. Sherif, Dr. W. E. Bull and Mr. D. F. Harnish.

REFERENCES

(1) Stokes, H. N., Am. Chem. J., 19, 782 (1897).
(2) Bull, W. E., Thesis, University of Illinois, 1957.
(3) Otto, R. J. A., and Audrieth, L. F., J. Am. Chem. Soc., 80, 3575 (1958).
(4) Stock, A., Ber., 39, 1967 (1906).
(5) Grundmann, C., and Rätz, R., Z. Naturforsch., 10a, 116 (1955).
(6) Otto, R. J. A., and Audrieth, L. F., J. Am. Chem. Soc., 80, 5894 (1958).
(7) Goubeau, J., and Reyling, J., Z. anorg. allgem. Chem., 294, 96 (1958).

Research On Sulfur-Phosphorus-Nitrogen Polymers

by

Dr.Margot Becke - Goehring
Professor of Chemistry
First Department of Inorganic Chemistry
Chemisches Institut Universität Heidelberg

Contract No. AF 61(052)-35

The research reported in this document has been sponsored by the

Wright Air Development Center

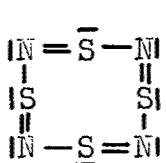
of the Air Research and Development Command, United States Air Force, through its European Office.

I. Polymeric Sulfur-Nitrogen Compounds

A. Thiodithiazyl chloride

a. Preparation

We began our research with the aim of preparing the green and stable sulfur-nitrogen chloride of the emperical formula S_3N_2Cl. This compound (thiodithiazyl chloride) was first obtained in 1880 by Demarçay from the products of the action of S_2Cl_2 on S_4N_4 (I) at low temperatures (1).

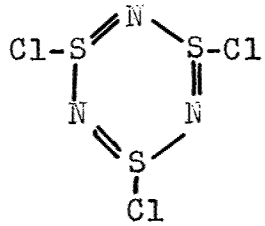


I

(This is only one resonance hybride)

To prepare thiodithiazyl chloride we used at first the reaction of trithiazyl chloride $(SNCl)_3$ (II), with nitrous oxide, NO. We carried out the reaction in nitromethane as a solvent and obtained the desired product in 80% yield.

We were able to obtain thiodithiazyl chloride in still better yield, when we allowed S_4N_4 to react with nitrosyl chloride, NOCl.



II

b. Physical and chemical properties:

Thiodithiazyl chloride is a black crystalline product with a greenish metallic luster. It is insoluble in all organic solvents as well as in water. However, with water it undergoes hydrolysis froming a yellow-brownish solution and a black precipitation. S_3N_2Cl does not react with sulfur dioxide nor with chlorine. On the contrary it reacts with sulfur trioxide forming a sulfur trioxide adduct. By heating up to 100° C decomposition occurs. When heated in high vacuum up to 100° C S_4N_3Cl is formed in a good yield.

B. Thiodithiazyl bromide

The bromide S_3N_2Br, analogous to the above described compound, could be prepared by allowing tetrasulfur tetranitride (I) to react with S_2Br_2 at low tempera-

tures.This bromide S_3N_2Br was a yellowish green crystalline substance. Also this compound appeared to be insoluble in organic solvents.With water hydrolysis occurs.

C. Constitution of Thiodithiazyl halogenides.

Nothing certain can as yet be said about the constitution of the green compounds.The substances are polymeric.In any case they are no simple adducts of SCl_2 or SBr_2 e.g. S_2Cl_2 or S_2Br_2 and S_4N_4.Though the reaction formally may be described by the equation

$$S_4N_4 + S_2Cl_2 \rightarrow S_6N_4Cl_2$$

investigation with radioactive sulfur dichloride, S_2Cl_2, containing S^{35} has shown that the formed reaction product has the composition of S_3N_2Cl and contains changing amounts of sulfur originating from S_2Cl_2. In the maximum it contains 66% sulfur from S_2Cl_2.The formed product,however,does not exchange its sulfur with the one from S_2Cl_2.Figure 1 shows a possible constitution formula for the high polymeric substance.Only one resonance structure is given.The double bonds are suggested not to be localized.

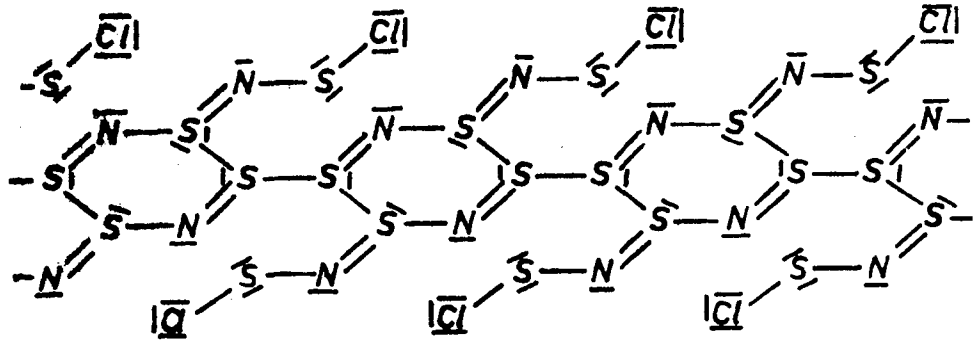


Figure 1.

BEST AVAILABLE COPY

D. Thiotrithiazyl chloride.

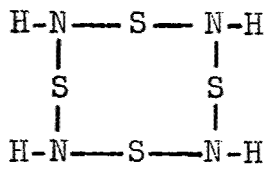
a. Preparation.

The compound S_4N_3Cl was first obtained in 1880 by Demarçay (1) from the products of the action of S_2Cl_2 on S_4N_4 (I). The compound has since be made by the reaction of S_4N_4 with S_2Cl_2 (2). This reaction was examined by MacDiarmid (3), who found that HCl with a trace of moisture would produce S_4N_3Cl from S_4N_4. He concluded that the action of S_2Cl_2 was due to traces of HCl. We have found that at first an adduct $[S_4N_4]\cdot 4\ HCl$ is formed. With traces of water the following reaction occurs:

$$S_4N_4 \cdot 4\ HCl \rightarrow S_4N_3Cl + NH_4Cl + Cl_2$$

Thiotrithiazyl chloride may also be obtained if trithiazyl chloride (II), in boiling carbon tetrachloride is treated with excess of sulfur monochloride, S_2Cl_2. The yield of S_4N_3Cl is here small, at the highest 20%.

In a very good yield it can be obtained by the action of trithiazyl chloride on tetrasulfur tetraimide, $H_4N_4S_4$, (III). At this point it may be mentioned, that trithiazyl chloride (II) is obtained by chlorination of S_4N_4 (4), tetrasulfur tetraimide by reduction reactions with S_4N_4 (5).



III

We established that when S_3N_2Cl was heated for a short time at 80° C under carbon tetra chloride it was converted into thiotrithiazyl chloride S_4N_3Cl in a yield of 95% according to the equation:

$$6\ S_3N_2Cl \rightarrow 4\ S_4N_3Cl + S_2Cl_2$$

The good yield is only obtained when S_2Cl_2 in excess is added.

b. Physical and chemical properties.

Thiotrithiazyl chloride is a bright yellow solid and insoluble in all organic solvents. Hydrolysis with cold water results in black precipitations with variant compositions. These compounds are stable only for a short time. Finally sulfur, sulfur dioxide and thiosulfate beyond ammonium ion results.

The thermal stability of S_4N_3Cl is higher than that of S_3N_2Cl, however, it is not unlimited. When the substance is heated up to 170° C in high vacuum S_4N_4 is formed which may be collected on a sublimation finger.

The oxidation number of sulfur in S_4N_3Cl is + 2.5 (6). The substance is polymeric. Figure 2 shows a possible constitution formula, which may be discussed.

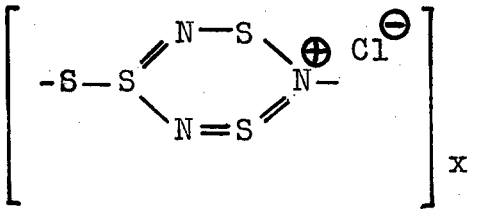


Figure 2

E. Thiodithiazyl-benzene.

a. Preparation.

We tried to prepare SN - chains with organic groups. For this purpose we reacted tetrasulfur tetranitride S_4N_4 with aromatic Grignard compounds in the following manner:
The aryl magnesium bromide which has been prepared in the usual manner, was added to a benzene solution of S_4N_4 at room temperature. The reaction product was poured into diluted acid and the benzene layer evaporated after drying with $CaCl_2$. The crude product was purified by recrystallization. The obtained compounds have the composition IV.

$$R-S-N=S=N-S-R$$

IV

R = C_6H_5-
ClC_6H_4-
BrC_6H_4-
CH_3O-C_6H_4-

b. Chemical and physical properties.

The compounds are very stable in the air. They are well crystallized and intensively colored.

$S_3N_2(C_6H_5)_2$	orange leaflets	m.p. 105° C
$S_3N_2(C_6H_4Cl)_2$	red-brown needles	m.p. 160° C
$S_3N_2(C_6H_4Br)_2$	red-brown leaflets	m.p. 135° C
$S_3N_2(C_6H_4OCH_3)_2$	goldshiny leaflets	m.p. 125° C

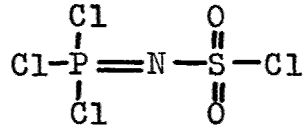
There seems to be a possibility to react these compounds a second time with Grignard reagent and a second time with S_4N_4. By such reactions polymeric substances could be expected.

II. Polymeric Sulfur-Nitrogen-Phosphorus Compounds.

A. Triamido phosphazo sulfamide

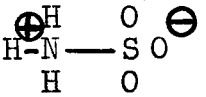
a. Preparation.

We tried to obtain polymeric products in which sulfur is bond to nitrogen and phosphorus. As a starting material V was used. This compound is made according to a procedure of Kirsanov (7) from amidosulfuric acid, VI, and PCl_5:



V

$$H_2N\text{-}SO_3H + 2\ PCl_5 \rightarrow OPCl_3 + Cl_3P{=}N\text{-}SO_2\text{-}Cl + 3\ HCl$$



VI

At first the hydrolysis of this compound was looked at. We could show that the hydrolysis doesn't result in polymeric products, even when only very small quantities of water were used, but gives always amidosulfuric acid, phosphoric acid and hydrogen chloride.

$$Cl_3P{=}N\text{-}SO_2\text{-}Cl + 5\ H_2O \rightarrow H_3PO_4 + H_2NSO_3H + 4\ HCl$$

Then the compound was subjected to ammonolysis. For this purpose ammonia was passed into a benzene solution of the compound V at room temperature excluding any water. An exothermic reaction took place. When no NH_3 is resorbed by the solution any more a colorless precipitation is present, which consists of ammonium chloride and a phosphorus-sulfur amide:

$$Cl_3P{=}N\text{-}SO_2\text{-}Cl + 8\ NH_3 \rightarrow 4\ NH_4Cl + (H_2N)_3P{=}N\text{-}SO_2\text{-}NH_2$$

In order to separate from ammonium chloride the product was suspended in chloroform, then diethylamine has been added and the mixture was refluxed. The following reaction occurs:

$$NH_4Cl + HN(C_2H_5)_2 \rightarrow NH_3 + [H_2N(C_2H_5)_2]Cl$$

Diethylammonium chloride is soluble in chloroform, ammonia escapes and the amide was expected to remain. We obtained a smeary sample with a strong ammonia smell.

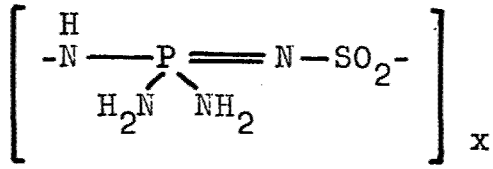
b. Physical and chemical properties.

It has not been possible to separate triamido phosphazo sulfamide completely from ammonium chloride. The compound is easily soluble in water and in liquid ammonia just like ammonium chloride. It is insoluble in organic solvents. The product is unstable, ammonia is released even at room temperature.

B. Diamido phosphazo sulfimide

a. Preparation.

The product described on page 6 could be condensed. We heated in a water-jet vacuum up to 80° C until the ammonia smell disappeared. The wanted condensation product with formula VII resulted.



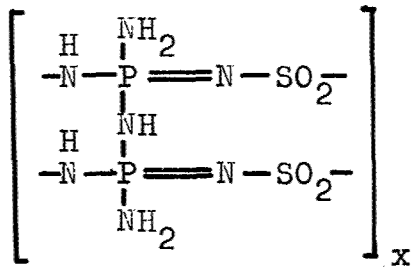
VII

b. Physical and chemical properties.

Compound VII is amorphous and forms a white powder. It is no more soluble in liquid ammonia. With water dissolution occurs only after heating under decomposition. Condensing ammonia on the compound and keeping the reaction product for some time under pressure at room temperature the sample absorbs ammonia again. The ammonia can be removed once more by reducing the pressure. The quantitative investigation of this reaction showed that the following equilibrium is existing:

$$(\text{-NH-P(NH}_2)_2\text{=N-SO}_2\text{-})_x + x\ \text{NH}_3 \rightleftharpoons x\ (\text{H}_2\text{N})_3\text{P=NSO}_2\text{NH}_2$$

When product VII is heated in high vacuum up to 100 - 200° C the compound is splitting off more NH_3 under condensation to higher polymeric products. This condensation is finished within 30 minutes. A compound is formed which has the formula VIII according to the analysis. This sample is colorless and X-ray amorphous. It is insoluble in ammonia and in organic solvents. With water no dissolution or reaction occurs. Hot acids, however, hydrolize the product. Heating up to 150° C doesn't effect any reaction. Heating above 200° C



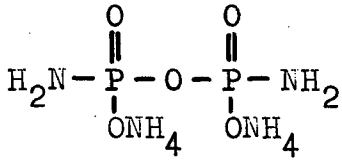
VIII

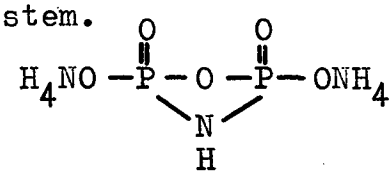
effects further condensation. Ammonia is released and a sulfur and nitrogen containing product can be collected in a cooling trap. This substance probably is a reaction product of SO_2 and ammonia. A brown sample remains which contains phosphorus, nitrogen and sulfur. This substance is insoluble in water and other solvents.

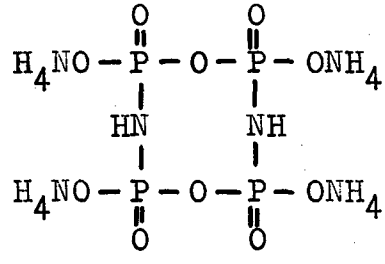
III. Polymeric Phosphorus-Nitrogen Compounds.

A. The Reaction between Phosphorus Pentoxide and Ammonia.

The reaction between P_4O_{10} and NH_3 has been the subject of many investigations (8). Woodstock (9) carried out the reaction between dry NH_3 and P_4O_{10} and heated the reaction mixture in the presence of dry NH_3 to at least 150° C. He thereby obtained products having a P:N ratio of less than 1.5 : 1. Woodstock also used liquid ammonia as reactant, and yet other procedures, i.e. suspending the P_4O_{10} in an inert organic solvent through which he passed the gaseous NH_3. He supposed the first product produced in this reaction to be the diammonium salt of diamidodiphosphoric acid, $P_2O_3(ONH_4)_2(NH_2)_2$, after which this was supposed to undergo condensation with formation of a 4- or 8- membered ring system.







Fischer (10) obtained considerable confirmation of Woodstock's observations. However, he maintained that there was as yet no certain knowledge concerning the mechanism of reaction between P_4O_{10} and NH_3.

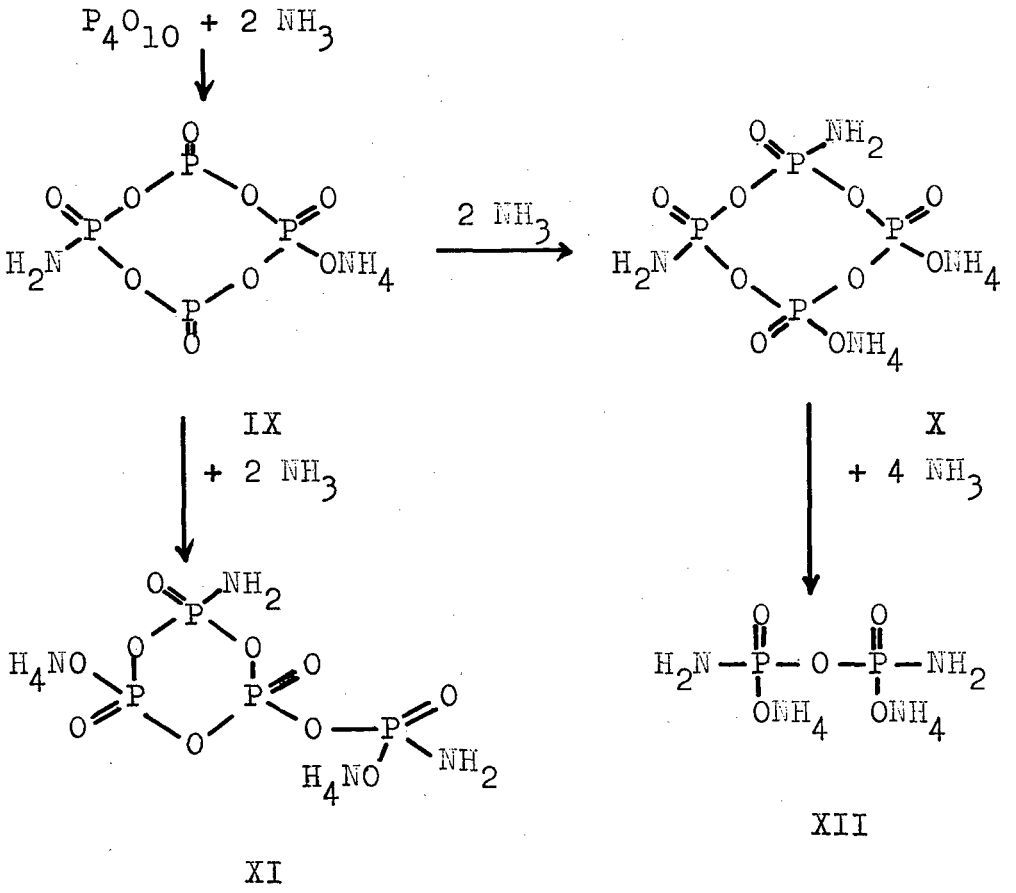
This system appeared, therefore, to be a promising one for further study. We investigated the reaction of liquid NH_3 with P_4O_{10} and found that the substance underwent rapid reaction, but that the surface of the P_4O_{10} soon became inaccessible to the NH_3, thus bringing the reaction to a standstill. In a sealed tube it took about 5-6 weeks for completion of the reaction, when P_4O_{10} could no longer be detected on the X-ray diagram of the product. However, the reaction can be carried out very rapidly in an autoclave, fitted with a magnetic stirrer, at temperatures between 40 and 50° C. In this way reaction was complete after 24 hrs. The atomic ratio P:N:ammonium-N was 1:1.79:1.16. This ratio was also found by Fischer in some of his experiments (10).

A uniform product was obtained by heating the reaction-product to temperatures between 100 and 110° C. Unlike Woodstock (9) we carried out this heating under normal atmospheric conditions for several hours. NH_3 is liberated and the substance becomes puffed up to give a solid product, having an atomic ratio of P:N:ammonium-N 3 1:1.5:1.06.

This product is a light-grey powder, which dissolves slowly in cold water, but rather quickly when it is heated. The solution has an almost neutral reaction and coagulates albumen in acetic acid solution instantaneously. Chromatograms showed the presence of polyphosphate and of oligophosphate, the latter being supposedly obtained by hydrolysis of the polyphosphate. Solutions of our reaction product in water prove to have considerable ability to bind Ca. The binding was complete with an atomic ratio of Ca:P = 1:5.4 .

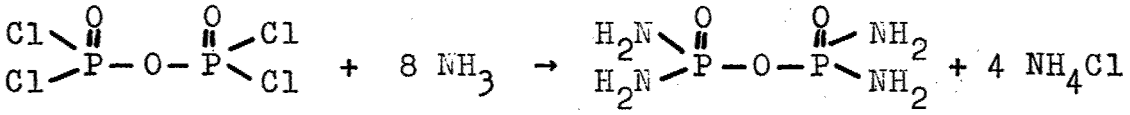
We should like to interprete the reaction as follows: It is supposed that firstly the compound IX is formed by ammonolysis from P_4O_{10}, while further reaction could yield either X or XI. Thilo and coworkers (11) have shown by the solvolysis of P_4O_{10} witha polar solvent e.g. water derivatives of tetrametaphosphoric

acid are mainly obtained. On the other hand one obtains derivatives of isotetrametaphosphoric acid, X, when for example ether is used. On these grounds X is proposed as the principle product in the reaction between NH_3 and P_4O_{10}. It is fairly certain, that the compound XI was not obtained. Since the compound XI was not obtained. Since the compound X is also liable to undergo further reaction after a while it is possible that we obtained the compound XII in the manner shown.



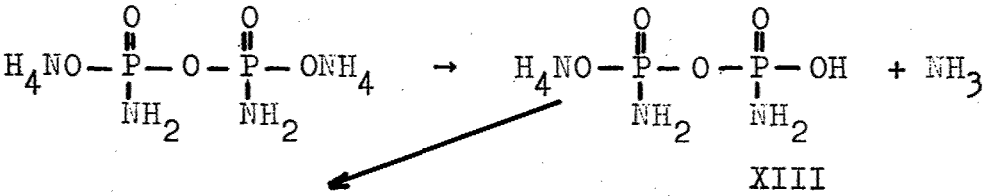
The ammonolysis does not go farther than this, as we have shown (12) that the ammonolysis of $P_2O_3Cl_4$

gives $P_2O_3(NH_2)_4$,

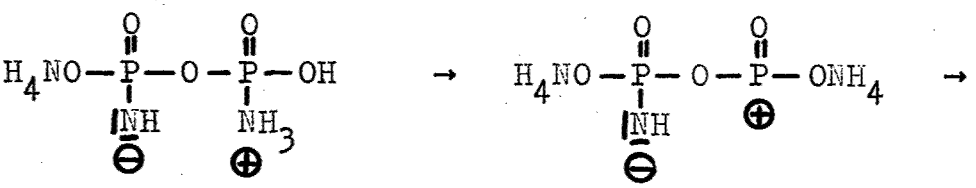


and no derivatives of orthophosphoric acid were produced.

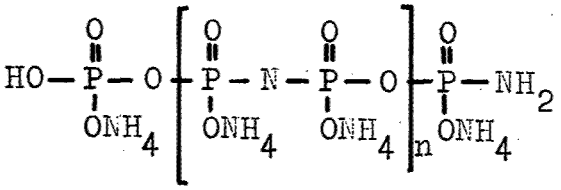
Thus, from the reaction between P_4O_{10} and liquid NH_3 a mixture of reaction products was obtained, which, we believe, include the compounds X and XII. On heating this reaction product, condensation occurs with simultaneous cleavage of NH_3, as the final product shows an atomic ratio of P:N:ammonium-N of about 1 : 1.5 : 1. This latter reaction can occur by either an intra- or intermolecular process. In the first case the reaction may be depicted as follows: the ammonium salt of diamido diphosphoric acid XIII is formed, after which rearrangement takes place analogous to a reaction which has been previously described for amidophosphoric acid (13). This substance will polymerize to a product XV in which each P-atom is connected with 4 ligands.



XIII

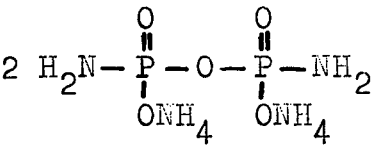


XIV XVa

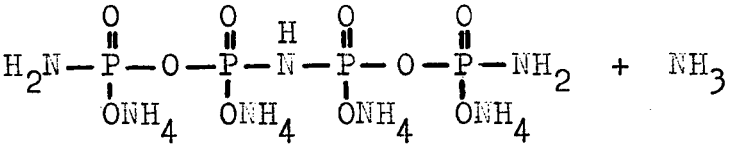


XV

In the case of an intermolecular process the condensation will occur between 2 molecules of the diammonium salt of diamidophosphoric acid to give firstly a derivative of an imidotetraphosphoric acid XVII which will be able to take part in further condensation reactions. This reaction would be analogous to the behaviour of triamidophosphoric acid towards reagents which react with cleavage of NH_3 (14):

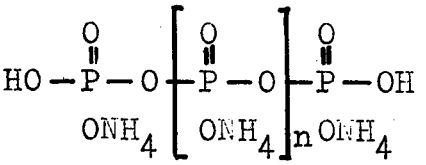


XVI

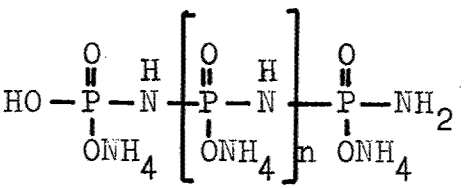


XVII

In both cases an ammonium salt of a polyphosphoric acid is obtained, the P-atoms of which will be linked by O - bridges as well as by NH-bridges. It is quite understandable that this ammonium salt has a great ability to bind calcium. For an ammonium polyphosphate XVIII which is obtained by the rearrangement of amidophosphoric acid (13), as well as an ammonium-polyphosphimate, obtained by the analogous rearrangement of diamido phosphoric acid both have the ability to bind Ca. The substance XV therefore should possess the properties of both XVIII and IXX. In fact the ability to bind Ca is as great with XV as with XVII. The analytical data prove the end product to have the given formula XV. n should be about 1 - 4, the chromatograms showing more probability for n = 4.



XVIII



IXX

B. Hydrolysis of Polymeric Phosphonitrilic chloride.

a. Preparation of the polymeric phosphonitrilic chlorides.

Phosphonitrilic chloride is produced by the reaction of phosphorus pentachloride with ammonium chloride according to:

$$PCl_5 + NH_4Cl \rightarrow 1/n \ (PNCl_2)_n + 4\ HCl$$

The best reaction temperature lies about 150° C. At present there are three preparative methods in use:

1. The old high pressure Method of Stokes, which is carried out in a sealed tube or better in an autoclave (15),

2. Schenck and Römer's solution method (16), whereby a high boiling, inert solvent is used, e.g. tetrachloroethane,

3. the normal pressure method of Steinmann, Schirmer and Audrieth (17) in which method an open tube is used as a reaction vessel.

The phosphonitrilic chloride mixture obtained by one of the above methods then requires separation to give the constituent homologues in a pure state. The only complete separation (15) consists essentially in vacuum-fractional distillation, and yields pure samples of the homologues with n = 3 to 7 besides the so called nitrilo-hexachloro-phosphorus nitride; the residue from the distillation is a thick oil for which Stokes found $\bar{n}$ = 11 as the average gedree of polymerisation. He found further, that the lower and middle homologues produced a rubber-like high polymer at temperatures of ca. 250° C. Strong heating at 500° C causes depoly-

merization of this substance to a mixture of middle and lower molecular weight homologues (18,19),while slow heating at this temperature produces mainly a brittle inelastic substance of obviously still greater molecular weight (16,19).

For the preparation of the required starting material we have used both the "high pressure" and the "solution" methods.The product from the high pressure method contains greater amounts of the intermediate range polymers than that obtained by Schenck and Römer's method which favours the formation of the two lowest molecular weight polymers.

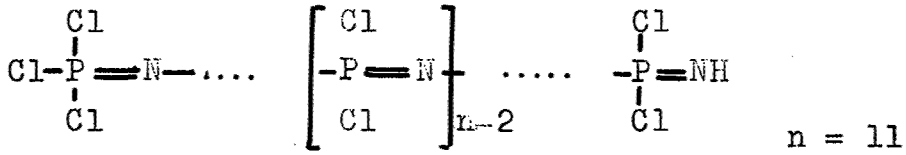
Our treatment of the phosphonitrilic chlorides mixture obtained by one of these two methods differs in many respects from that of Stokes.In particular, it is not possible to treat the reaction product with hot water to remove unreacted phosphorus pentachloride and ammonium chloride as Stokes has desribed,since the higher polymers are very sensitive towards moisture and are immediately decomposed by hot water.The procedure we have used to this end is described as follows:

To remove most of the tri- and tetraphosphonitrilic chloride the raw product was extracted four or five times with boiling petroleum ether under exclusion of water.The phosphonitrilic chloride oil remaining after this extraction still contains crystalls of unreacted ammonium chloride.The oil was dissolved in benzene and freed from these crystalls by filtration. The benzene was distilled off.The small residue of tri- and tetraphosphonitrilic chlorides still present in the oil were now distilled off in high vacuum. The middle homologues (n=5-7) were the distilled off in high vacuum as rapidly as possible.We found that the product can be heated until to temperatures of 280° C without polymerization.Phosphonitrilic chloride rubber,however, is not formed below 400° C under these pressure conditions

After distilling off the middle fraction an oil remains in the distilling flask.The average degree of polymerization is n = 15.For preparative purposes

a sufficient purification of the oily phosphonitrilic chloride can be made by firstly removing the formed trimeric compound by numerous extractions with boiling petroleum ether and then treating a solution of the residue in benzene with absolutely dry alkali-free active charcoal.The residue may be distilled in high vacuum with a bath temperature of about 400° C.

The nuclear magnetic resonance spectrum of the oily phosphonitrilic chlorides (20) showed two resonance peaks,the chemical shift of which was found to be 7.7 p.p.m. and 16.8 p.p.m.This means that there are two kinds of phosphorus atoms in the molecule.From these measurements the following structure can be concluded:



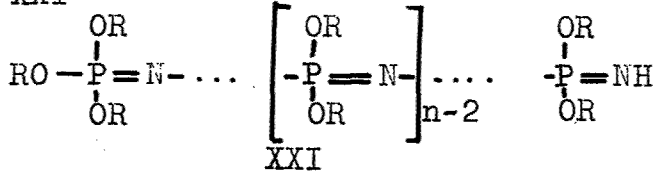
XX

n = 11

b. Solvolysis of oily phosphonitrilic chlorides.

The chlorine in $(PNCl_2)_n$ can be substituted by other groups (21).In these reactions the oily oligomers react much easier than the low homologues.For example the oily oligomers react easily with water and during their preparation and treatment the moisture has to be excluded carefully.This is probably connected with the fact,that the higher oligomers represent chainlike substances without aromatic character.

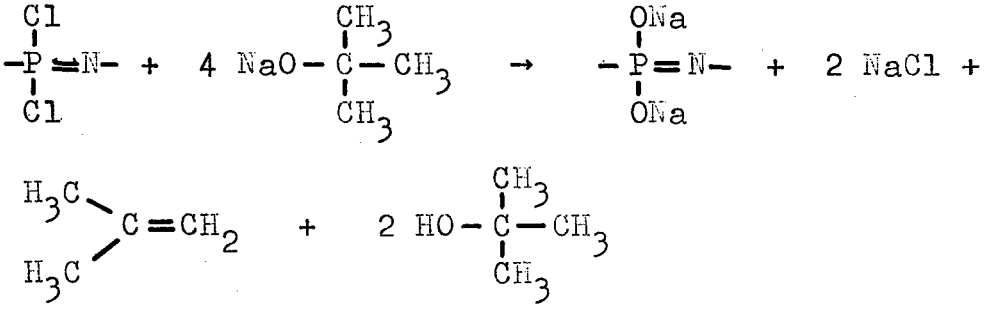
At first we investigated the alcoholysis of the oily phosphonitrilic chlorides. By reacting the oil with a solution of sodium methylate in absolute methanol we obtained the methyl ester as a tough,nearly colorless liquid.Carefully treated the ester has the same polymerisation degree like the oily phosphonitrilic chloride,with which the reaction has been started.The analysis of the compound is in agree with the "open chain" structure XXI



XXI

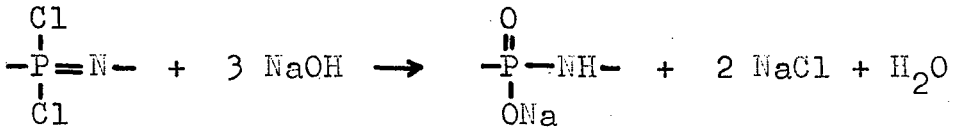
This proposal for the structure is also in agree with the nuclear magnetic resonance spectrum.The nmr spectrum shows an intensive peak at 4.2 p.p.m. with a small peak at a lower field,which may be due to the left end-group in the compound XXI.

Using alkali tet. butylate instead of alkali methylate for the saponification,another reaction goes on.The ester which may be present primarily is immediately decomposed under mild conditions froming isobutylene and the sodium salt of a metaphosphimic acid:



From the obtained salt mixture the free metaphosphimic acid can be prepared by adding concentrated hydrochloric acid and methanol to a water solution.Polymetaphosphimic acid precipitates as a white,X-ray amorphous powder. According to the analysis a monohydrate of this compound is fo med,i.e. the compound contains 1 mol. H_2O per NPO_2H_2-group.

The same,in water easily soluble acid can be prepared by hydrolysis of the oily phosphonitrilic chloride with aqueous alkali:



The hydrolysis of oily phosphonitrilic chloride with aqueous acid,however,results besides water soluble products in a slightly soluble substance with acid properties and with the composition of a metaphosphimic acid hydrate.As it is shown later,we have here higher condensated polymetaphosphimic acids with oxygen-

bridges.

The soluble polymetaphosphimic acid froms in acid solution slightly soluble colorless precipitations with many metals, e.g. with Ag^{+}, Cu^{++}, Mg^{++}, Ca^{++}, Ba^{++}, Zn^{++}, Al^{+++}, Fe^{+++}. Only the silver salts were investigated. We found that the silver content of the precipitation depends strongly on the pH of the solution. If the silver salt is precipitated from a solution which has been brought to a pH of 9 - 10 by adding sodium hydroxide to the polymetaphosphimic acid, its composition corresponds after drying to the one of a primary salt, i.e. only one half of the present protons of the acid are substituted by Ag^{+} : $P_nN_nO_{2n+1}Ag_nH_{n+2}$.

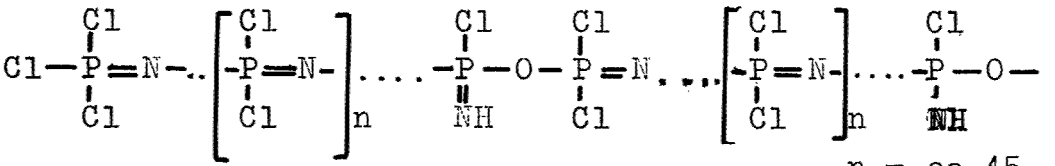
By adding a sufficient excess of $AgNO_3$ and adding more NaOH, the originally colorless precipitation accepts a yellowish coloring which is increasing more and more. Is more NaOH added until a black precipitation of silver oxide is formed and is it removed by diluted acetic acid, the intensively yellow precipitation $P_nN_nO_{2n+1}Ag_{2n}H_2$ remains.

c. Solvolysis of phosphonitrilic chloride caoutchouc.

In a work which has been carried out beyond this contract we could show that oily phosphonitrilic chloride reacts with a small amount of water forming a phosphonitrilic caoutchouc with the polymerization degree of about 90. For the preparation of this caoutchouc the oily phosphonitrilic chloride has to be dissolved in an organic solvent and reacted with water, which is adsorbed by charcoal or silica gel. The following reaction is going on:

$$x\ P_nN_nCl_{2n+1}H + x\ H_2O \rightarrow (P_nN_nCl_{2n-1}OH)_x + x\ HCl$$

The caoutchouc has the following structure:



XXII

n = ca.45

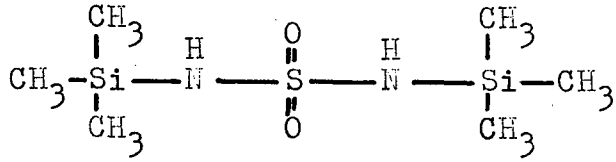
The reaction of this phosphonitrilic chloride caoutchouc with sodium tert.butylate results in the sodium salt of the metaphosphimic acid which corresponds to the caoutchouc and from which the free acid in the hydrate form can easily be prepared.The acid which is colorless and X-ray amorphous,is slightly soluble in hydrochloric acid,better in water.Evidently this acid is identical with the slightly soluble metaphosphimic acid,which is obtained by the acid hydrolysis of the oily phosphonitrilic chloride.The yield,however,is better,when the caoutchouc is used as a starting material.

IV. Sulfur-Nitrogen-Silicon Compounds.

We succeeded in preparing compounds with S-N-Si - linkages.As yet no polymer substances have been prepared. However,if a methyl group connected with Si is substituted by chlorine and is hydrolized carefully the formationsof polymer silicones are to be expected,in which silicon is partially linked with sulfur and nitrogen.

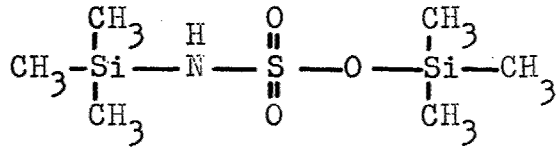
a. Preparation.

1.Hexamethyldisilazan and sulfamide react in an organic solvent producing N,N'-bis-(trimethylsilyl)-sulfamide, (XXIII).The same product could be obtained by the reaction of hexamethyldisilazan with sulfuryl chloride or of trimethyl-N-methylaminosilane with sulfamide. In all preparations the yield was very good.



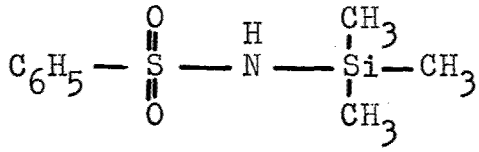
XXIII

2.Chlorosulfuric acid ethyl ester reacts with hexamethyldisilazan producing N-trimethylsilyl-amidosulfuric-acid-trimethylsilyl ester XXIV.



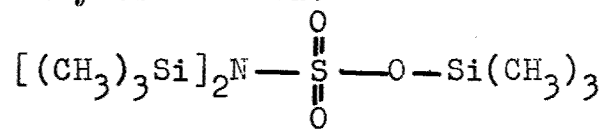
XXIV

3. Benzenesulfamide, $C_6H_5-SO_2-NH_2$ reacts with hexamethyldisilazan producing N-trimethylsilyl-benzenesulfamide XXV. The same compound is obtained by the reaction of benzenesulfamide with trimethyl-N-methylaminosilane.



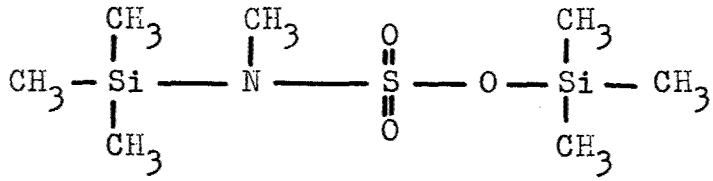
XXV

4. Chlorosulfuric acid reacts with hexamethyldisilazan forming N-bis-(trimethylsilyl)-amidosulfuric-acid-trimethylsilylester XXVI:



XXVI

5. Chlorosulfuric acid ethyl ester reacts with trimethyl-N-methylaminosilane in an organic solvent producing N-methyl-N-trimethylsilyl-amidosulfuric-acid-trimethylsilyl-ester XXVII:



XXVII

b. Physical and chemical properties.

Compound XXIII: white needle shaped crystals, m.p. 104-105°C, soluble in ether, benzene, acetone, dioxane, slightly soluble in 1,2-dichloroethane, carbon tetrachloride and chloroform. On warming with damp ether sulfamide and hexamethyldisiloxan are liberated.

Compound XXIV: colorless needles, m.p. 44°C, b.p. 84°C (0.001 mm Hg), soluble in benzene, ether, petroleum ether, chloroform, carbon tetrachloride. Hydrolysis yields amidosulfuric acid and hexamethyldisiloxan.

Compound XXV: Colorless platelets, m.p. 63°C, soluble in ether, slightly soluble in petroleum ether, very slightly soluble in chloroform and carbon tetrachloride.

Compound XXVI: colorless needles, m.p. 17.5°C, b.p. 78°C (0.05 mm Hg), soluble in benzene, ether, petroleum ether, 1,2-dichloroethane, chloroform, carbon tetrachloride, dioxane; hydrolysis yields amidosulfuric acid and hexamethyldisiloxan.

Compound XXVII: colorless oil, b.p. 72 °C (0.05 mm Hg), soluble in benzene, ether, chloroform, carbon tetrachloride, dioxane, acetone. Hydrolysis yields N-methyl-amidosulfuric acid and hexamethyldisiloxan.

References:

1. E.Demarcay,Compt.rend.hebd.Séances Acad.Sci. 91, 854 (1880)
2. W.Muthmann and E.Seitter,Ber.dtsch.chem.Ges. 30, 627 (1897);H.Wölbling,Z.anorg.allg.Chem. 57, 284 (1908)
3. A.G.MacDiarmid,Nature [London] 164, 1131 (1949)
4. W.Muthmann and E.Seitter,Ber.dtsch.chem.Ges. 30, 627 (1897); A.Meuwsen,Ber.dtsch.chem.Ges. 64, 2311 (1931)
5. H.Wölbling,Z.anorg.allg.Chem. 57, 281 (1908); A. Meuwsen and M.Lösel,Z.anorg.allg.Chem. 271, 217 (1953)
6. M.Goehring and D.Schuster,Z.anorg.allg.Chem. 271, 281 (1953)
7. Zhur. Obshchei Khim. 22, 88 (1952)
8. H.Schiff,Liebigs Ann.Chem. 103, 168 (1857);J.H. Gladstone, J.Chem.Soc. 21, 64 (1868); A.Mente, Liebigs Ann.Chem. 248, 245 (1888); A.Sanfourche,A. Hernette and M.Fau,Bull.Soc.Chim.France [4] 47, 273 (1930)
9. W.H.Woodstock,U.S.Patent 2 122 122 (1938)
10. H.Fischer:Über die Reaktionsprodukte aus Phosphorpentoxyd und Ammoniak und deren Eignung zur Wasserenthärtung.Verlag M.Dittert u.Co.,Dresden 1941.
11. E.Thilo and W.Wieker,Z.anorg.allg.Chem. 277, 27 (1954)
12. M.Goehring and K.Niedenzu,Chem.Ber. 89, 17 (1956)
13. M.Goehring and J.Sambeth,Chem.Ber. 90, 232 (1957)
14. M.Goehring and K.Niedenzu,Chem.Ber.89, 1771 (1956)
15. H.N.Stokes,Amer.chem.Journ.19, 782 (1897)
16. R.Schenck and G.Römer,Ber.dtsch.chem.Ges.57, 1343 (1924)
17. R.Steinman,F.B.Schirmer and L.F.Audrieth,J.Am. Chem.Soc. 64, 2377 (1942)

18. H.N.Stokes, Am.Chem.Journ. 17, 275 (1895)
19. A.M.de Ficquelmont, Compt.rend.204, 689 (1937)
20. J.R.Van Wazer and E.Fluck,private communication
21. L.F.Audrieth,R.Steinman and A.D.F.Toy,Chem.Rev. 32, 109 (1943)

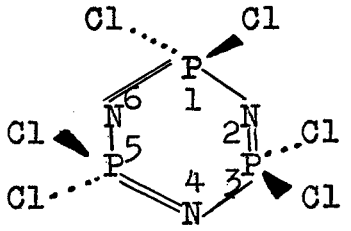
SOME ASPECTS OF PHOSPHONITRILIC HALIDE CHEMISTRY

by R.A. Shaw

Birkbeck College (University of London)

In the phosphonitrilic halide field two distinct types of polymers can be visualised, addition polymers and condensation polymers. The former are of the "inorganic rubber" type which can be produced, amongst others, from the fluorides, chlorides, and bromides. This class will not be further considered in this paper. The second type are condensation polymers and here the degree of cross-linking and its stereochemistry will be factors of major importance. Within recent years the stereospecific aspects of polymerisation processes have been studied and significant advances have been made in this field. This paper will deal mainly with the sterochemistry of the cyclic trimer $(PNX_2)_3$ which is known to be a six-membered ring system. Published structure determinations are few and in the six-membered ring system have been confined to the chloride, $(PNCl_2)_3$. This has been shown by electron diffraction of its vapour[1] and X-ray diffraction of its solid[2] to possess a planar six-membered ring with all P...N distances equal, and with the two chlorine atoms attached to each phosphorus atom projecting above and below the plane of the ring.

Figure 1



If we now make the tentative assumption that most, or perhaps all, the known trimer derivatives also possess a planar ring structure we can attempt to discuss their stereochemistry.

In the benzene system, if the ring is progressively substituted by only one type of substituent R, twelve derivatives $C_6H_{6-n}R_n$ (n=1,2,...6) (excluding enantiomorphs) in all are possible, which are pictured in figure 2.

The only type of isomerism frequently met in this field is positional, as stereoisomerism is precluded by the fact that the substituents are also in the plane of the ring. On occasions, when two particularly bulky ortho substituents are present, optical isomerism has been observed.

The position is different in the phosphonitrilic halide field. If we take as a specific example the trimeric chloride $(PNCl_2)_3$ and substitute it progressively by one type of substituent R, again twelve derivatives $P_3N_3Cl_{6-n}R_n$ (n=1,2,...6) (excluding enantiomorphs) in all are possible, which are displayed in figure 3.

In this series possibilities for positional, stereo, and optical isomerism abound.

Let us consider what evidence we have for the existence of structures I to XII. Until recently virtually all known reactions of the trimeric phosphonitrilic chloride have yielded products where two, four or six chlorine atoms had been substituted.[3,4] This led to the implied or expressed suggestions[4,5] that the chlorine atoms reacted in pairs and that these pairs resided on the same phosphorus atoms, i.e. structures of type II, VIII and XII. Very recent work at Heidelberg University and Birkbeck College, London, has shown however that the situation is much more complex than was once believed and evidence has been adduced that the older views are by no means universally correct. At once we must say that no complete series is known so far, and that the examples have been chosen from a variety of compounds some containing different substituents. But it is hoped that these will suffice to illustrate the different structural types. A monobromide $P_3N_3Cl_5Br$ has been synthesised from phosphorus pentachloride and ammonium bromide[6] and more recently mono(dialkylamino) derivatives have been isolated,[7] which are incidentally the first compounds of type I ($P_3N_3Cl_5R$) which have been prepared by substitution in the trimeric system.

Considering now the three disubstituted derivatives II ⟶ IV we know with certainty that Bode and

FIGURE 2

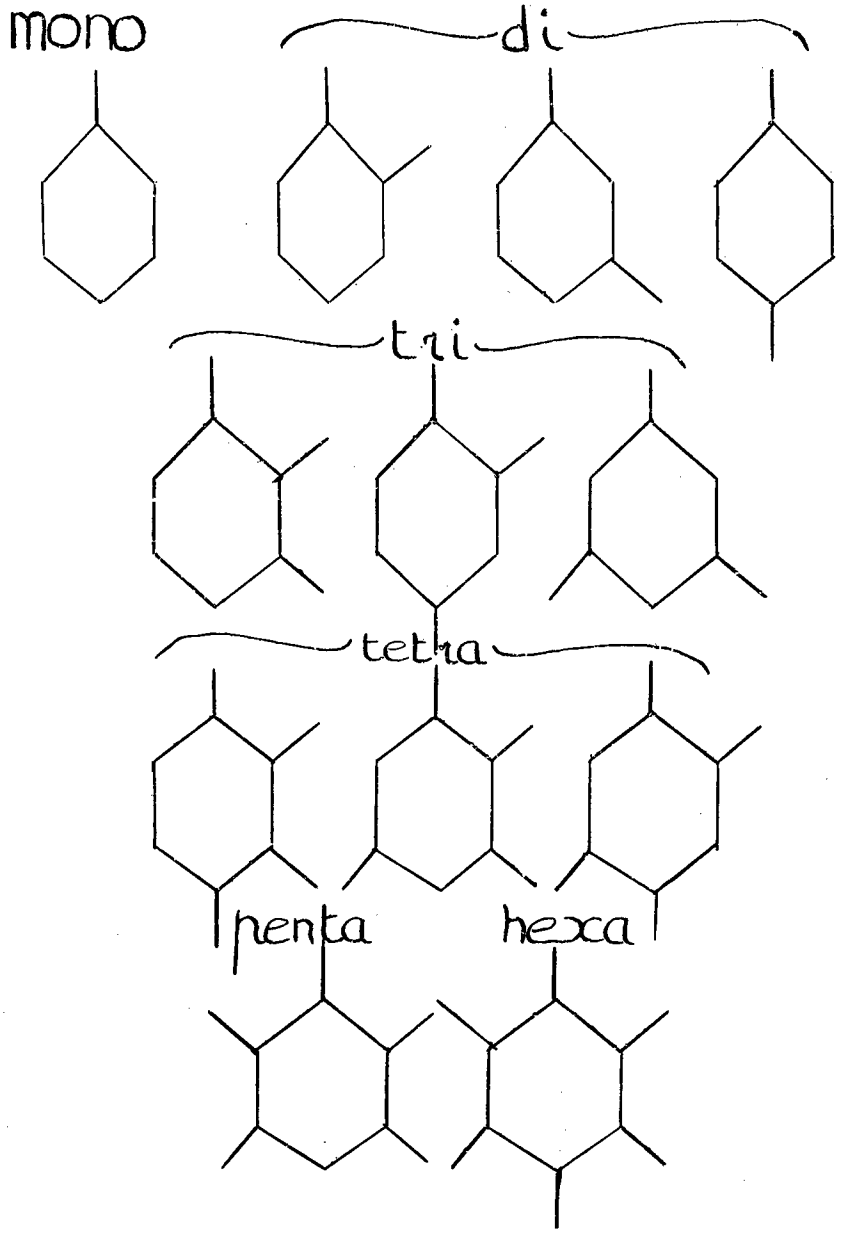
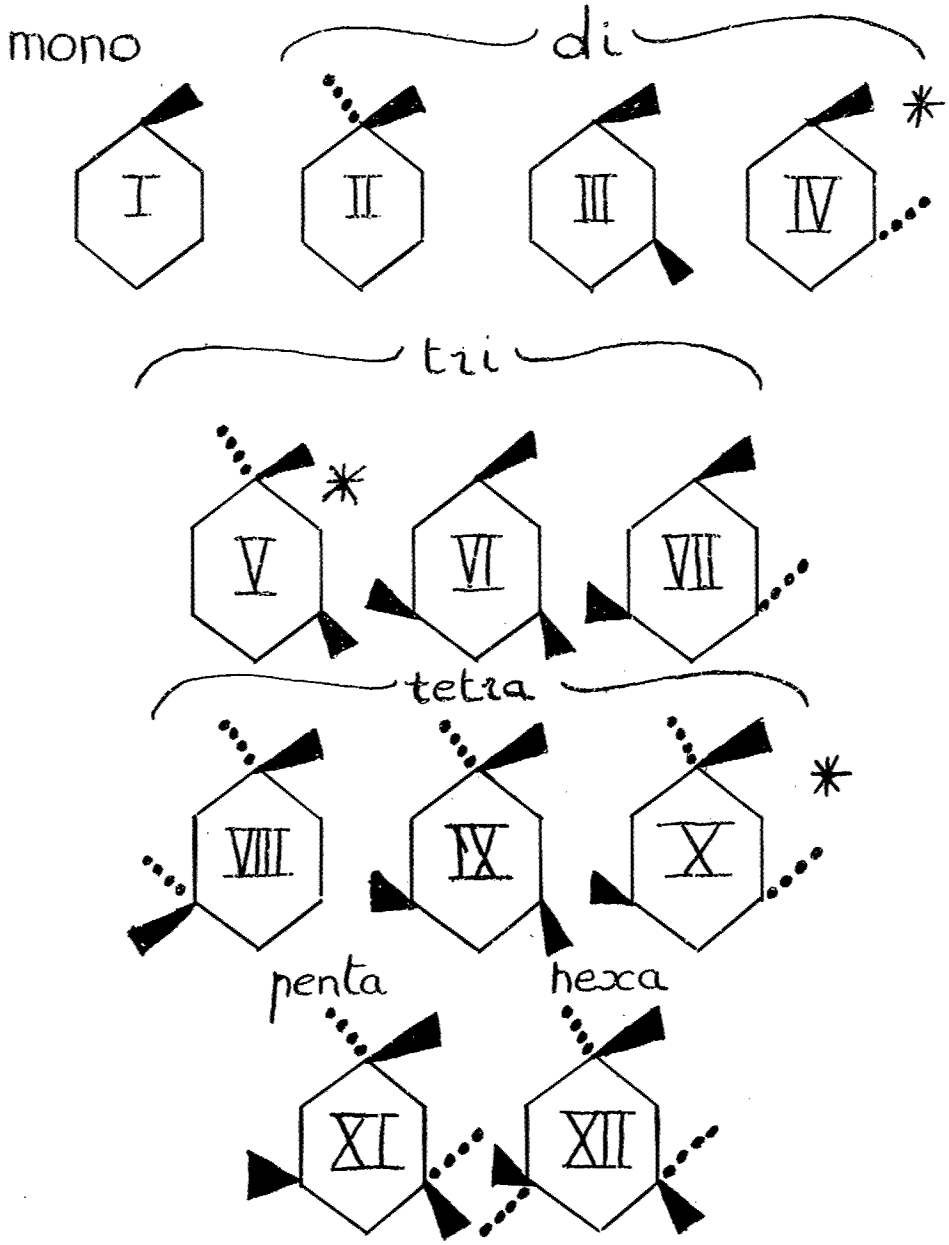


FIGURE 3



* Indicates absence of a plane or centre of symmetry

Bach have obtained by a Friedel-Craft's reaction a diphenyl derivative $P_3N_3Cl_4Ph_2$ of the type II whose structure they proved by degradation. The elegant work of Becke-Goehring and John[8] on the amides and substituted amides of the trimer provide examples of other structural types. These authors suggest that the first three amino residues are placed on three different phosphorus atoms thus producing di- and tri-substituted compounds of the 1,3- and 1,3,5- types. We consider that many of the di- and tri- substituted amides prepared in our laboratory[7,9] possess a similar structure. So far no conclusive evidence has emerged whether these di-substituted amides represent the cis (III) or trans (IV) types or possibly both. The same problem of cis-trans isomerism (VI and VII) is posed by the above-mentioned tri-substituted amides. The isomeric 1,1,3- structure (V) has so far not been reported.

Recently we have prepared a tetraphenyl derivative $P_3N_3Cl_2Ph_4$,[10] to which we tentatively assign the structure VIII. Tetrasubstituted amides presumably of the 1,1,3,5-type have been prepared by the Heidelberg workers[8] and by us[7,9] and again it is not yet clear whether they represent the structural types IX, X, or both. Pentasubstituted compounds (XI) are unknown, but numerous examples of hexasubstituted trimer derivatives have been reported.[3,4,7,8,9]

We can thus see that many of the twelve structural types represented in figure 3 are already known, although in many cases these structures have so far not been rigidly proved. Furthermore it seems that different reaction mechanisms can provide different isomers in this system. It is expected that the problems of structure and the isolation of the remaining species will be solved in the not too distant future, and we hope that work at present in progress at Birkbeck College will make a contribution to this.

Finally a brief mention of similar problems in the tetramer field will be made. Recently Shaw and Stratton[11] have isolated two stereoisomeric tetraphenyl derivatives $P_4N_4Cl_4Ph_4$ the data for which is summarised below.

	Found		Calculated for $P_4N_4Cl_4Ph_4$
	A	B	
m.p.	248°	148°	
M.W.	645,619	648	630
C	44.8%	44.4%	45.7%
H	3.2%	3.7%	3.2%
N	8.8%	8.8%	8.9%
Cl	22.4%	22.3%	22.5%
P	20.0%	20.2%	19.7%
I.R.	1313,1294,1282cm.$^{-1}$	1308,1292, 1275cm.$^{-1}$	Characteristic of tetramer derivatives[12,13]
Hydrolytic degradation	$PhP(O)(OH)_2$	$PhP(O)(OH)_2$	

This is the first reported example of stereoisomerism in the phosphonitrilic halide field, as well as, to the best of our knowledge, the first authenticated isomerism of this type in a purely inorganic ring system.

Other partially and fully substituted tetramer derivatives are also under investigation.[14,15]

It is hoped that this short paper on the stereochemistry of the phosphonitrilic halides will have demonstrated the scope and importance of fundamental studies of structure and the need for the examination of reaction mechanisms in this field.

References

[1]Brockway, L.O. & Bright, W.M., J. Amer. chem. Soc., 1943, 65, 1551

[2]Wilson, A. & Carroll, D.F., Chem. & Ind., 1958, 1558

[3]Audrieth, L.F., Steinman, R. & Toy, A.D.F., Chem. Rev., 1943, 32, 109

[4]Bode, H. et al., Ber. dtsch. chem. Ges., 1942, 75, 215 et seq.

[5]"Phosphonitrilic chlorides", information pamphlet, Albright & Wilson (Mfg.) Ltd.

[6]Rice, R.G., Daasch, L.W., Holden, J.R. & Kohn, E.J., J. inorg. nucl. Chem., 1958, 5, 190

[7]Ray, S.K. & Shaw, R.A., unpublished results

[8]Becke-Goehring, M. & John, K., Angew. Chem., 1958, 70, 657

[9]Ray, S.K. & Shaw, R.A., Chem. & Ind., 1959, 53

[10]Shaw, R.A. & Wells, F.B.G., unpublished results

[11]Shaw, R.A. & Stratton, C., Chem. & Ind., 1959, 52

[12]Daasch, L.W., J. Amer. chem. Soc., 1954, 76, 3403

[13]Shaw, R.A., Chem. & Ind., 1959, 54

[14]Matalia, A.V. & Shaw, R.A., unpublished results

[15]Fitzsimmons, B.W. & Shaw, R.A., unpublished results

Wright Air Development Center, Ohio
CONFERENCE ON HIGH TEMPERATURE POLYMER AND FLUID RESEARCH, by Polymer Branch, Materials Laboratory. October 1959, 484p. incl. illus. (Proj. 7340, Task 73404) (WADC TR 59-427) Unclassified Report

This report is a compilation of the papers presented at the conference on "High Temperature Polymer and Fluid Research". This conference was held on 26-28 May 1959 at the Dayton Biltmore Hotel, Dayton 2, Ohio.

The agenda included polymers containing M-O-M Bonds, Silicon-containing materials, novel polymers and polymerization

(over)

techniques, inorganic polymers and a session on general interest.

UNCLASSIFIED

I. Polymer Branch, Materials Laboratory, WADC, Wright-Patterson Air Force Base, Ohio

UNCLASSIFIED

UNCLASSIFIED

Wright Air Development Center, Ohio
CONFERENCE ON HIGH TEMPERATURE POLYMER AND FLUID RESEARCH, by Polymer Branch, Materials Laboratory. October 1959, 484p. incl. illus. (Proj. 7340, Task 73404) (WADC TR 59-427) Unclassified Report

This report is a compilation of the papers presented at the conference on "High Temperature Polymer and Fluid Research". This conference was held on 26-28 May 1959 at the Dayton Biltmore Hotel, Dayton 2, Ohio.

The agenda included polymers containing M-O-M Bonds, Silicon-containing materials, novel polymers and polymerization

(over)

techniques, inorganic polymers and a session on general interest.

UNCLASSIFIED

I. Polymer Branch, Materials Laboratory, WADC, Wright-Patterson Air Force Base, Ohio

UNCLASSIFIED

UNCLASSIFIED