UNCLASSIFIED

AD NUMBER
AD370788
CLASSIFICATION CHANGES
TO: **UNCLASSIFIED**
FROM: **CONFIDENTIAL**
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 31 DEC 1965. Other requests shall be referred to Defense Advanced Research Projects Agency, 3701 North Fairfax Drive, Arlington, VA 22203-1714.**
AUTHORITY
ONR ltr dtd 4 May 1977 ONR ltr dtd 4 May 1977

THIS PAGE IS UNCLASSIFIED

SECURITY MARKING

The classified or limited status of this report applies to each page, unless otherwise marked.
Separate page printouts MUST be marked accordingly.

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 AND 794. THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. 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.

BLANK PAGES
IN THIS
DOCUMENT
WERE NOT
FILMED

Report RMD 5043-65F

Contract No. NOnr 4364(00)

82078

(U)
ADVANCED OXIDIZER RESEARCH

Report Period: 1 January 1965 to 31 December 1965

Research reported in this publication was supported by the Advanced Research Projects Agency.

GROUP 4
DOWNGRADED AT 3-YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS

Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

Thiokol
REACTION MOTORS DIVISION

(U)

ADVANCED OXIDIZER RESEARCH

Report RMD 5043-65F

Report Period: 1 January 1965 to 31 December 1965

Report Date: 31 December 1965

Contract No. NOnr 4364(00), ARPA Order No. 417, Amendment No. 2

Submitted by: Donald D. Perry
DONALD D. PERRY
Supervisor, Synthetic
Chemical Research Section

Approved by: Murray S. Cohen
MURRAY S. COHEN
Manager, Chemistry
Department

David J. Mann
DAVID J. MANN
Director of Research

FOREWORD

This final report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of advanced oxidizer chemistry being conducted at this Division under the sponsorship of the Advanced Research Projects Agency. This work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer.

The report consists of Sections I, II and III covering Tasks 51, 53 and 55, respectively. The body of each task represents the results of completed studies in the form of preprints of manuscripts prepared for publication. Progress in areas in which data are incomplete or experimentation is expected to continue is summarized in an appendix.

ABSTRACT

This report describes research conducted during the past year at Thiokol Chemical Corporation, Reaction Motors Division, on advanced solid oxidizers. The effort was divided into three major tasks covering the areas of organic difluoramine chemistry, inorganic oxidizer synthesis, and thermal stability of inorganic perchlorates.

Task 51 - Organic Difluoramine Chemistry

The thermally initiated reaction between t-butyl iodide and tetrafluorohydrazine was found to provide a convenient synthetic route to t-butyldifluoramine. The latter reacts with organolithium reagents to yield a mixture of azo compound, dialkyldifluorohydrazine, tertiary amine, and hydrocarbon. Under similar conditions, triphenylmethyldifluoramine gives benzophenone anil and n-octane. t-Butyldifluoramine was attacked by concentrated nitric acid to yield a complex mixture of products, including nitrates and nitrites, while triphenylmethyldifluoramine gave mainly triphenylcarbinol.

The synthesis and properties of some geminal and vicinal bis(difluoramino)-alkanes and phenyl-substituted bis(difluoramino)alkanes are described. Gas chromatographic methods were employed for the purification of some of the bis(difluoramino)alkanes. Pairs of geometric and configurational isomers were successfully separated and purified to >99%.

Some base-catalyzed elimination reactions of difluoramines have been found to give products other than the expected simple ketofluorimines or nitriles. Conditions under which a typical bis(difluoramino)fluoraminomethoxy-alkane eliminates the elements of HNF_2 to yield an N,N,N'-trifluoroalkoxy-formamidine were also studied.

Attempts were made to develop an efficient method for the synthesis of cyclohexyldifluoramine by the fluorination of ethyl N-cyclohexylcarbamate and by other routes, but yields of more than 10% could not be obtained. Some preliminary results on the reactions of difluoramines and ketofluorimes with organic peroxides and with strong fluoride-ion acceptors were also carried out.

Task 53 - Inorganic Oxidizer Synthesis

An adduct of N_2F_4 with AsF_5 can be obtained by the reaction of N_2F_4 with liquid AsF_5 at -78°, or by the reaction of N_2F_4 with $HAsF_5$ in HF -78°. At low temperatures the composition of the adduct approximates $N_2F_4 \cdot 2AsF_5$ and at room temperature $N_2F_4 \cdot AsF_5$. The fact that it may be prepared by the reaction of N_2F_4 with $HAsF_6$ ($H_2F^+AsF_6^-$) leads to the hypothesis that it has the ionic structure, $N_2F_3^+AsF_6^-$. Infrared and F^{19} n.m.r. data appear to support this hypothesis. The X-ray pattern of $N_2F_3AsF_6$ has been indexed on a cubic unit cell with $a_0 = 7.65$ Å. The $N_2F_3^+$ ion is stable in the presence of ClO_4^-. Thus, the possibility is open for the synthesis of $N_2F_3ClO_4$ from $N_2F_3AsF_6$, if a proper reaction medium can be found.

Efforts to prepare O_2ClO_4, O_2ClF_4, and N_2FClF_4 were unsuccessful. Studies of the reaction of $NONF_2$ with AsF_5 have been initiated, the objective being the synthesis of $NONF^+AsF_6^-$.

Task 55 - Thermal Stability of Advanced Solid Oxidizers

The thermal decomposition of hydroxylammonium chloride was studied between 130° and 160° as a preliminary phase of a study of the thermal decomposition of hydroxylammonium perchlorate. Reaction products were analyzed and the reaction was found to follow two paths concurrently, one producing nitrogen and the other nitrous oxide. Stoichiometries for these paths previously reported in the literature were found to hold true, but the influence of temperature on the rate of each path was found to be considerable, in contrast to the reported absence of temperature dependency. The activation energy of the nitrogen-producing path is 63 kcal/mole; that of the nitrous oxide producing path is 37 kcal/mole.

The thermal decomposition of hydroxylammonium perchlorate was studied between 120° and 150° in sealed systems, and at 180° in an open system. The reaction in closed systems was found to be rate-controlled by a different step from that which is rate-controlling for either path in the decomposition of the chloride; the activation energy is 44.3 kcal/mole. A stoichiometry was obtained in mass-balance experiments in sealed systems and the mechanism of the reaction outlined. Experiments in the open system, while inconclusive by themselves, do show that removal of the perchloric acid produced in the reaction leads to production of some NH_4ClO_4; the experimental results were related to those recently reported from USNOTS, China Lake, to yield a comprehensive integration of the data obtained on sealed systems of both the chloride and perchlorate.

The results of a small number of experiments on hydrazinium diperchlorate have been recorded in an appendix, as well as results of long-term "order of magnitude" comparative thermal stability tests on hydroxylammonium perchlorate and hydrazinium diperchlorate at 70°.

SECTION I

TASK 51

ORGANIC DIFLUORAMINE CHEMISTRY

Section I

ORGANIC DIFLUORAMINE CHEMISTRY (U)

Harry F. Smith
and
Joseph J. Dvorak

Contributors

J. A. Castellano
D. G. Chowanec
J. A. Creatura
R. Crooker
A. W. Fremmer
D. F. Kates
D. N. Pregler
P. Shapiro
M. J. Socha
E. St. Cyr
W. H. Wieting
D. Y. Yee

CONTENTS

		Page
I.	INTRODUCTION	1
II.	MANUSCRIPTS OF PAPERS FOR PUBLICATION	2
	A. Some Reactions of Alkyl- and Arylakyldifluoramines	3
	B. Preparation and Properties of Some Bis(difluoramino)alkanes and arylalkanes	29
	C. Gas Chromatographic Separation of Some Bis(difluoramino)alkanes	51
	D. Some Elimination Reactions of Organic Difluoramines	65
III.	APPENDIX	79
	A. Discussion	79
	1. Synthesis of Cyclohexyldifluoramine	79
	2. Addition Reactions of Ketofluorimines	84
	3. Peroxyacid Oxidation of Ketofluorimines	86
	4. Reactions of Nitrogen-Fluorine Compounds with Lewis Acids	86
	B. Experimental	88
	1. Attempted Reaction of Trifluoropentoxyformamidine with Benzoyl Peroxide	88
	2. Reaction of Trifluoropentoxyformamidine with AsF_5	88
	3. Rection of 1,2-Bis(difluoramino)cyclohexane with AsF_5	89
	4. Reaction of 1,2-Bis(difluoramino)cyclohexane with BF_3	89
IV.	REFERENCES	90

ILLUSTRATIONS

MANUSCRIPT B

Figure		Page
1	Infrared Spectrum of 1,1-Bis(difluoramino)hexane	32
2	Infrared Spectrum of 1,1-Bis(difluoramino)heptane	33
3	F^{19} N.m.r.. Spectrum of α-2,3-Bis(difluoramino)-pentane	33
4	F^{19} N.m.r.. Spectrum of β-2,3-Bis(difluoramino) pentane	35
5	Proton N.m.r.. Spectrum of α-2,3-Bis(difluoramino) pentane	37
6	Proton N.m.r. Spectrum of β-2,3-Bis(difluoramino)-pentane	37
7	Infrared Spectrum of 2-Difluoramino-2-hydroxyphenyl-ethane	41
8	Infrared Spectrum of α,α-Bis(difluoramino)toluene	41
9	Infrared Spectrum of 1,2-Bis(difluoramino)phenylethane	42
10	Infrared Spectrum of 1,1-Bis(difluoramino)phenylethane	42
11	Infrared Spectrum of 2,2-Bis(difluoramino)phenylethane	43

MANUSCRIPT C

1	G. C. Separation of cis- and trans-1,2-Bis(difluoramino)-cyclohexane on Dodecyl Phthalate	55
2	Infrared Spectrum of trans-1,2-Bis(difluoramino)-cyclohexane	55

ILLUSTRATIONS (cont)

MANUSCRIPT C

Figure		Page
3	Infrared Spectrum of cis-1,2-Bis(difluoramino)-cyclohexane	55
4	G. C. Separation of cis- and trans-1,2-Bis(difluoramino)cyclohexane on Silicone	58
5	G. C. Separation of Diastereoisomers of 2,3-Bis-difluoramino)pentane	60
6	Infrared Spectrum of α-2,3-Bis(difluoramino)pentane	60
7	Infrared Spectrum of β-2,3-Bis(difluoramino)pentane	61
8	G. C. Separation of 2,3-Bis(difluoramino)-2,3-dimethylbutane	63
9	Infrared Spectrum of 2,3-Bis(difluoramino)-2,3-dimethylbutane	63

TABLES

MANUSCRIPT A

		Page
I	Principal Mass Peaks of Di-n-butyl-t-butylamine and Tri-n-butylamine	8
II	Reactions of t-Alkyldifluoramines with Organolithium Reagents	8
III	Reactions of t-Alkyldifluoramines with 70% Nitric Acid	12

MANUSCRIPT B

I	Properties of 1,1-Bis(difluoramino)alkanes	32
II	Properties of 2,3-Bis(difluoramino)alkanes	40
III	Properties of Phenyl-substituted Bis(difluoramino)-alkanes	40

MANUSCRIPT C

I	Gas Chromatographic Conditions	53
II	Mass Spectra of 1,2-Bis(difluoramino)cyclohexanes	56
III	Physical Properties of 1,2-Bis(difluoramino)cyclohexanes	57

TABLES (cont)

MANUSCRIPT C

		Page
IV	Analyses and Physical Properties of 2, 3-Bis(difluoramino)-pentanes	59
V	Analyses and Melting Points of 2, 3-Bis(difluoramino)-2, 3-dimethylbutane	62

MANUSCRIPT D

I	Partial Mass Spectrum of Dehydrofluorination Product	68

APPENDIX

I	Aqueous Fluorination of Ethyl N-Cyclohexylcarbamate	81

I. INTRODUCTION

The principal objective of this research program has been to investigate the chemical properties of alkyldifluoramines and related organic nitrogen-fluorine compounds, and to elucidate the mechanisms of those reactions which were found to occur. In addition, certain bis(difluoramino) compounds have been synthesized and highly purified, for the evaluation of thermal shock sensitivity and thermodynamic data.

Earlier reports (Ref 1, 2, 3) have dealt with the reactions of alkyldifluoramines with a variety of reagents, with the preparation and chemical properties of bis(difluoramino)cyclohexenes, and with the reactions of the ketofluorimino group. The latter study was directed toward defining the scope and generality of the active-hydrogen addition reactions characteristic of perfluoroguanidine, and a determination of the extent to which the ketofluorimine group resembles carbonyl, olefin, or oxime groups.

This report presents the results of further studies along these lines. It includes, in addition, a discussion of the synthesis and purification of selected bis(difluoramino)alkanes for sensitivity and thermochemical investigations, formerly treated separately as Task 52 (Ref 4, 5, 6). The appendix to this report also includes the results of some preliminary experiments on the reactions of organic nitrogen-fluorine compounds with peroxides and with Lewis acids such as arsenic pentafluoride. This research will be continued during the coming year.

II. MANUSCRIPTS OF PAPERS FOR PUBLICATION

A. Some Reactions of Alkyl- and Arylalkyldifluoramines

Accepted for publication in a forthcoming issue of the Advances in Chemistry Series

B. Preparation and Properties of Some Bis(difluoramino)alkanes and -arylalkanes

Prepared for submission, when declassified, to Journal of Chemical and Engineering Data

C. Gas Chromatographic Separation of Some Bis(difluoramino)-alkanes

Prepared for submission, when declassified, to Journal of Gas Chromatography

D. Some Elimination Reactions of Organic Difluoramines

Prepared for submission, when declassified, as a Note to Journal of Organic Chemistry

Some Reactions of Alkyl- and Arylalkyldifluoramines

Harry F. Smith, Joseph A. Castellano and Donald D. Perry

Contribution from the Chemistry Department
Thiokol Chemical Corporation
Reaction Motors Division
Denville, New Jersey

ABSTRACT

The thermally initiated reaction between t-butyl iodide and tetrafluorohydrazine provides a convenient synthetic route to t-butyldifluoramine. Tertiary alkyldifluoramines have been found to react with organolithium reagents and with concentrated nitric acid. The reaction of triphenylmethyldifluoramine with n-butyllithium produced benzophenone anil and n-octane. t-Butyldifluoramine reacted with organolithium reagents to yield a mixture of azo compound, dialkyldifluorohydrazine, tertiary amine, and the hydrocarbon resulting from the coupling of two free radicals derived from the organometallic reagent. A mechanism involving two successive one-electron reduction steps, to give first nitrogen radicals and then nitrenes as intermediates, is compatible with all of the products observed. t-Butyldifluoramine was attacked by concentrated

nitric acid to yield a complex array of products, including alkyl nitrates and nitrites, while triphenylmethyldifluoramine gave principally triphenylcarbinol.

INTRODUCTION

The continuing search for more energetic rocket propellant compositions has focused attention on several previously unexplored fields of chemistry. Compounds containing fluorine bound to nitrogen offer attractive prospects in such applications. Since effective utilization of any chemical system requires an understanding of the components involved, we have undertaken a study of the reactions of some simple model compounds of this class.

SYNTHESIS OF t-BUTYLDIFLUORAMINE

The first synthesis of an N, N-difluoroalkylamine (alkyldifluoramine) in 1936 [14] introduced a new family of organic compounds. The perfluoroalkyldifluoramines obtained by fluorination of various carbon-nitrogen compounds [1, 2, 3, 7, 12] have more recently been supplemented by a limited number of analogous compounds containing non-fluorinated alkyl groups [5, 6, 13]. This paper is devoted to the study of the chemical properties of these interesting compounds.

A reported synthesis [13] of t-butyldifluoramine capitalized on the equilibrium dissociation of tetrafluorohydrazine into NF_2 free radicals [9], by generating t-butyl radicals via the decomposition of azoisobutane in the

presence of tetrafluorohydrazine. The synthesis of azoisobutane has been accomplished by two methods [4, 16]. Using the more efficient of these methods [16], which in our hands gave a 30% yield of the intermediate, the overall yield of t-butyldifluoramine obtained in the two-step reaction sequence was only 6% of theoretical.

Ethyl-and methyldifluoramine have been prepared by reaction of the respective iodides with tetrafluorohydrazine excited by ultraviolet radiation [5]. We therefore investigated the free radical reaction of t-butyl iodide with tetrafluorohydrazine and found that it produced the desired t-butyldifluoramine routinely in 40% yield. The reaction is believed to take place by the following steps:

$$2(CH_3)_3CI \longrightarrow 2(CH_3)_3C\cdot + I_2 \qquad (1)$$

$$N_2F_4 \longrightarrow 2NF_2\cdot \qquad (2)$$

$$(CH_3)_3C\cdot + NF_2\cdot \longrightarrow (CH_3)_3CNF_2 \qquad (3)$$

t-Butyldifluoramine was obtained by exposing a mixture of the reactants to light or, more conveniently, by heating. The yield of product in the thermal reaction was not increased by a 50% increase in reaction time.

The product was identified by boiling point and elemental analysis. Its infrared spectrum and fragmentation pattern in the mass spectrometer were also consistent with the assigned structure.

The presence of small amounts of C_8 and C_{12} olefins (telomers of isobutene) among the reaction products attests to the occurrence of disproportionation between t-butyl radicals (equation 4). Coupling of t-butyl radicals (equation 5) also occurred to a minor extent, as evidenced by the appearance of traces of tetramethylbutane.

$$2(CH_3)_3C\cdot \longrightarrow (CH_3)_3CH + (CH_3)_2C{=}CH_2 \qquad (4)$$

$$2(CH_3)_3C\cdot \longrightarrow (CH_3)_3CC(CH_3)_3 \qquad (5)$$

REACTIONS WITH ORGANOMETALLIC REAGENTS

Triphenylmethyldifluoramine (I) has been found to react rapidly with n-butyllithium to yield n-octane and benzophenone anil (II). With equimolar quantities of the reactants the reaction was incomplete and some I was recovered. Only 40% of the fluorine was converted to fluoride ion under these conditions. Increasing the amount of organometallic reagent to two molar equivalents resulted in complete disappearance of the difluoramine; 77% of the total fluorine was recovered as fluoride ion and the yield of II was 70% of theory.

t-Butyldifluoramine (III) reacted rapidly with either n-butyllithium or phenyllithium to produce n-octane and biphenyl, respectively. Recovery of fluoride ion was 20-27% in equimolar systems and increased to approximately 50% when more than one equivalent of n-butyllithium was used

Two additional products, present in small quantity, were detected by infrared and mass spectral methods. The first was identified as azoisobutane (IV) and the second appeared, on the basis of mass spectral evidence, to be 1,2-difluoro-1,2-di-t-butylhydrazine (V).

$(CH_3)_3CN{=}NC(CH_3)_3$ IV

$(CH_3)_3CNNC(CH_3)_3$ V
F F

The reaction of III with two or four equivalents of n-butyllithium resulted in the formation of a new product, N, N-di-n-butyl-t-butylamine (VI), in yields up to 16% of theory. This previously unknown tertiary amine was identified by infrared and mass spectrometric analyses. A comparison of the mass spectrum of VI with that of the known tri-n-butylamine (Table I) shows that the same major peaks appear but in quite different relative intensities. The mass peaks due to rearrangements were generally more intense and two such peaks (m/e = 86, 114) which do not occur in tri-n-butylamine were observed.

The results of this series of experiments are summarized in Table II.

PROPOSED MECHANISM OF ORGANOLITHIUM REACTIONS

The various products obtained in the experiments described above can be explained on the assumption that the organometallic reagents reduced the tertiary alkyldifluoramines via a succession of one-electron transfer steps.

TABLE I

PRINCIPAL MASS PEAKS OF DI-n-BUTYL-t-BUTYLAMINE AND TRI-n-BUTYLAMINE

m/e	Ionic Species	Relative Intensity $(n\text{-Bu})_2N\text{-}t\text{-Bu}$	Relative Intensity $(n\text{-Bu})_3N$[a]
41	$C_3H_5^+$	90	21.40
42	$C_3H_6^+$	34	16.00
43	$C_3H_7^+$	85	7.80
57	$C_4H_9^+$	100	13.40
58	C_4H_{10} or $C_3H_3NH_2^+$ (Rearrangement)	75	5.00
72	$C_4H_9NH^+$ (Rearrangement)	91	1.16
86	$C_4H_9NHCH_2^+$ (Rearrangement)	92	4.26
99	$C_4H_9N(CH_2)_2^+$ (Rearrangement)	12	----
100	$C_4H_9NH(CH_2)_2^+$ (Rearrangement)	8	26.30
113	$C_4H_9\text{-}N\text{-}(CH_2)_3^+$	8	----
114	$C_9H_9\text{-}NH(CH_2)_3^+$ (Rearrangement)	4	0.25
128	$(C_4H_9)_2N^+$	68	1.03
142	$(C_4H_9)_2NCH_2^+$	63	100.00
170	$(C_4H_9)_2NC_3H_6^+$	26	0.14
185	$(C_4H_9)_3N^+$	8	5.22

a. Mass Spectral Data, A. P. I., Serial No. 1132

TABLE II

REACTIONS OF t-ALKYLDIFLUORAMINES WITH ORGANOLITHIUM REAGENTS

RNF_2	Reactants R'Li	Molar Ratio	Products % R'R'	Products % F^-	Products Others
I	n-BuLi	1:1	---	40.1	I, II
I	n-BuLi	1:2	Present	77.0	I, 42+% II
I	n-BuLi	1:2	---	----	72% II
III	ØLi	1:1	Present	21.1	III, IV, V
III	ØLi	1:1	50.8	19.5	III
III	n-BuLi	1:1	88.0	25.6	III
III	n-BuLi	1:1	Present	25.6	III
III	n-BuLi	1:2	Present	48.8	VI
III	n-BuLi	1:4	---	52.0	16.2% VI

A possible alternative for the step shown in equation 2 would be interaction of the R' radical derived from the organometallic reagent with the fluoramino

$$R_3CNF_2 + R'Li \longrightarrow R_3C\dot{N}F + R'\cdot + LiF \qquad (1)$$

VII a, R = CH_3
b, R = ϕ

$$R_3C\dot{N}F + R'Li \longrightarrow R_3C\dot{N}\cdot + R'\cdot + LiF \qquad (2)$$

VIII a, R = CH_3
b, R = ϕ

radical (VII). Such a process would also produce the nitrene (VIII), but would require different stoichiometry. No trace of the fluorocarbon by-products which would be formed in this process has been detected.

$$R_3C\dot{N}F + R'\cdot \longrightarrow R_3C\dot{N}\cdot + R'F \qquad (3)$$

The array of final products obtained in any one experiment was found, as expected, to depend upon the reactant ratio and the order and rate of addition. The reactive intermediate species are capable of interacting in various combinations and products arising from several of these possibilities have been detected.

In each case the hydrocarbon produced by the coupling of two of the radicals derived from the organometallic reagent was a prominent product. Diphenyl and n-octane were obtained from phenyllithium and n-butyllithium, respectively. When an equimolar quantity of phenyllithium was added slowly to

t-butyldifluoramine (III), the homogeneous coupling product (V) of the amino radical (VII a) was detected among the products, along with the coupling product (IV) of the nitrene (VIII a). The diradical nature of nitrenes, which leads

$$2(CH_3)_3C\dot{N}F \longrightarrow (CH_3)_3C\overset{F}{\underset{|}{N}}\text{-}\overset{F}{\underset{|}{N}}C(CH_3)_3 \qquad (4)$$

VII a V

$$2(CH_3)_3C\dot{N}\cdot \longrightarrow (CH_3)_3CN{=}NC(CH_3)_3 \qquad (5)$$

VIII a IV

to dimerization and the production of azo compounds, is well known[8]. The cross-coupling of VIII a with the n-butyl radical has been observed when an excess of n-butyllithium was used.

$$(CH_3)_3C\dot{N}\cdot + 2\dot{C}H_3(CH_2)_3 \longrightarrow (CH_3)_3CN(CH_2CH_2CH_2CH_3)_2 \qquad (6)$$

VIII a VI

In reactions involving triphenylmethyldifluoramine (I), rearrangement of the nitrene (VIII b) appears to be favored energetically, since benzophenone anil (II) was the only product found. II has been reported as the principal product of thermal decomposition of triphenylmethyl, N-triphenylmethylhydroxylamine, and a number of related compounds[10, 15, 17] presumably also via the nitrene intermediate. An analogous rearrangement of the t-butyl nitrene:

$$\phi_3C\dot{N}\cdot \longrightarrow \phi_2C{=}N\phi \qquad (7)$$

VIII b II

(VIII a), if it occured, would yield the imine (IX) which would be subsequently hydrolyzed to acetone and methylamine. A careful search failed to reveal the presence of any volatile base.

$$(CH_3)_3CN\cdot \longrightarrow (CH_3)_2C{=}NCH_3 \xrightarrow{H_2O} (CH_3)_2C{=}O + CH_3NH_2 \qquad (8)$$

VIII a IX

REACTIONS WITH NITRIC ACID

Since concentrated nitric acid exhibits both oxidative and electrophilic properties, one can anticipate several possible modes of attack on a tertiary alkyldifluoramine. The difluoramine might be protonated and subsequently hydrolyzed, oxidation might produce an amine oxide analog, oxidative cleavage might occur at N-F, C-N, or C-C bonds, or a nitroalkane might be produced. It has been reported, for example, that triphenylmethyldifluoramine is protonated in concentrated sulfuric acid and decomposes with the liberation of difluoramine[6]. We have confirmed this observation and found, furthermore, that a secondary alkyldifluoramine is similarly protonated but decomposes with the evolution of hydrogen fluoride. Triphenylmethyldifluoramine has been found to dissolve in glacial acetic acid and to be recovered unchanged upon dilution with water. It was not affected by contact with concentrated hydrochloric acid at room temperature.

The room temperature reactions of t-butyldifluoramine and triphenylmethyldifluoramine with concentrated nitric acid, in equimolar quantites and

with a large excess of acid, have been studied. Table III presents a summary of the products obtained in each case, as determined chiefly by infrared spectral evidence.

TABLE III

REACTIONS OF t-ALKYLDIFLUORAMINES WITH 70% NITRIC ACID

	t-Butyldifluoramine		Trityldifluoramine	
Product	Equimolar Acid	Excess Acid	Equimolar Acid	Excess Acid
NO_2	-----	Large	Present	Large
N_2O	Present	Present	-------	Present
CO_2	------	Large	-------	-------
NO_3F	Trace	Trace	-------	Trace
NOCl or NO_2F	------	------	-------	Trace
SiF_4	Present	Present	-------	Present
Alkyl Nitrate	Present	Present	-------	Present
Alkyl Nitrite	------	Present	-------	Present
Nitroalkane	------	------	-------	Present
Carbinol	------	------	-------	Major
Alkyldifluoramine	Present	------	Major	------

Several points are worth considering in some detail. The large amount of nitrogen dioxide obtained when excess acid was used is apparently the result of decomposition of nitric acid catalyzed by the difluoramine or one of the reaction products. This interpretation is supported by the fact that the quantities of gas obtained were greatly in excess of stoichiometric, based on the difluoramine, and by the observed exponential pressure rise following a protracted induction period.

The presence of carbon dioxide among the products of the reaction of t-butyldifluoramine with excess nitric acid is a clear indication that C-C bond

cleavage occurred. The nitrate and nitrite esters produced in this experiment were mixtures of various alkyl derivatives, and not solely t-butyl derivatives, as in the other cases where nitrate esters were detected. The relative stability of trityldifluoramine toward oxidative cleavage is fully in accord with known differences between aromatic and aliphatic systems.

The appearance of silicon tetrafluoride, during an investigation of organic fluorine compounds in glass equipment, is generally understood to imply the transient formation of hydrogen fluoride; this interpretation should be applied here. An interesting point, not yet fully understood, is the appearance of nitroalkane and carbinol only in the reaction of trityldifluoramine with excess acid.

In general, the results observed are best understood as the consequences of electrophilic attack on the alkyldifluoramines. The fact that such attack did not occur when triphenylmethyldifluoramine was treated with hydrochloric acid, an even stronger electrophile, tends to cloud this simple picture. It becomes necessary to invoke the simultaneous participation of an oxidative process in some way which is not yet clear.

Assuming that protonation of the alkyldifluoramine does occur, elimination of difluoramine and formation of a tertiary carbonium ion would logically follow.

$$R_3CNF_2 + H^+ \longrightarrow R_3\overset{+}{C}NF_2H \qquad (9)$$

$$R_3\overset{+}{C}NF_2H \longrightarrow R_3C^+ + HNF_2 \qquad (10)$$

The failure of difluoramine to appear among the final products is not particularly surprising. In the presence of nitric acid and/or nitrogen oxides, it might easily be oxidized and may well constitute the source of the silicon tetrafluoride. The formation of a carbonium ion from trityldifluoramine would be favored by resonance stabilization. In the t-butyl case, on the other hand, this driving force is not present and formation of the ion would be expected to occur less readily. In addition, both the t-butyl carbonium ion and the difluorammonium ion from which it is derived would be more subject to a variety of side reactions than the corresponding trityl species.

Reaction of the carbonium ion with water or with nitrate ion would produce the carbinol and the ester, respectively. Alternatively, the carbinol might be

$$R_3C^+ + H_2O \longrightarrow R_3COH + H^+ \qquad (11)$$

$$R_3C^+ + NO_3^- \longrightarrow R_3CONO_2 \qquad (12)$$

$$R_3COH + HNO_3 \longrightarrow R_3CONO_2 + H_2O \qquad (13)$$

esterfied by nitric acid. For the reasons cited above these reactions contributed substantially to the overall result only in the triphenylmethyldifluoramine reactions.

EXPERIMENTAL

Materials

The phenyllithium and n-butyllithium used in this work were commercial products supplied by Foote Mineral Company in ether-benzene and hexane

solutions, respectively. Triphenylmethyldifluoramine was obtained from Peninsular ChemResearch and purified by recrystallization from methanol, m.p. 80-81.5°. t-Butyl iodide was obtained from K and K Laboratories, Jamaica, New York, and purified before use either by distillation or by washing with aqueous sodium thiosulfate and drying.

Synthesis of t-Butyldifluoramine

A 2-l. Pyrex bulb, fitted with a freeze-out tip and a vacuum stopcock terminating in a standard ball joint, was charged with 6.0 g. (0.0307 mole) of t-butyl iodide in a nitrogen atmosphere. The liquid was frozen at -78° and the bulb was evacuated. After three additional freeze-thaw cycles with intermittent evacuation, the tip of the flask was cooled to -196° and 4.16 g. (0.040 mole, measured by volume assuming ideal gas properties) of tetrafluorohydrazine was condensed into the bulb. The bulb was then transferred to a heating jacket and heated to 95 ± 5° for 4 hr. Following this, the bulb was cooled to room temperature, the contents were condensed in the tip at -78° and any volatile components were removed under vacuum. The crude t-butyldifluoramine was then distilled under vacuum from the bulb at 28° into a trap at -78°. The synthesis was repeated four times and the combined product was fractionated to yield 5.8 g. (43.3%) of colorless liquid, b.p. 55-56° (760 mm.).

A sample was chromatographed using a Wilkens Autoprep with a 20 ft. by 3/8 in. column packed with 30% SF-96 Silicone on Chromosorb P. Retention time at 35° and a flowrate of 100 ml./min. was 40 min.

Anal. Calcd. for $C_4H_9NF_2$: C, 44.03; H, 8.31; N, 12.84.

Found: C, 44.46; H, 8.31; N, 12.45.

The infrared spectrum showed very strong absorptions at 880 and 970 $cm.^{-1}$ and a weak band at 930 $cm.^{-1}$, indicative of NF_2 groups. The expected symmetrical and asymmetrical CH_3-C deformation bands (1480 and 1375 $cm.^{-1}$, respectively)and the C-H stretching band (2990 $cm.^{-1}$) were also observed. The mass spectrum, although lacking the molecule ion peak, did show the following significant fragments (m/e, assignment, relative intensity): 94, $C_3H_6NF_2^+$, 6.3; 57, $C_4H_9^+$, 100; 33, NF^+, 4.5.

In the photolytic process, a 500 ml. Pyrex bulb containg 1.5 g. (8.3 mmoles) of t-butyl iodide and 1.58 g. (15.2 mmoles) of tetrafluorohydrazine was illuminated with a 300-watt Reflectorflood lamp at a distance of 15 cm. for 24 hr. Upon working up the reaction mixture as described above, 0.4 g. of t-butyldifluoramine was obtained.

Reaction of t-Butyldifluoramine with Phenyllithium

t-Butyldifluoramine (0.55 g. 0.005 mole) was dissolved in 10 ml. of sodium-dried ether and the solution was cooled to 0.5°. In a dropping funnel under nitrogen, 2.5 ml. (0.005 mole) of phenyllithium solution in benzene-ether

(Lithium Corporation of America) was diluted with dry ether to 10 ml. This solution was added to the stirred difluoramine solution during one hour. A red-brown color appeared and deepened gradually during the addition. A gentle stream of nitrogen was passed through the reaction flask and then bubbled into a standardized solution containing 5.27 meq. of acid, while 20 ml. of distilled water was added dropwise to the reaction mixture (20 min.). Stirring was continued for one hour. The acid solution was titrated with base and 5.19 meq. was found. The decrease (1.5%) was not considered to be significant. The aqueous and organic phases of the reaction mixture were separated. The water layer was washed with 15 ml. of ether. The wash and the organic layer were combined and washed with three 10-ml. portions of distilled water. These washes were combined with the aqueous solution, which was subjected to analyses as discussed above.

The ether-benzene solution was dried first over Drierite and then over anhydrous sodium sulfate and distilled at atmospheric pressure. The flask was heated in a bath at 55-60° throughout distillation of the bulk of the solvents and raised to 95-100° for 20 min. at the end. The distillate, collected at Dry Ice temperature, was shown by infrared analysis to consist of unreacted t-butyldifluoramine and ethyl ether. A residue weighing 1.10 g. remained. The mass spectrum of this fraction contained peaks at 33 (NF), 41 (C_3H_5), 45 (CNF), and 57 (C_4H_9) mass units. The trace of ether observed

(m/e = 59) was not sufficient to account for the intensity of the peak at 45. The most probable source of these fragments is the substituted hydrazine (V).

The several components of the less volatile fraction were separated by vapor phase chromatography, using a Perkin-Elmer Model 154 C instrument. The six foot column was packed with di-n-decyl phthalate on firebrick and was maintained at 90° with a helium flowrate of 53 ml./min. Since fractions were expected to be too small to be collected individually, the effluent stream was fed directly into the inlet of a Bendix time-of-flight mass spectrometer. In one fraction, mass peaks at 57 (C_4H_9) and 71 ($C_4H_9N_2$) units were observed in relative intensities identical to those found in azoisobutane (IV).

Reaction of t-Butyldifluoramine with n-Butyllithium

A solution of 1.1 g. (0.01 mole) of t-butyldifluoramine in 10 ml. hexane was treated with 26.0 ml. (0.04 mole) of n-butyllithium solution, by adding the organometallic reagent dropwise over a one hour period at 5-10°. The dark brown mixture was stirred for 2.5 hr. at 10-25° and then treated with water. The organic solution was separated and dried over anhydrous Na_2SO_4 while the aqueous solution was analyzed and found to contain 0.197 g. (0.0104 mole, 52.0%) of fluoride ion. The solvent was evaporated from the organic solution and the residual brown oil was distilled to yield 0.32 g. of a liquid, b.p. 79-82° (0.3 mm.). On the basis of infrared and mass spectral data, the liquid product was identified as N, N- di-n-butyl-t-butylamine.

Reaction of Triphenylmethyldifluoramine with n-Butyllithium

1. A solution of 5.9 g. (0.02 mole) of triphenylmethyldifluoramine, m.p. 80-81°, in 40 ml. of hexane was cooled to 0° in a 200 ml. three-neck flask while 25.8 ml. (0.04 mole) of n-butyllithium solution was added dropwise with stirring over a 1.5 hr. period. A deep red color developed as the butyllithium came into contact with the hexane solution, but the color changed to a bright yellow on continued stirring at 5-10°. At the completion of the addition, the solution was allowed to come to room temperature and it was stirred at 25° for 2 hr. Water was then added to the mixture, the organic phase was separated, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated, leaving 5.72 g. of brown semi-solid. The material was kept under 0.5 mm. pressure for 1 hr., a liquid nitrogen trap being employed to collect any liquid distillate. A liquid (0.3 g.) was obtained and submitted for infrared analysis. It showed very strong absorptions indicative of O-H, aliphatic C-H, $C-CH_3$, C-OH and $-(CH_2)n>4$. In addition, a medium strength band at 1710 $cm.^{-1}$ (C=O) was also present.

The residue was recrystallized from MeOH to yield 2.15 g. (42%) of yellow crystals, m.p. 112-113°, which were identified by infrared and elemental analysis as benzophenone anil.

Anal. Calcd. for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44.

Found: C, 88.85; H, 5.86; N, 5.61.

The physical constants were in excellent agreement with the literature, m.p. 113-114° [18].

The methanol solution from the recrystallization was evaporated to dryness to yield 3.3 g. of a mixture of triphenylmethyldifluoramine and benzophenone anil. In addition, the infrared spectrum of this material showed weak absorptions due to aliphatic C-H, C=O and C=N or C=C.

2 A solution of 1.48 g. (0.005 mole) of triphenylmethyldifluoramine in 30 ml. hexane was treated with 6.5 ml. (0.01 mole) of n-butyllithium solution as in section I. Water was added to the reaction mixture and the organic phase was separated and washed with four 100 ml. portions of distilled water. The combined aqueous washings were transferred to a 500 ml. volumetric flask and adjusted to volume with distilled water. This solution was found to contain 146 mg. F^- (0.0077 mole, 77%) and 0.0028 mole OH^-.

The hexane solution was dried over Na_2SO_4 and the solvent evaporated. The residue was taken up in CH_2Cl_2 and chromatographed on alumina. The chromatogram was followed by the yellow band which moved down the column. This yellow CH_2Cl_2 eluate was evaporated to dryness and the residue was recrystallized from ether to yield 0.92 g. (0.0036 mole, 72%) benzophenone anil, m.p. 112-113°. The column was eluted with MeOH and the solvent was evaporated to give 0.13 g. of brown solid. The infrared spectrum of this material showed strong absorptions indicative of aliphatic C-H, aromatic C-H,

C=N or C=O (1660 cm.$^{-1}$), a trace of N-F, and substituted aromatic.

t-Butyldifluoramine and Nitric Acid

1. t-Butyldifluoramine (1.02 g., 9.3 mmoles) was condensed under vacuum into a flask containing 10 ml. (150 mmoles) of concentrated HNO_3. The mixture was warmed to room temperature and stirred. The pressure rose to 210-220 mm. and remained constant for 16 hr. After this period, the pressure rose within 1.5 hr. to 730 mm., with the evolution of brown gas. On cooling the reaction flask to -70°, the pressure dropped to 340 mm. A sample of this gas was subjected to infrared analysis and found to contain C-H (3000 and 1480 cm.$^{-1}$), C-CH_3 (1375 cm.$^{-1}$), N_2O (2220 cm.$^{-1}$)N_2O_4 (1750 and 1625 cm.$^{-1}$), N-F (attributed to starting material, 970 and 880 cm.$^{-1}$), NO_3F (920, 790, and 720 cm.$^{-1}$), CO_2 (2300 and 625 cm.$^{-1}$), SiF_5 (1025 cm.$^{-1}$), and NOCl (presumably from attack on NaCl window, 1810 and 1790 cm.$^{-1}$). Mass spectrometric analysis confirmed the presence of starting difluoramine, CO_2 and/or N_2O, SiF_4, and NO_3F, and established the absence of H_2 and O_2. A second gas sample taken at 0° was found to contain some of these components, but no additional products. The acid solution was extracted with pentane to remove organic products. Infrared analysis of this extract revealed the presence of alkyl nitrite and nitrate (C-H at 2850 and 1450 cm.$^{-1}$, possible C-CH_3 at 1375 cm.$^{-1}$, C-ONO at 1560 cm.$^{-1}$, and C-ONO_2 at 1640 cm.$^{-1}$).

2. Concentrated nitric acid (0.67 ml., 10.0 mmoles) was delivered by pipet into a 50 ml. round-bottomed flask, which was fitted with a magnetic stirring bar and a suitable adapter, and attached to a vacuum line. The acid was frozen in a liquid N_2 bath and the flask was evacuated. The acid was melted and refrozen twice, with evacuation to effect degassification. t-Butyldifluoramine (1.09 g., 10.0 mmoles) was evaporated into an evacuated calibrated storage bulb to the calculated pressure and then condensed into the flask with liquid N_2. The reactor portion of the line with manometer was closed off, and the flask was allowed to warm to room temperature. The mixture was stirred at 26-29° for 24 hr., during which the pressure remained essentially constant (186-198 mm. Hg). The liquid mixture became yellow, but no brown fumes appeared in the vapor space.

Gas samples for infrared and mass spectral analyses were taken, with the reaction flask at 25° and -78°. Both samples contained an alkyl nitrate, N_2O, t-butyldifluoramine and some additional N-F material, and a trace of NO_3F.

The liquid reaction mixture was extracted with CCl_4. Infrared analysis of the extract did not indicate any additional products. The aqueous residue was evaporated to dryness at room temperature and a few needle crystals were recovered. The infrared spectrum of this solid showed only absorptions due to water. Attempts to dehydrate the small amount of product which remained were unsuccessful.

Triphenylmethyldifluoramine and Nitric Acid

1. Recrystallized triphenylmethyldifluoramine (1.0 g., 3.4 mmoles, m.p. 80-81.5°) and a small magnetic stirring bar were placed in the bottom of a reaction tube having a small side chamber. Concentrated (70%) nitric acid (2.5 ml., 38 mmoles) was placed in the side chamber and the tube was connected to a vacuum line by means of standard taper joints. The nitric acid was frozen by immersion in a liquid nitrogen bath and the system was evacuated. The cold bath was removed. Then the tube was rotated so that the nitric acid, as it melted, flowed onto the triphenylmethyldifluoramine.

The resulting slurry was stirred at 22-25° for 24 hr. The reaction mixture bubbled and became progressively darker and brown fumes were observed in the vapor space. The pressure rose exponentially to reach a maximum of approximately 400 mm. in 2.5 hr. (system volume - 180 ml.) and then remained constant.

After 24 hr., the reaction mixture was cooled to -78° and a gas sample was taken for analysis. Infrared and mass spectrometric examination revealed the presence of NO_2, N_2O, SiF_4, and either NOCl or NO_3F.

The reaction tube was then warmed to room temperature, flushed with nitrogen, and opened. The reaction mixture was diluted with distilled water (color changed from dark brown to bright orange) and the solid product was removed by filtration. The filtrate was neutralized with

Na_2CO_3 (color changed from pale amber to brown) and extracted with benzene. No residue was obtained upon evaporation of an aliquot of the benzene extract. Reacidification of the aqueous layer lightened the color, but not to the original shade. The remaining color was too intense to permit the determination of fluoride ion.

The orange solid product was washed with water, dried in vacuum over P_2O_5, and chromatographed on an alkaline alumina column. The first fraction, 420 mg., yellow to pale orange crystals eluted with pentane-benzene, proved to be the principal constituent of the mixture. It was recrystallized from pentane-benzene to give a nearly colorless compound, m.p. 162.5-163°. Its infrared spectrum was identical with that of triphenylcarbinol, lit. m.p. 162.5° (11).

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.20

Found: C, 87.06/87.21; H, 6.29/6.41.

2. Triphenylmethyldifluoramine (2.95 g., 10 mmoles) was placed, along with a small magnetic stirring bar, in a test tube having a standard taper glass joint. The tube was flushed with dry nitrogen and placed in a liquid nitrogen bath. Concentrated HNO_3 (0.67 ml., 10 mmoles) was introduced slowly and allowed to freeze on the side of the tube without contacting the triphenylmethyldifluoramine. The reaction tube was then connected via a suitable adapter to a vacuum system, evacuated, and allowed to warm to

room temperature. After the mixture was stirred for 18 hr. at 25-28°, a sample of the gaseous products (p= 55 mm. in 180 ml.) was taken in an evacuated cell. The system was then filled with nitrogen to atmospheric pressure. The reaction mixture was diluted with distilled water and the yellow insoluble product was removed by filtration. The yellow aqueous filtrate was extracted three times with methylene chloride, the third extract contained very little color, although the aqueous solution remained a strong yellow. On standing, the combined extracts became orange in color, as did the solid product on the filter.

Infrared analyses of the gas sample and the methylene chloride extract (differential vs. solvent) showed no significant absorptions. The aqueous solution was found to contain 7.41 meq. of free acid and 25 mg. (1.3 meq.) of fluoride ion. The infrared absorption spectrum of the bright yellow-orange solid (m.p. 79-81°) was superimposable upon that of triphenyl-methyldifluoramine.

ACKNOWLEDGEMENT

The research reported herein was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research, under Contract Number NOnr 1878(00).

The authors wish to thank Dr. Murray S. Cohen of these laboratories for his interest and encouragement during the course of this work. Analytical

assistance by Alan Fremmer, John A. Creatura, Raymond N. Storey, Donald Y. Yee, Daniel G. Chowanec and Donald N. Pregler, is gratefully acknowledged.

LITERATURE CITED

1. Attaway, J. A., Groth, R. H., Bigelow, L. A., J. Am. Chem. Soc., 81, 3599 (1959).

2. Bigelow, L. A., Fundamental Research in Organic Fluorine Chemistry, Terminal Report, Office of Naval Research, AD No. 207549, 31 August 1958.

3. Coates, G. E., Harris, J., Sutcliffe, T., J. Chem. Soc. 1951, 2762.

4. Farenhorst, E., Kooyman, E. C., Rec. trav. chim., 72, 993 (1953).

5. Frazer, J. W., J. Inorg. Nucl. Chem. 16, 23 (1960).

6. Graham, W. H., Parker, C. O., J. Org. Chem., 28, 850 (1963).

7. Haszeldine, R. N., Research, 4, 338 (1951).

8. Horner, L., Christmann, A., Angew. Chem. (Int'l. Ed.) 2, 599 (1963).

9. Johnson, F. A., Colburn, C. B., J. Am. Chem. Soc., 83, 3043 (1961).

10. Jones, L. W., Fleck, E. E., ibid., 50, 2022 (1928).

11. Lange, N. A., Handbook of Chemistry , 6th Ed., p. 370, Handbook Publishers, Inc., Sandusky, Ohio, 1946.

12. Pearson, R. K., Dresdner, R. D., J. Am. Chem. Soc., 84, 4743 (1962).

13. Petry, R. C., Freeman, J. P., ibid., 83, 3912 (1961).

14. Ruff, O., Giese, M., Ber., 69B, 598 (1936).

15. Saunders, W. H., Ware, J. C., J. Am. Chem. Soc., 80, 3328 (1958).

16. Stevens, T. E., J. Org. Chem., 26, 2531 (1961).

17. Stieglitz, J., et al., J. Am. Chem. Soc., 36, 272 1914; ibid., 38, 2081, 2718 (1916); ibid., 44, 1270, 1293 (1922).

18. Weston, A. W., Michaels, R. J. Jr., ibid., 73, 1381 (1951).

Preparation and Properties of Some Bis(difluoramino)alkanes and -arylalkanes

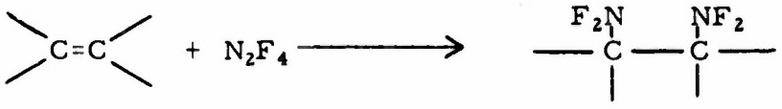
Harry F. Smith, Warren H. Wieting, David F. Kates, and Donald D. Perry

Thiokol Chemical Corporation
Reaction Motors Division
Denville, New Jersey

Representative members of three series of bis(difluoramino)alkanes and -arylalkanes have been prepared by the addition of tetrafluorohydrazine to olefins and by the acid-catalyzed reaction of difluoramine with carbonyl compounds. The compounds were characterized by means of elemental analysis, infrared and n.m.r. spectra, and physical properties.

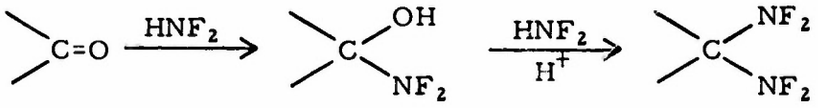
An interest in recent years in the potential application of organic difluoramine derivatives as high-energy propellant ingredients has resulted in a proliferation of new compounds of this class. In this paper, the synthesis and properties of several new compounds are described, along with new data on a few related compounds which were reported earlier but not thoroughly characterized. The types of compounds described include 1,1-bis(difluoramino)alkanes, 2,3-bis(difluoramino)alkanes, and phenyl-substituted bis(difluoramino)alkanes. These were prepared by one of two established

methods: the addition of tetrafluorohydrazine to an olefin to yield a vicinal bis(difluoramine)[8] as in equation 1, or the reaction of difluoramine with



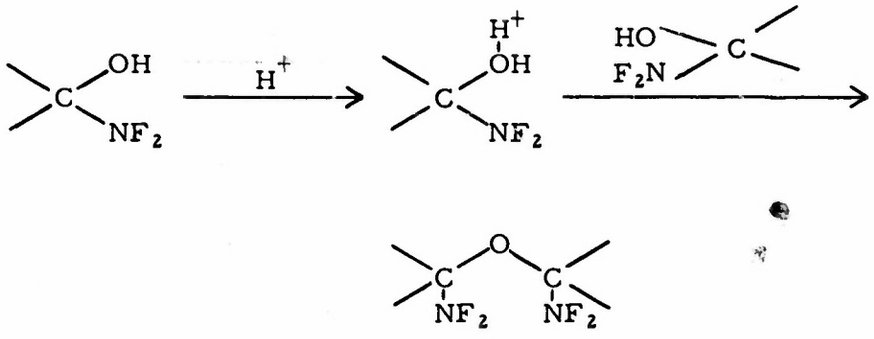
(1)

a carbonyl compound in the presence of fuming sulfuric acid to yield a geminal derivative.[1] The second procedure is understood to take place in two steps (equation 2), an uncatalyzed addition followed by protonation and displacement of hydroxyl.[9] The course of this reaction is strongly dependent



(2)

upon relative concentrations of reactants and, hence, upon order and rates of introduction. The intermediate hydroxydifluoramines are susceptible to condensation, in acidic medium, forming the corresponding ethers (equation 3).



(3)

Hexanal and heptanal reacted with difluoramine to give the expected gem-bis(difluoramines) in 40-65% yields. Their properties are summarized in Table I. Infrared spectra are reproduced in Figures 1 and 2.

Two vicinal bis(difluoramines) were prepared by the free radical addition of tetrafluorohydrazine[2] to the appropriate olefins. The first, 2,3-bis(difluoramino)-2,3-dimethylbutane, had been synthesized earlier,[6] but in the present work purification by gas chromatography[10] gave a product of higher purity. A melting point 20° higher than that previously observed was obtained. The fact that this compound is a solid while related compounds of similar or higher molecular weight are liquids can be attributed to the high order of symmetry in the molecule.

The second product in this series, 2,3-bis(difluoramino)pentane, contains two unlike asymmetric carbon atoms and so is capable of existence in four configurations. The two diastereoisomeric pairs of enantiomorphs were successfully separated by gas chromatographic methods.[10] The prefixes α- and β- have been used to designate the isomers having shorter and longer retention times, respectively.

The F^{19} and proton n.m.r. spectra of the α- and β-isomers provide some interesting information, and permit a tentative assignment of structure. The F^{19} n.m.r. spectrum of the α-dl pair, shown in Figure 3, is readily decomposed into two large unsymmetrical AB quartets, both further split by coupling

TABLE I

PROPERTIES OF 1,1-BIS(DIFLUORAMINO)ALKANES, $RCH(NF_2)_2$

R	b.p. (mm.)	b.p. (760 mm.)	n_D^{25}	C%		H%		N%		F%	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
n-Hexyl	45° (17)	140°	1.3740	38.30	37.94	6.43	6.43	14.89	14.57	---	---
n-Heptyl	48° (4.5)	162°	1.3830	41.58	41.36	6.98	7.25	13.85	14.04	37.59	37.45

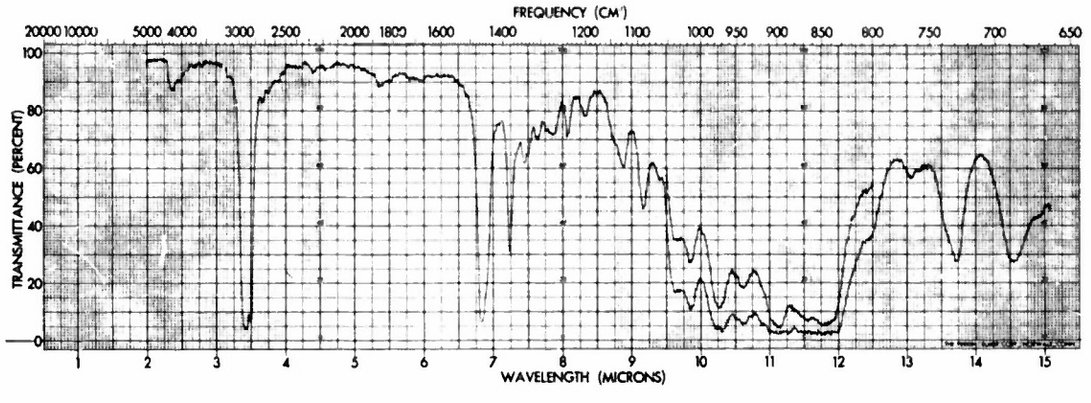


Figure 1. 1,1-Bis(difluoramino)hexane

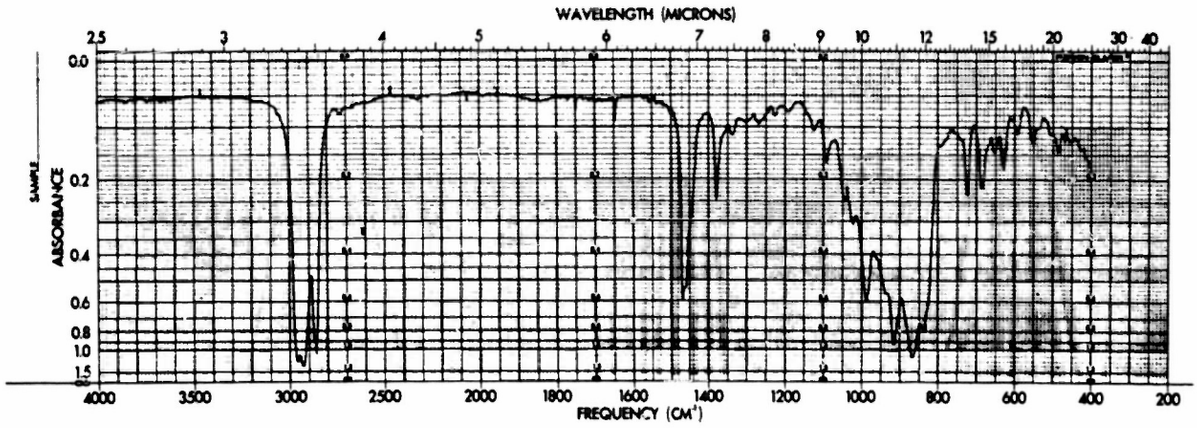


Figure 2. Infrared Spectrum of 1, 1-Bis(difluoroamino)heptane

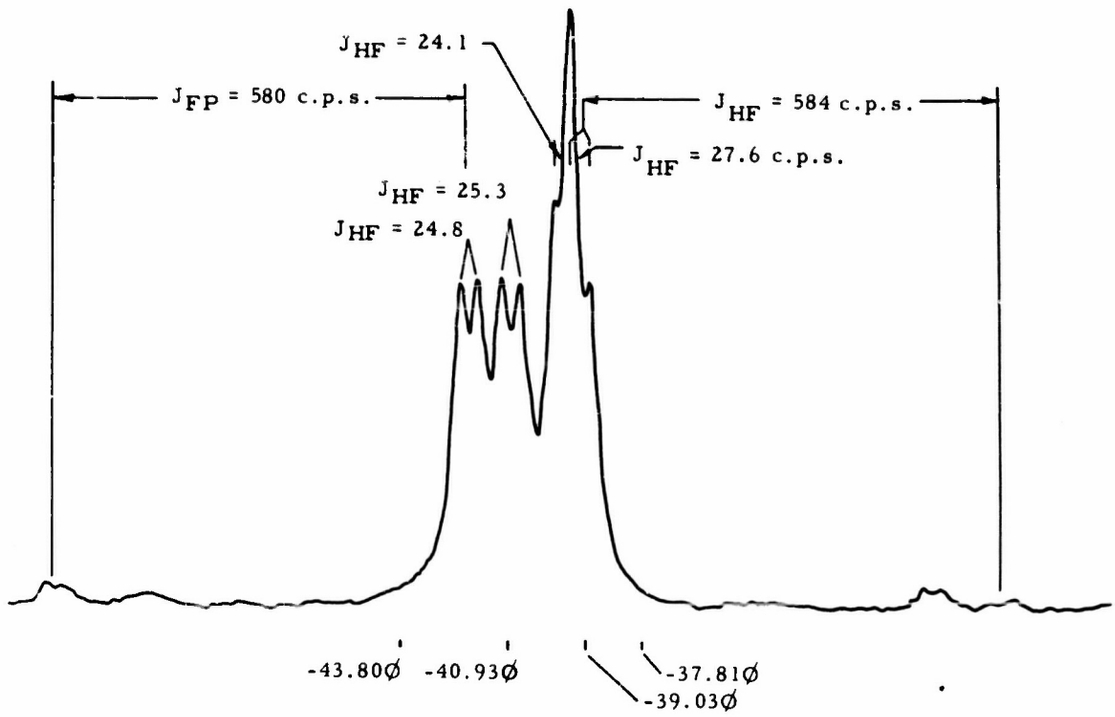


Figure 3. F^{19} N.M.R. Spectrum of α-2,3-Bis(difluoramino)pentane

to the gem hydrogens to form two eight-line ABX patterns. The central lines of one ABX group overlap to form a triplet. The chemical shifts of the fluorines in this NF_2 group are -40.93 Ø and -[illegible] 81 Ø. Coupling constants are J_{FF} = 584 c.p.s. with one J_{HF} = 27.6 c.p.s. and the other J_{HF} = 24.1 c.p.s. The chemical shifts of the fluorines in the NF_2 group associated with the large central quartet are -43.80 Ø and -39.03 Ø. Coupling constants are J_{FF} = 580 c.p.s., one J_{HF} = 25.3 c.p.s. and the other J_{HF} = 24.8 c.p.s. No assignment of the NF_2 groups to positions on the carbon chain was possible on the basis of these data alone.

The F^{19} n.m.r. spectrum of the β-dl pair is shown in Figure 4, and despite the smaller number of lines observed than in the α-isomer spectrum, it actually represents a much more complex case. The central lines of the ABX pattern from the fluorines of one NF_2 group may overlap to form a large doublet, dropping the intensity of the outer lines to zero. However, this cannot explain the unusual pattern of the outer lines. It is probable that the spectra of the NF_2 groups cannot be treated independently, since there is fluorine-fluorine coupling between the NF_2 groups via the "through space" mechanism.[4,5]

Figure 2 of reference 5 predicts a J_{FF} of about 20 c.p.s. at an internuclear distance of 2.65 Å. Due to the relatively small chemical shift differences, a coupling constant of this magnitude could produce the observed

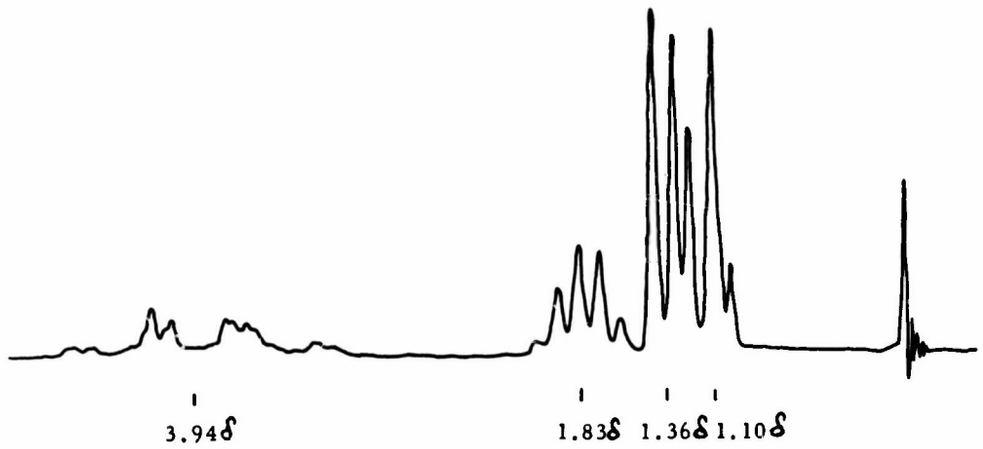


Figure 4. F^{19} N.M.R. Spectrum of β-2,3-Bis(difluoramino)pentane

spectrum. Exact chemical shifts and coupling constants can only be obtained from a full theoretical analysis of the spectrum.

The H^1 spectrum of the α form is shown in Figure 5. The gem protons form a complex multiplet centered approximately at 3.94 δ. The C_1-methyl appears as a slightly distorted doublet at 1.36 δ with J_{HH} = 7.1 c.p.s. The ethyl group forms an A_3B_2 pattern with the methyl proton appearing as a distorted triplet centered at 1.10 δ and the methylene protons centered at 1.83 δ. The latter probably appears as a distorted quintet due to equal coupling constants between the CH_2 protons and the CH_3 protons and the CH_2 protons with the gem proton. The H^1 spectrum of the β-dl pair is shown in Figure 6. The gem protons form a highly complex pattern centered approximately at 3.67 δ. The methyl protons of C_1 appear as a doublet centered at 1.39 δ with J_{HH} = 6.9 c.p.s. The ethyl group again appears as an A_3B_2 with the center of the distorted methyl triplet at 1.09 δ and the methylene multiplet centered at about 1.85 δ.

The two pairs of enantiomorphs which constitute 2,3-bis(difluoramino)-pentane can be represented, each in one of its possible staggered conformations, by the Newman projections[3] shown. The view is along the line of the bond between C_2 and C_3. C_2, nearer the observer, is indicated by the radii spaced at 120° angles. C_3, farther from the eye, is designated by the circle with radial extensions.

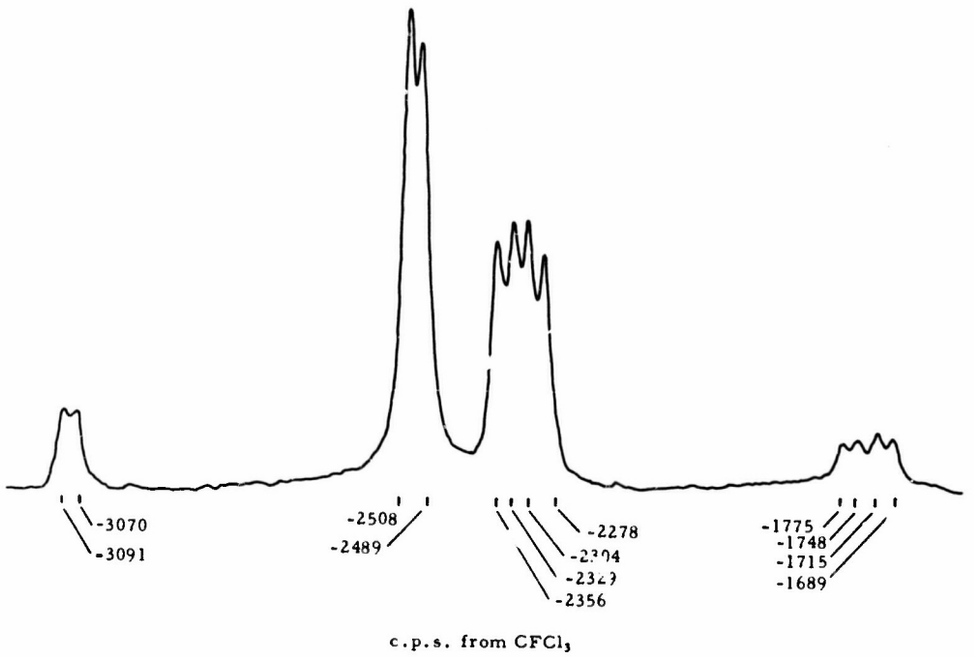


Figure 5. Proton N.M.R. Spectrum of α-2,3-Bis(difluoramino)pentane

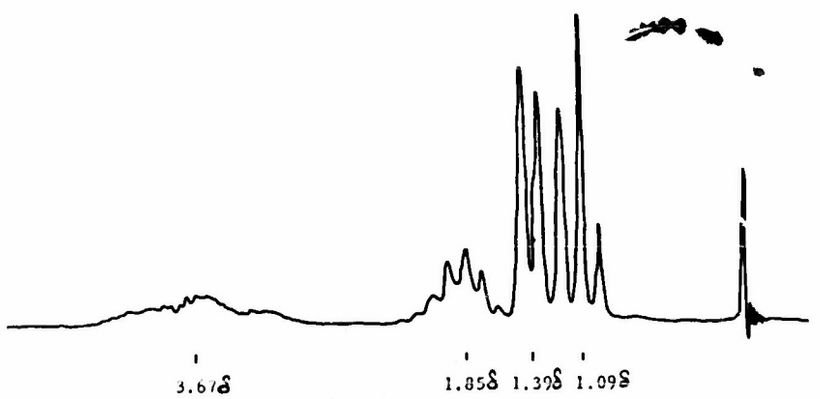
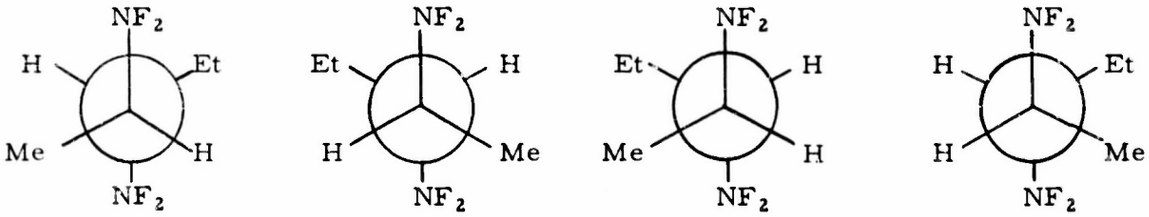


Figure 6. Proton N.M.R. Spectrum of β-2,3-Bis(difluoramino)pentane



A B C D

A and B, a mirror-image pair, are probably in their most stable conformations as shown, since it is possible for both the difluoramino groups and the alkyl groups to be in the preferred trans positions with respect to each other. other. In the other pair, C and D, a trans relationship between difluoramino groups requires a gauche conformation between the methyl and ethyl groups. The same two enantiomorphs can also be drawn as below, with trans alkyl groups and gauche difluoramino groups. It is possible that this conformation,

C' D'

which brings the fluorine atoms into close enough juxtaposition for through-space coupling to occur, would be favored. For this reason, we tentatively suggest that the racemic mixture of A and B constitutes the isomer we have designated α, while β consists of the racemic mixture of C and D, with the preferred conformations being represented by C' and D'.

Some analytical data and physical properties of 2,3-bis(difluoramino)-2,3-dimethylbutane and the isomers of 2,3-bis(difluoramino)pentane are listed in Table II.

Of the phenyl-substituted bis(difluoramines) (Table III), 1,2-bis(difluoramino)phenylethane[7] was synthesized by the tetrafluorohydrazine addition method, and α,α-bis(difluoramino)toluene and 2,2- and 1,1-bis(difluoramino)phenylethane[11] were obtained from the difluoramine reaction. The latter compound could not be prepared in one step. Under the usual reaction conditions either the aldehyde decomposed, or the only product obtained was bis(1-difluoramino)-2-phenylethyl ether. The successful synthesis involved initial reaction of phenylacetaldehyde with difluoramine to give the hydroxydifluoramine (Figure 7), followed by addition of this intermediate to difluoramine refluxing over fuming sulfuric acid. Even this procedure was sensitive to minor changes in agitation and addition rate, and could not be duplicated. Physical properties are listed in Table III, and infrared spectra are shown in Figures 8 through 11.

EXPERIMENTAL

1,1-Bis(difluoramino)heptane - To an aqueous solution containing 1.0 mole of difluorourea was added dropwise 8.0 ml. of concentrated H_2SO_4.

TABLE II

PROPERTIES OF 2,3-BIS(DIFLUORAMINO)ALKANES, $R-\underset{R'}{\overset{NF_2}{C}}-\underset{R'}{\overset{NF_2}{C}}-R''$

R	R'	R''	b.p. (mm.)	b.p. (760 mm.)	n^{25}_D	C% Calcd.	C% Found	H% Calcd.	H% Found	N% Calcd.	N% Found
CH_3	CH_3	CH_3	---	83.5-84.5° [a]	---	38.30	38.44	6.43	6.60	14.89	14.72
(α) CH_3	H	C_2H_5	48-50° (51)	119°	1.3688	34.48	34.60	5.79	5.63	16.09	15.13
(β) CH_3	H	C_2H_5	54-55° (51)	123°	1.3728	34.48	34.88	5.79	5.63	16.09	15.34

a. Melting Point

TABLE III

PROPERTIES OF PHENYL-SUBSTITUTED BIS(DIFLUORAMINO)ALKANES

Compound	b.p. (mm.)	b.p. (760 mm.) [a]	n^{25}_D	C% Calcd.	C% Found	H% Calcd.	H% Found	N% Calcd.	N% Found	F% Calcd.	F% Found
$\phi CH(NF_2)_2$	39 (2.2)	183	---	43.31	43.63	3.12	3.50	14.43	18.60	---	---
$\phi CH(NF_2)_2CH_2NF_2$	44 (0.5)	220	1.4620	46.16	46.19	3.87	3.83	13.46	13.33	---	---
$\phi CH(NF_2)_2CH_3$	34 (0.06)	242	---	46.16	47.41	3.87	4.27	13.46	12.56	36.51	35.35
$\phi CH_2CH(NF_2)_2$	48 (1.0)	210	---	46.16	46.32	3.87	3.92	13.46	13.37	---	---

a. Extrapolated

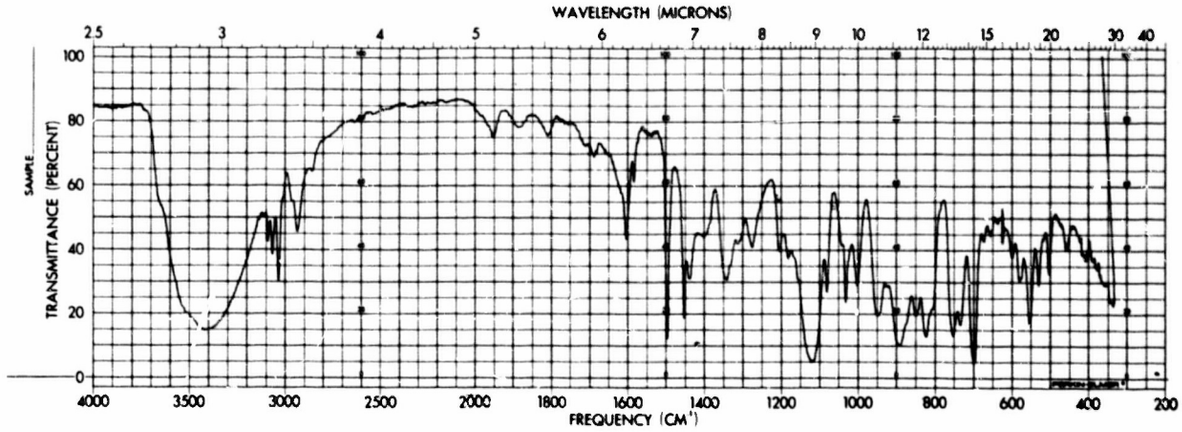


Figure 7. Infrared Spectrum of 2-Difluoramino-2-hydroxyphenylethane

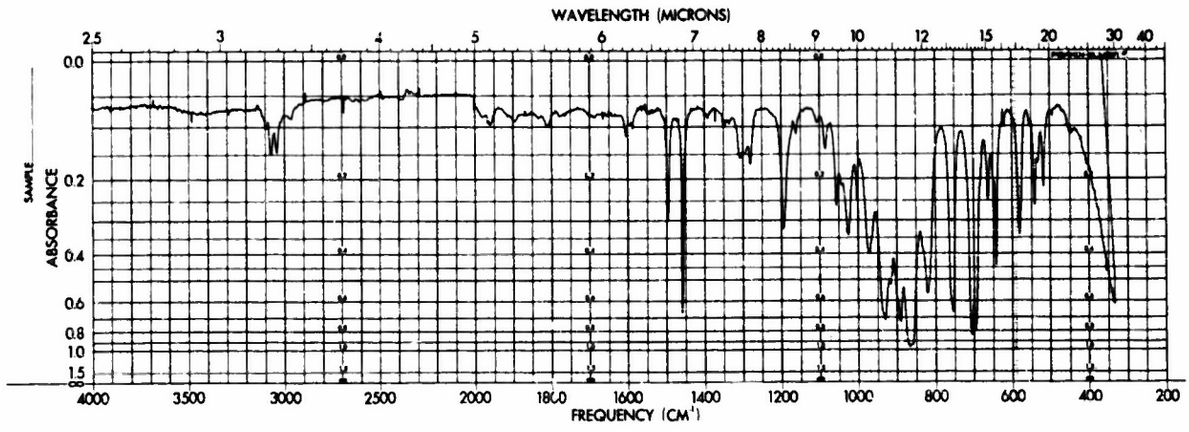


Figure 8. Infrared Spectrum of α,α-Bis(difluoramino)toluene

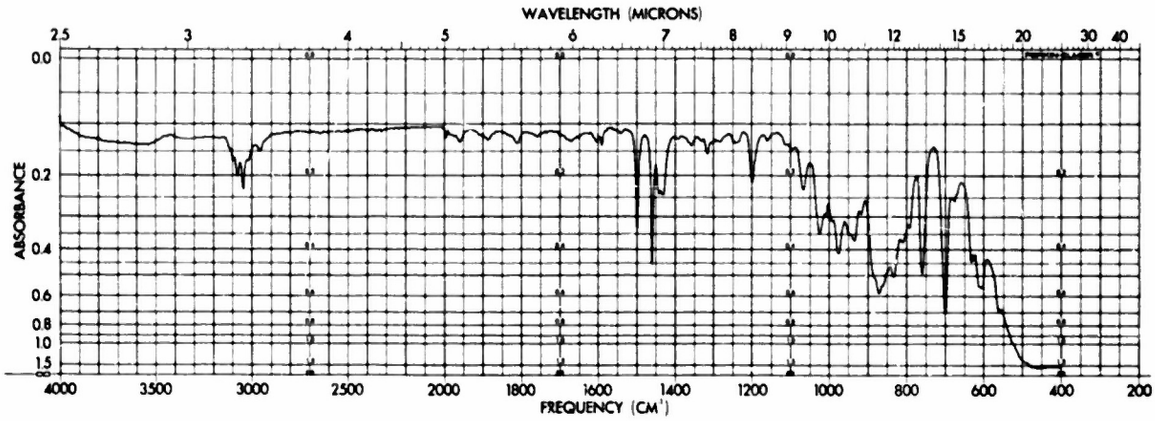


Figure 9. Infrared Spectrum of 1,2-Bis(difluoramino)phenylethane

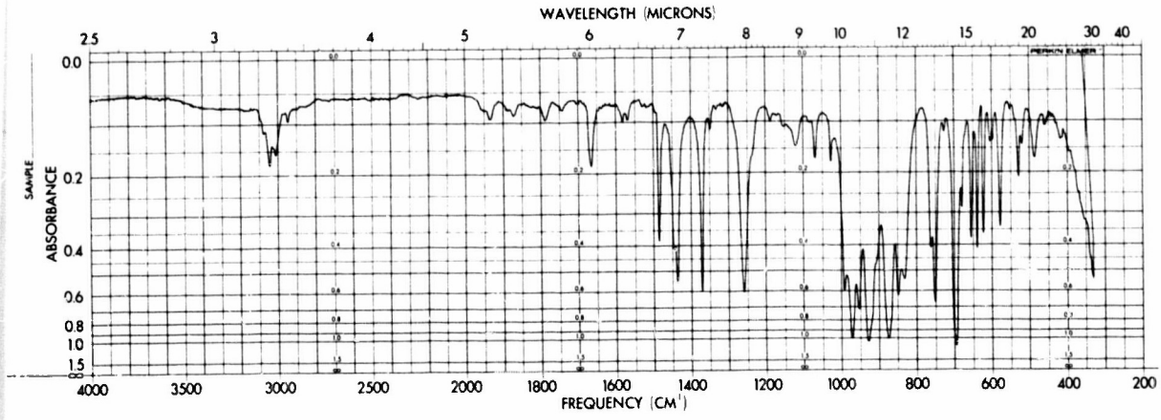


Figure 10. Infrared Spectrum of 1,1-Bis(difluoramino)phenylethane

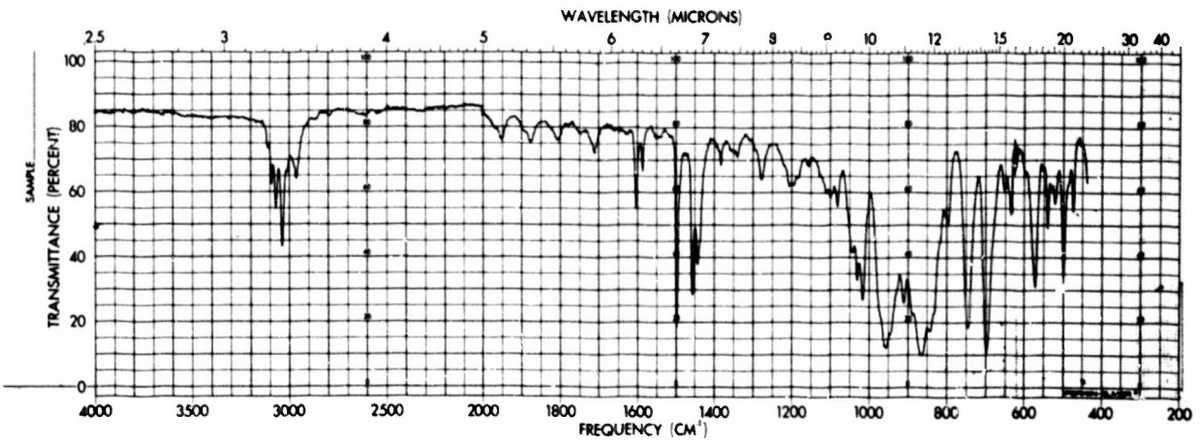


Figure 11. Infrared Spectrum of 2,2-Bis(difluoramino)phenylethane

The difluoramine liberated was collected under Dry Ice reflux in a flask containing 7.0 ml. of fuming sulfuric acid (104%). To this was added dropwise a solution of 5.10 g. (0.045 mole) heptanal (K and K Laboratory) in 10 ml. Freon-113. After 0.5 hr. of additional stirring, an additional 20 ml. of Freon-113 was added and the organic layer was separated.

To the combined organic layers from two such runs was added 20 ml. 98% sulfuric acid, and the mixture was stirred vigorously for 20-30 min. The organic solution was then decanted off, washed with water and aqueous bicarbonate, dried, and stripped of solvent. The 8.0 g. of residue was distilled at 48° (4.5 mm.) to yield 5.5 g. of pure product.

2,3-Bis(difluoramino)-2,3-dimethylbutane - A solution of 2.85 g. (34 mmoles) of 2,3-dimethylbutene-2 in 20 ml. of Freon-113 was placed in a 60-ml. stainless steel Hoke cylinder. The mixture was degassed by freezing at -78° and evacuating, and alternately melting at room temperature, through three cycles. Then 89 mmoles of N_2F_4, measured by volume, assuming ideal gas properties, was condensed into the cylinder at -196°. The mixture was agitated on a reciprocating rocker arm while being heated to 50° for 15 hr., after which the excess N_2F_4 was pumped off at -78°. This procedure was repeated with a 50% increase in the amount of reactants. The combined reaction mixtures were chromatographed without prior work-up to give 6.0 g. (26%) of pure 2,3-bis(difluoramino)-2,3-dimethylbutane.

2,3-Bis(difluoramino)pentane - In a 75 ml. stainless steel cylinder were mixed 3.90 g. (56.5 mmoles) of pentene-2 (Fisher Scientific Co., 99% pure) and 20 ml. Freon-113. To this was added, by condensing at -160°, 134 mmoles (3 l. at 760 mm.) of tetrafluorohydrazine. The mixture was heated with shaking to 80° for 15 hr. The crude products from this and three identical preparations (30.4 g., 78.5%) were combined and distilled. Material boiling in the range 48-52°(51 mm.)was diluted with Freon-113 to permit automatic injection and chromatographed on 20% SF-96 Silicone on A. W. Chromosorb P at 60°. The isomers, α (having the shorter retention time) and β, were cleanly separated, but a mechanical malfunction in the collector permitted the α sample to be contaminated with a small amount of β, necessitating a second pass. Final yields were 4.5 g. of α and 6.1 g. of β.

1,2-Bis(difluoramino)phenylethane - Styrene (5.89 g., 56.5 mmoles) was treated with 134 mmoles of N_2F_4 and worked up in the same manner described for N_2F_4 adducts above. After the solvent was removed, 10.40 g. of crude product remained. This was combined with the product from a second identical run and distilled twice to give 5.3 g. (22.6% yield) of pure 1,2-bis(difluoramino)-phenylethane.

1,1-Bis(difluoramino)phenylethane - A solution of 7.18 g. (60 mmoles) acetophenone in 20 ml. methylene chloride was added dropwise to a stirred flask containing 0.5 mole HNF_2 refluxing over 5 ml. of 104% H_2SO_4 at 0-5°. After 4 hr, the HNF_2 was allowed to distill off. The solvent layer was decanted, washed three times with water, once with aqueous $NaHCO_3$, and again with water. The

yield of crude material obtained from four such preparations, after solvent removal, was 38.7 g. Distillation gave 14.0 g., b.p. 60° (3.0 mm.). This material gave a single sharp v.p.c. peak on the Silicone SF-96 column. The sample

Anal. Calcd. for $C_8H_8N_2F_4$: C, 46.16; H, 3.87; N, 13.46.

Anal. Calcd. for ($C_8H_8N_2F_4 + C_8H_8O$): C, 58.53; H, 4.91; N, 8.53.

Found: C, 58.05; H, 4.84; N, 8.61.

was dissolved in 30 ml. Freon-113 and stirred with 40 ml. 98% H_2SO_4 for 0.5 hr., separated, washed with water and $NaHCO_3$, and dried. The residue remaining after removal of solvent still showed a small carbonyl absorption. The acid treatment and washing were repeated to yield 3.4 g. of material from which the carbonyl contaminant had been removed, as indicated by the infrared spectrum.

Reaction of Difluoramine with Phenylacetaldehyde in Sulfuric Acid - A solution of 7.5 g. (62.5 mmoles) phenylactaldehyde (K and K Laboratories) distilled at 48° (1.3 mm.), in 20 ml. dried Freon-113 was added slowly to 0.5 mole of refluxing HNF_2 over 7 ml. 104% H_2SO_4. The acid layer became black and viscous. After workup as above, 0.5 g. of polymeric residue was obtained. The synthesis was repeated as above three times, except that only 4 ml. of H_2SO_4 was used and 10 ml. Freon-113 was added before the introduction of the aldehyde was begun. A total of 16.15 g. of crude NF product was obtained. This material could be distilled only by removing the short fractionating column, b.p. 114° (0.05 mm.). The high boiling point indicated that the product obtained was actually bis(1-difluoramino-2-phenylethyl) ether and the infrared spectrum confirmed this conclusion.

1-Difluoramino-2-phenylethanol - Difluoramine (0.25 mole) was generated and collected under Dry Ice reflux as above, in a flask containing 10 ml. Freon-113. To this was added, during 4 hr., a solution of 7.7 g. phenylacetaldehyde (K and K Laboratories, distilled at 65°/1.7 mm.) in 10 ml. Freon-113. The reaction mixture was then warmed to room temperature to remove excess difluoramine. A portion, approximately 67%, was stripped of solvent, and distilled (b.p. 76°/0.3 mm.)to yield 5.75 g. of liquid.

Anal. Calcd. for $C_8H_9NF_2O$: C, 55.49; H, 5.24; N, 8.09.

Found: C, 55.54; H, 5.24; N, 7.78.

2,2-Bis(difluoramino)phenylethane - A solution of 5.75 g. (33.3 mmoles) of 1-difluoramino-2-phenylethanol in 15 ml. Freon-113 was added during 4 hr. to 0.25 mole of difluoramine refluxing over 4.0 ml. 104% fuming sulfuric acid and 10 ml. Freon-113. After workup as described above, a crude yield of 2.0 g. (29%) of liquid product, b.p. 48° (1.0 mm.) was obtained. The infrared spectrum contained the expected absorption bands for a mono-substituted aromatic compound with NF_2 groups. Attempts to duplicate this procedure revealed that results were extremely variable. Low yields of geminal compound and substantial amounts of the ether were ofter encountered.

Spectra - The infrared spectra were recorded on a Perkin-Elmer Model 521 Infrared Spectrometer. N.m.r. spectra were obtained on a Varian DP 60 Spectrometer, operated at 56.4 Mc for fluorine resonance. Compounds were

present as 70% by volume solutions in $CFCl_3$ with 2% added TMS. Spectra were calibrated by the side-band method using $CFCl_3$ and RMS as internal references.

ACKNOWLEDGEMENTS

This research was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research, under Contract Number NOnr 4364(00).

The authors are indebted to Richard L. Hanson of the Office of Naval Research and Dr. Murray S. Cohen of these laboratories for their interest in and encouragement of this work.

Thanks are due to J. A. Creatura and D. N. Pregler for elementary analyses and to R. N. Storey and D. G. Chowanec for infrared spectra.

LITERATURE CITED

1. Aerojet-General Corporation, Report 0235-01-9, Research in Fluoro-Nitro Compounds, 1961 (Confidential Report).
2. Freeman, J. P., Advances in Chemistry Series, 36, "Free Radicals in Inorganic Chemistry," p. 128.
3. Newman, M. S., J. Chem. Educ., 32, 344(1955).
4. Ng, Soon and Sederholm, C. H., J. Chem. Phys., 40 2090(1964).

5. Petrakis, L. and Sederholm, C. H., ibid., 35, 1243 (1961).

6. Rohm and Haas Company, Report P-62-5, Quarterly Progress Report on A.R.P.A. Projects, 1962 (Confidential Report).

7. Rohm and Haas Company, Report P-60-10, Quarterly Progress Report on Physical Chemistry, 1960 (Confidential Report).

8. Rohm and Haas Company, Report P-58-18, Quarterly Progress Report on Synthetic Chemistry, Part II, "Organic Chemistry," 1958 (Confidential Report).

9. Rohm and Haas Company, Report P-61-6, Quarterly Progress Report on Synthetic Chemistry, Part II, "Organic Chemistry," 1961 (Confidential Report).

10. Smith, H. F. and Wieting, W. H., Gas Chromatographic Separation of Some Bis(difluoramino)alkanes, Preprint C, below.

11. U. S. Naval Propellant Plant, Indian Head, Maryland, Navweps Report 8571 (TR 147), Chemistry Research Quarterly Progress Report, 1964 (Confidential Report).

Gas Chromatographic Separation of Some Bis(difluoramino)alkanes[1]

Harry F. Smith and Warren H. Wieting

Thiokol Chemical Corporation
Reaction Motors Division
Denville, New Jersey

---

(1) This research was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research, under Contract Numbers 1878(00) and 4364(00).

ABSTRACT

The application of gas chromatographic methods to the purification of some bis(difluoramino)alkanes is described. Pairs of geometric isomers have been successfully separated, and characterized by means of their infrared, n.m.r., and mass spectra.

INTRODUCTION

As a consequence of a continuing search for more highly energetic rocket propellant constituents, much attention has been focused on the chemistry of organic nitrogen-fluorine compounds. We wish to report the separation of some selected materials of this class in exceptionally high purity, by gas chromatographic means.

The compounds discussed are vicinal bis(difluoramino)alkanes, synthesized by the addition of tetrafluorohydrazine[2] to the appropriate olefins[3]. Two

---

(2) C. B. Colburn and W. Kennedy, J. Am. Chem. Soc., 80, 5004 (1958).

(3) Rohm and Haas Company, Report P-58-18, Quarterly Progress Report on Synthetic Chemistry, Part II, "Organic Chemistry", 1958 (Confidential Report).

---

of the examples discussed involve the separation of pairs of geometric and diastero isomers having very similar physical properties. The third case consists of the separation of the desired product from unknown contaminants and illustrates a dramatic change in physical properties as a function of purity.

EXPERIMENTAL

Apparatus and Reagents

Standard commercial instruments were used for the separations and the characterization of the products:

1. Wilkens Autoprep Model A-700 Gas Chromatograph
2. Perkin-Elmer Model 154-C Vapor Fractometer
3. Perkin-Elmer Model 21 Infrared Spectrophotometer
4. Perkin-Elmer Model 521 Infrared Spectrophotometer
5. Varian DP-60 High Resolution N.m.r. Spectrometer
6. Bendix Model 12-101 Time-of-Flight Mass Spectrometer

7. Gas chromatographic columns were constructed of coiled copper tubing, which was passivated by exposure to fluorine gas.

8. Packing materials and stationary phases were obtained from Wilkens Instrument and Research, Inc.

Gas Chromatographic Separations

The columns and conditions utilized in this work are summarized in Table I. Results are discussed in more detail in the subsections which follow.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS

Instrument	Length (ft.)	Dia. (in.)	Packing	Column Temp. (°C)	Flowrate (ml./min.)	Application
Perkin-Elmer	6	1/4	25% Dodecyl Phthalate on 30-60 Firebrick	78/135	65	a
Autoprep	6	1/4	20% Silicone SF-96 on 30-60 AW Firebrick	70	100	a
Autoprep	10	3/8	20% Silicone SF-96 on 30-60 AW Chromosorb P	60	50	b
Autoprep	12	3/8	20% Silicone SF-96 on 30-60 AW Chromosorb P	70	100	c

a. Separation of cis- and trans-1,2-Bis(difluoramino)cyclohexane
b. Separation of α- and β-2,3-Bis(difluoramino) pentane
c. Purification of 2,3-Bis(difluoramino)-2,3-dimethylbutane

1. cis-and trans-1,2-Bis(difluoramino)cyclohexane

The title compound was prepared[4] and prepurified by distillation: b.p. 46-47° (6 mm.), 66-67° (35 mm.), 118° (135 mm.); $n_D^{27.5}$ 1.407; d_{25} 1.289.

Anal. Calcd. for $C_6H_{10}N_2F_4$: C, 38.71; H, 5.41; N, 15.05; F, 40.83.

Found: C, 38.70; H, 5.61; N, 14.86; F, 40.63.

(4) D. Grafstein and C. Vogel, Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 076-S1-61, Difluoramine Chemistry, 1961 (Confidential Report).

A 20-µl. sample of 1,2-bis(difluoramino)cyclohexane, b.p. 46-47° (6 mm.) was chromatographed at 78° as indicated in Table I. Two components, with retention times of 49 and 98 min. (Figure 1), were detected. An increase of column temperature to 135° gave satisfactory separation with larger samples, decreasing the retention times to 20 and 43 min., respectively. Infrared spectra of the two components are shown in Figures 2 and 3. The compound present in smaller amount and having the shorter retention time is assigned the cis-structure. The isomeric relationship between the two compounds is indicated by the similarity in their infrared spectra and in their mass spectrometric cracking patterns (Table II).

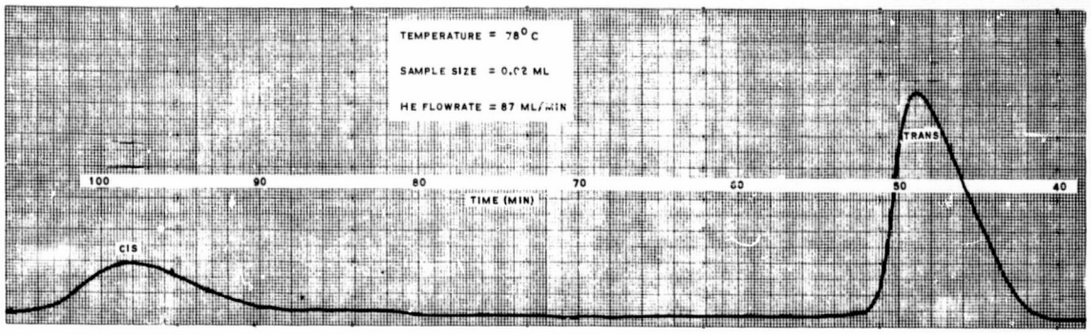


Figure 1. Vapor Phase Chromatographic Separation of trans and cis-1,2-Bis(difluoramino)cyclohexanes

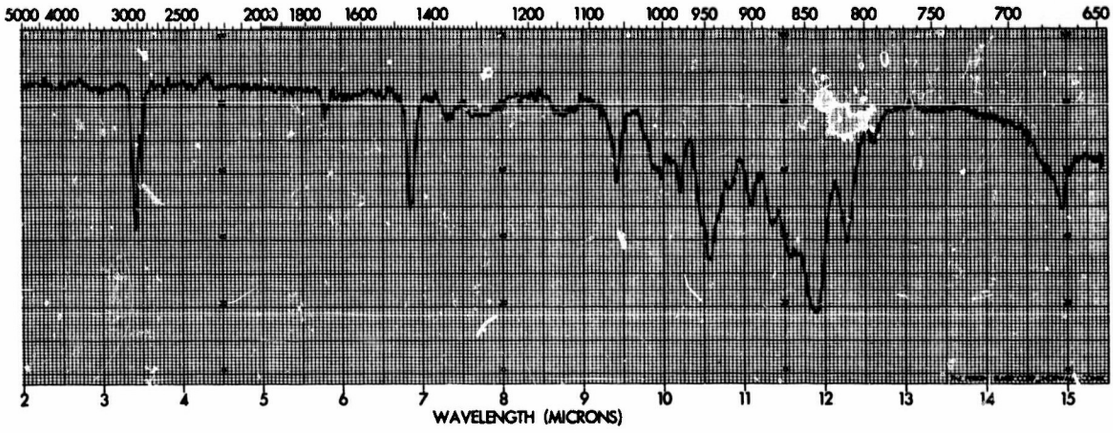


Figure 2. Infrared Spectrum of trans-1,2-Bis(difluoramino)cyclohexane

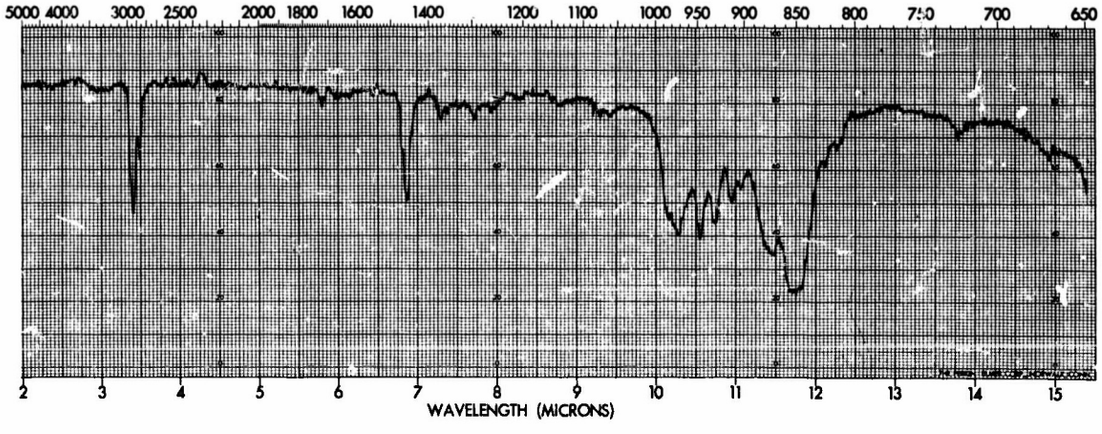


Figure 3. Infrared Spectrum of cis-1,2-Bis(difluoramino)cyclohexane

TABLE II

MASS SPECTRA OF 1,2-BIS(DIFLUORAMINO)CYCLOHEXANES

	Relative Intensities			Relative Intensities	
m/e	I trans	II cis	m/e	I trans	II cis
36	0.1	0.1	73	45.3	46.7
37	1.1	1.7	74	10.0	10.3
38	4.0	6.2	75	1.9	1.8
39	48.8	63.5	76	0.9	---
40	17.4	22.3	77	4.6	4.7
41	91.4	107.3	78	1.5	2.0
42	31.3	34.7	79	15.6	15.9
43	9.0	10.5	80	9.7	10.3
44	1.8	3.3	81	100.0	100.0
45	2.4	2.9	82	15.6	16.5
46	5.9	7.8	83	1.7	2.0
47	19.2	22.6	84	1.0	1.0
48	8.8	10.2	85	2.3	2.4
49	0.7	0.8	86	6.0	6.4
50	2.1	2.8	87	5.2	5.3
51	7.0	9.4	88	2.0	2.0
52	6.3	8.2	89	0.6	0.6
53	30.4	35.3	90	0.4	0.4
54	23.3	26.6	91	0.4	0.4
55	26.8	29.3	92	1.8	1.7
56	8.3	7.4	93	2.1	2.3
57	1.9	1.8	94	6.9	7.0
58	1.1	1.4	95	2.9	3.0
59	22.6	24.5	96	6.3	6.5
60	4.1	4.7	97	1.7	1.7
61	7.8	8.8	98	1.6	1.7
62	5.0	5.3	99	5.9	5.8
63	1.3	1.3	100	2.5	2.7
64	1.0	1.1	102	0.2	0.2
65	11.7	12.9	106	0.4	0.4
66	8.6	10.3	110	0.1	0.2
67	60.3	66.7	111	0.3	0.3
68	16.8	19.4	112	0.8	0.7
69	9.0	10.3	114	6.0	6.1
70	1.8	1.6	115	7.3	7.2
71	1.4	1.3	134	3.3	3.4
72	2.8	3.2			

Physical properties are summarized in Table III. The cis-and trans-isomers of 1,2-bis(difluoramino)cyclohexane were also separated conveniently on a silicone column (Table I), giving retention times of 17.6 and 29.6 min., respectively (Figure 4).

TABLE III

PHYSICAL PROPERTIES OF 1,2-BIS(DIFLUORAMINO)CYCLOHEXANES

Compound	n_D^{25}	d_{25}
Mixed isomers	1.4107[a]	1.289
cis	1.4125	1.293
trans	1.4095	1.275

a. $n_D^{27.5}$

2. α- and β-2,3-Bis(difluoramino)pentane

The title compound was prepared[5,6] and distilled:

b.p. 46.0° (38 mm.), 122° (760 mm.); n_D^{25} 1.3715;

Anal. Calcd. for $C_5H_{10}N_2F_4$: C, 34.49; H, 5.79; N, 16.09.

Found: C, 34.41; H, 5.91; N, 16.10.

(5) H. F. Smith, W. H. Wieting, and D. D. Perry, Preparation and Properties of Some Bis(difluoramino)alkanes and -arylalkanes, Preprint B, above.

(6) A. P. Kotloby and D. D. Perry, Thiokol Chemical Corporation, Reaction Motors Division, Report RMD AOR-ATS-63, Advanced Oxidizer Research, Section II, "Synthesis of Compounds for Structure-Sensitivity Study", 1963 (Confidential Report).

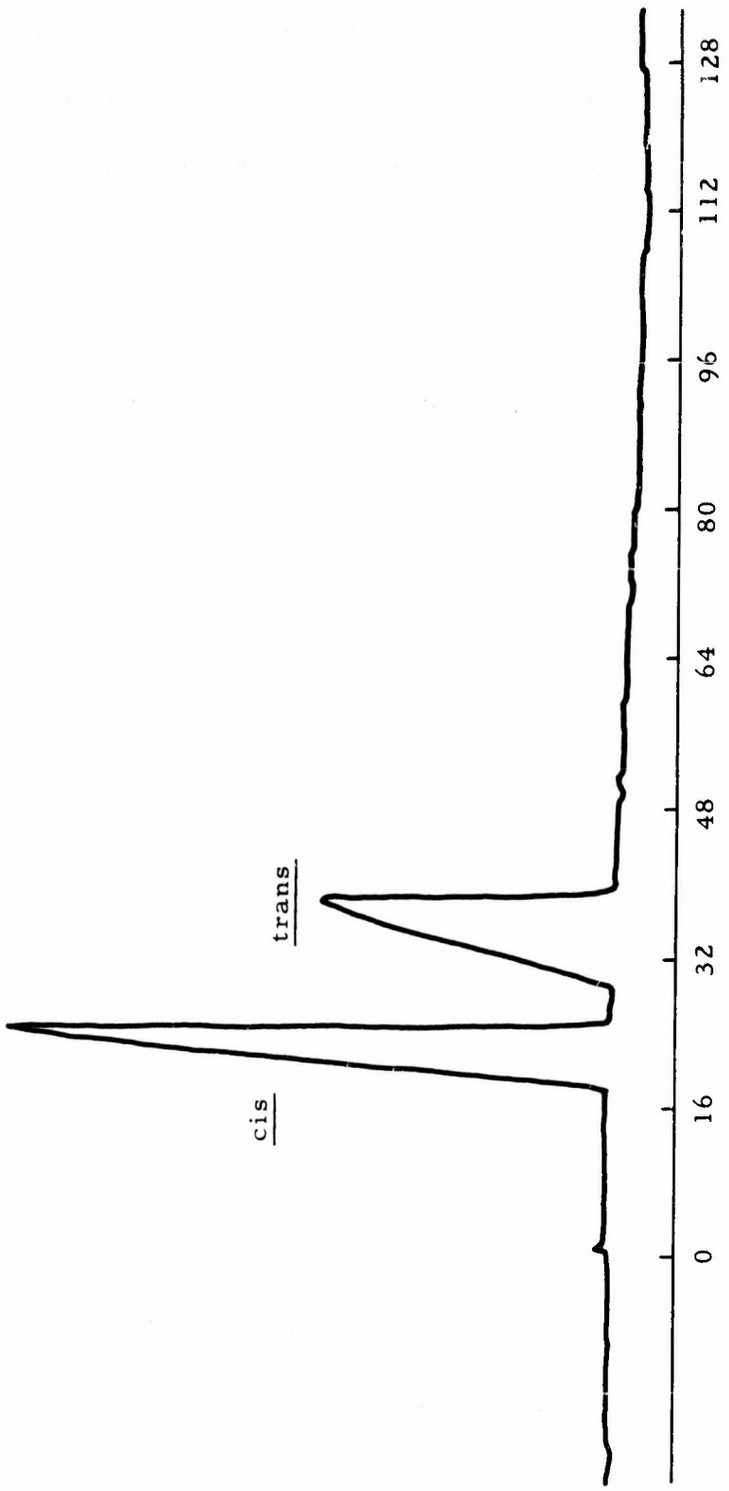


Figure 4. G. C. Separation of cis- and trans-1, 2-Bis(difluoramino)cyclohexane on Silicone

Crude 2,3-bis(difluoramino)pentane was distilled to give three fractions, b.p. 48-50°, 51-52°, and 54-55°(51 mm.). A Freon-113 solution of the first fraction was chromatographed (see Table I) with automatic injection and was separated into two components (Figure 5). The larger component, having a 51.2 min. retention time, was designated α, the other with a retention time of 66.4 min., β. These are diastereoisomers. Chromatographing the two higher boiling distillation fractions under the same conditions gave similar curves, with a progressive decrease in the first component and increase in the second. All three fractions were chromatographed to give a total of 4.5 g. of α and 6.1 g. of β, each >99% purity, from 30.4 g. of crude product before distillation.

The infrared spectra of the two isomers (Figures 6 and 7) are very similar and contain the expected absorptions. These spectra agree with the infrared spectrum of a sample of mixed isomers prepared earlier[5]. The F^{19} and proton n.m.r. spectra, discussed in detail elsewhere[5], were also in agreement with a geometrical isomeric relationship between the two compounds. Some analytical data and physical properties are listed in Table IV.

TABLE IV

ANALYSES AND PHYSICAL PROPERTIES OF
2,3-BIS(DIFLUORAMINO)PENTANES

Isomer	C	H	N	b.p. (760 mm.)	n_D^{25}
α	34.60	5.93	15.13	119°	1.3688
β	34.88	5.93	15.34	123°	1.3728
Theory	34.48	5.79	16.09	---	---

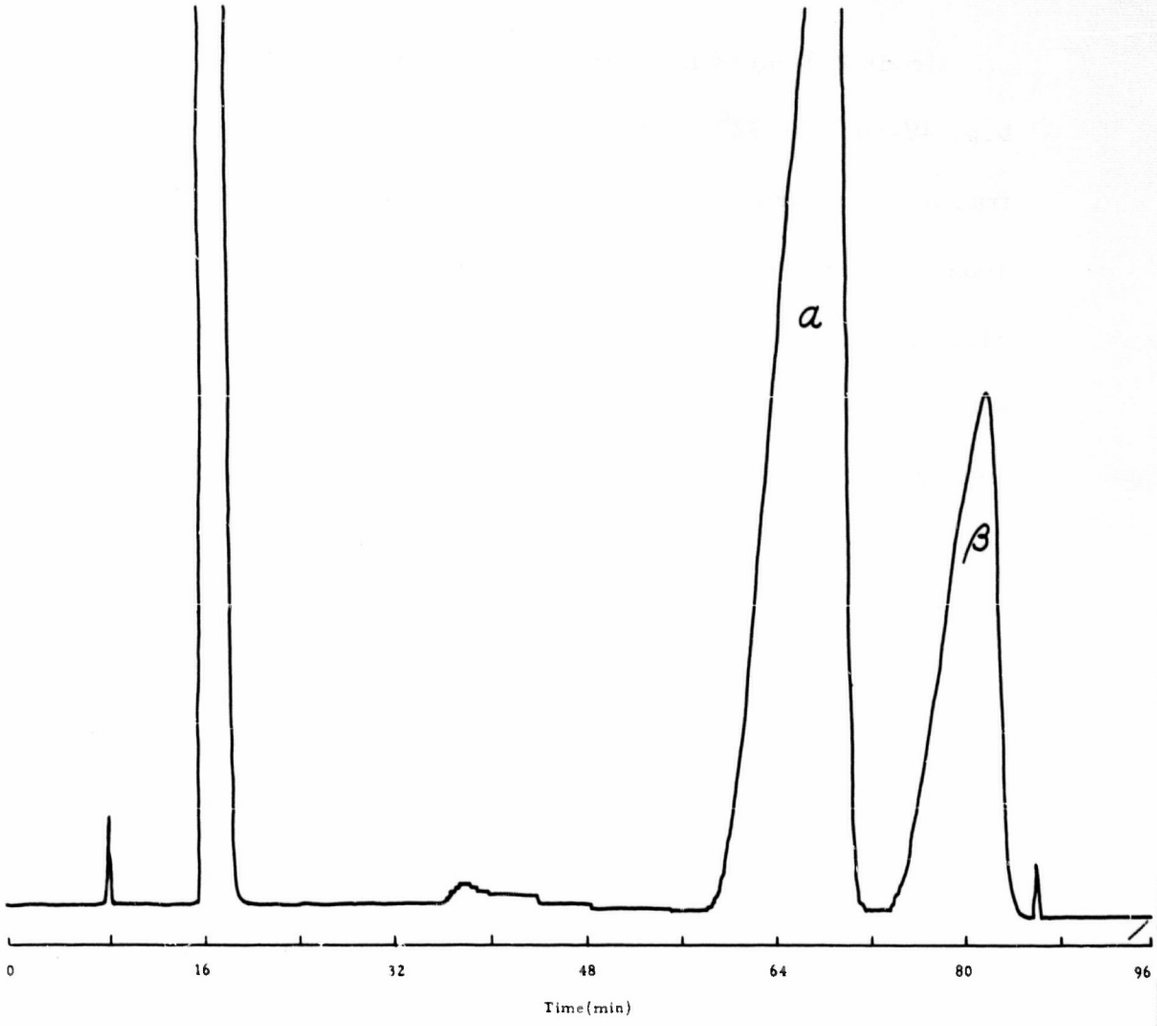


Figure 5. G. C. Separation of Diastereoisomers of 2,3-Bis(difluoramino)-pentane

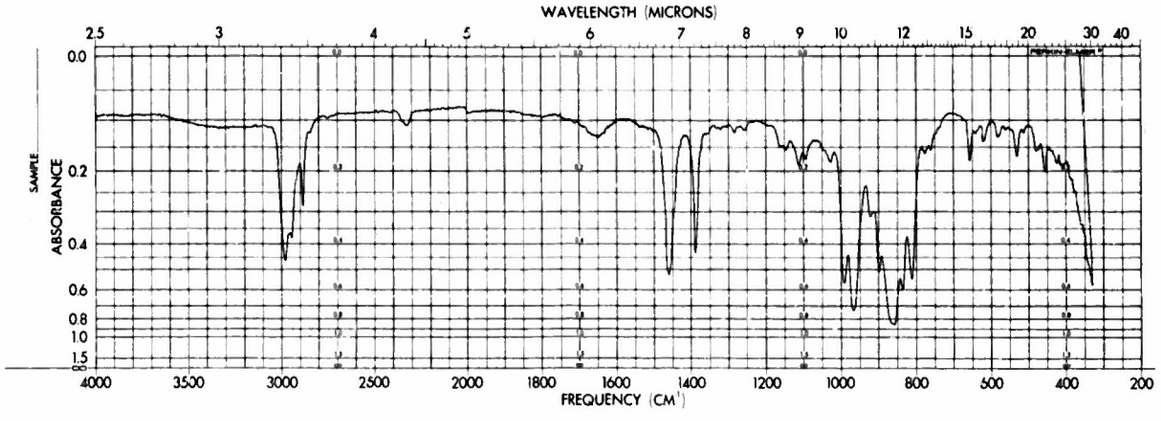


Figure 6. Infrared Spectrum of 2,3-Bis(difluoramino)pentane

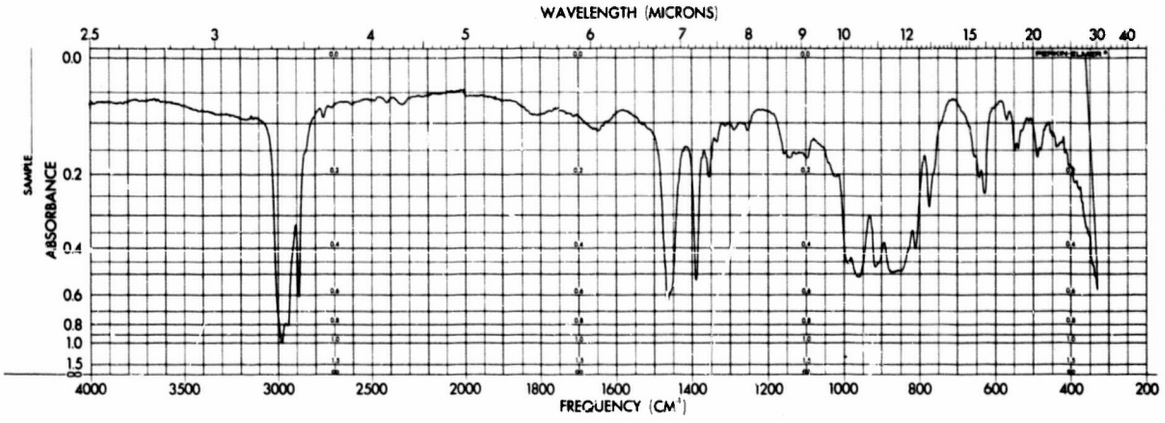


Figure 7. Infrared Spectrum of β-2, 3-Bis(difluoramino)pentane

3. 2,3-Bis(difluoramino)-2,3-dimethylbutane[5,7]

---

(7) Rohm and Haas Company, Report P-62-5, Quarterly Progress Report on A.R.P.A. Projects, 1962.

A sample of the title compound was prepared earlier[6] and purified by triple sublimation under nitrogen at 25-30° and atmospheric pressure. This material melted at 64-66° and gave a fair elemental analysis (Table V). A newly prepared sample was gas chromatographed in Freon-113 solution without preliminary purification, under the conditions given in Table I. The chromatographic trace is reproduced in Figure 8. A total of 6.0 g. of solid product, m.p. 83.5-84.5°, equivalent to 26% of the theoretical yield for the reaction, was recovered. The infrared spectrum is shown in Figure 9, and analytical data are listed in Table V. This represents a dramatic example of the efficiency of G.C. purification.

TABLE V

ANALYSES AND MELTING POINTS OF
2,3-BIS(DIFLUORAMINO)-2,3-DIMETHYLBUTANE

Sample	C	H	N	m.p.
Sublimed	36.91	6.60	14.06	64-66°
G.C.	38.44	6.43	14.72	83.5-84.5°
Theory	38.30	6.43	14.89	---

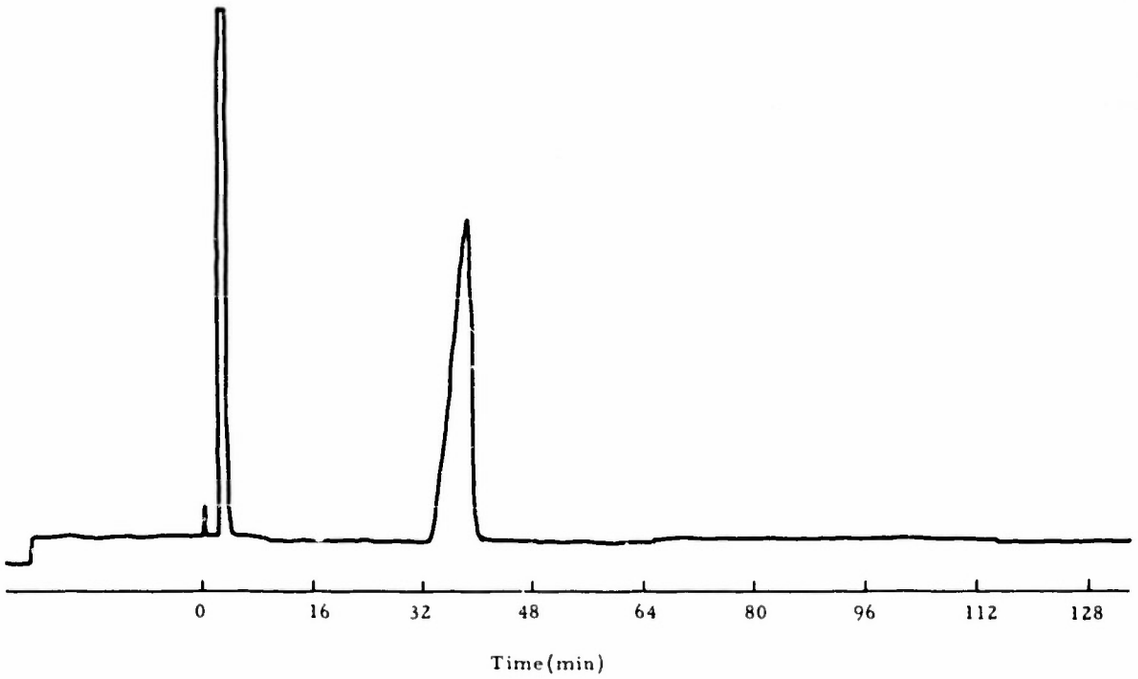


Figure 8. G. C. Separation of 2,3-Bis(difluoramino)-2,3-dimethylbutane

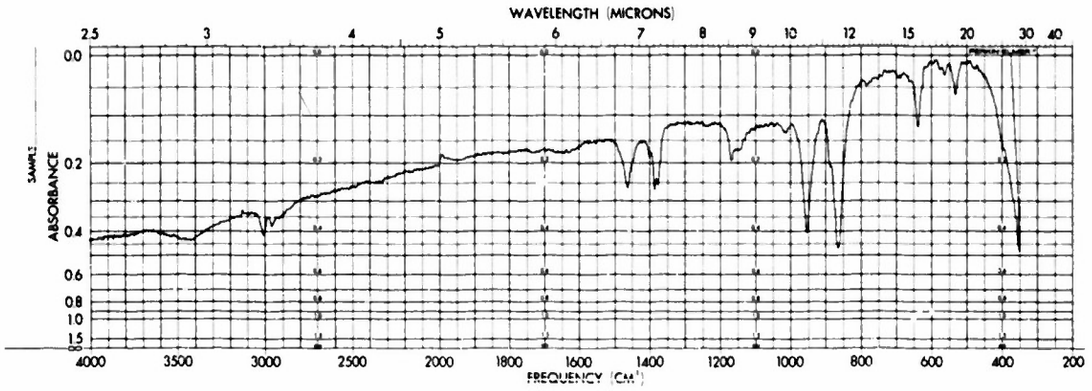


Figure 9. Infrared Spectrum of 2,3-Bis(difluoramino)-2,3-dimethylbutane

CONCLUSIONS

Gas chromatographic separations on dodecyl phthalate and Silicone SF-96 have proven effective in separating geometric isomers and diastereoisomers, and in obtaining levels of purity not previously reached, with several bis(difluoramino)alkanes.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. Richard L. Hanson of the Office of Naval Research and Drs. Donald D. Perry and Murray S. Cohen of these laboratories for their interest in and encouragement of this work. We are indebted to Raymond N. Storey for the gas chromatographic separation of the 1,2-bis(difluoramino)cyclohexane isomers and for infrared analyses, to Dr. David F. Kates for n.m.r. spectra, and to John A. Creatura and Donald N. Pregler for elemental analyses.

Some Elimination Reactions of Organic Difluoramines[1]

Harry F. Smith, Joseph J. Dvorak, and Donald D. Perry

Thiokol Chemical Corporation, Reaction Motors Division
Denville, New Jersey

---

(1) This research was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research, under Contract Number NOnr 4364(00).

Primary and secondary alkyldifluoramines are known[2, 3] to eliminate

---

(2) D. D. Perry, et al., Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 076-F, Superior Liquid Monopropellants, 15 July 1960 (Confidential report).

(3) Rohm and Haas Company, Report P-59-6, Part II, Quarterly Progress Report on Synthetic Chemistry, March 1959 (Confidential report).

---

hydrogen fluoride in the presence of a base to yield, respectively, nitriles and ketofluorimines:

$$RCH_2NF_2 + 2B \longrightarrow RC{\equiv}N + 2\,BHF \qquad (1)$$

$$R_2CHNF_2 + B \longrightarrow R_2C{=}NF + BHF \qquad (2)$$

We wish to report some novel compounds obtained by the base-induced dehydrofluorination of vicinal and geminal bis(difluoramines). Elimination of the elements of difluoramine from a bis(difluoramino)fluoraminomethyl ether, to yield a trifluoroformamidine derivative, is also described.

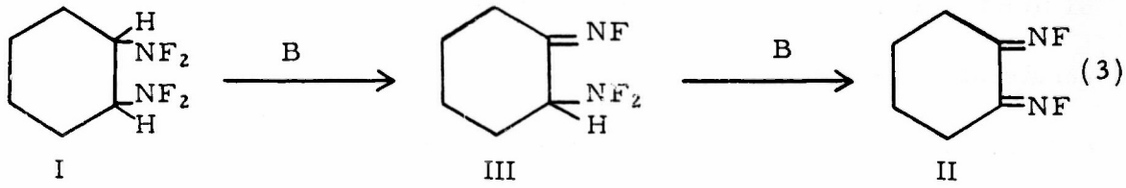
The dehydrofluorination of 1,2-bis(difluoramino)cyclohexane (I)[2] by treatment with a weakly basic ion-exchange resin, to yield 1,2-difluoriminocyclohexane (II), has been described in an earlier paper[4]. This reaction was carried

(4) H. F. Smith, J. A. Castellano, and D. D. Perry, The Chemistry of Alkyldifluoramines. III. The Synthesis and Some Reactions of 1,4-Bis(difluoramino)cyclohexene-2 and 1,2-Difluoriminocyclohexane, included in Report RMD 5043-64F, 31 December 1964 (Confidential Report).

out typically in ethyl ether solution at 30° to reflux temperature for 16 to 24 hr. Under these conditions the difluorimine was the only product obtained, although yields were neither quantitative nor consistent.

In a more recent experiment it was observed that the beads of ion exchange resin had disintegrated, an indication of neutralization, after only 6 hr, and the reaction was, therefore, quenched at this point by filtering the mixture. In contrast to previous experience, distillation of the crude reaction product gave three fractions. The first and predominant fraction consisted of unreacted I, and the third fraction consisted of II. The infrared spectrum of the second and smallest fraction, however, contained absorption bands due to both fluoramino ($-NF_2$) and fluorimino ($=NF$) groups, at 840-855 cm^{-1} and 822cm^{-1}, respectively, possibly in the same molecule. These observations suggest that dehydrofluorination of a difluoramino group in a position vicinal to a fluorimino group

proceeds somewhat more rapidly than the initial dehydrofluorination producing the first fluorimino group.



I III II (3)

When 1, 1-bis(difluoramino)heptane (IV)[5, 6] was treated similarly with the

---

(5) E. I. duPont de Nemours and Company, Report E Lab B-5-4, Synthesis of High-Energy Polymers and Solid Oxidizers, 1962, (Confidential report)

(6) H. F. Smith, W. H. Wieting, and D. D. Perry, Preparation and Properties of Some Bis(difluoramino)alkanes and -arylalkanes, Preprint B, above.

---

customary twofold excess of the ion-exhange resin, a liquid product containing nitrogen and fluorine was obtained. The results of elemental analysis revealed, however, that two equivalents of hydrogen fluoride had been removed. The infrared spectrum of the product included, in addition to the expected C-H and N- F absorptions, a band at 1642 cm^{-1} indicating unsaturation (C=C or C=N) and

$$C_6H_{13}CH(NF_2)_2 + 2B \not\longrightarrow C_6H_{13}C(=NF)(NF_2) + BHF + B \qquad (4)$$

a strong sharp band at 1550 cm^{-1}, probably due to a ring vibration.

Several plausible structures can be postulated for a compound having these features and the empirical formula $C_7H_{12}N_2F_2$. Mass spectral evidence (Table I)

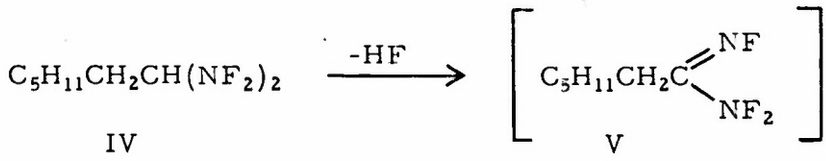
effectively eliminated any dimeric structure from consideration, since no mass peaks greater than 162 were observed. The boiling point, 35 to 38° (2.5 mm.), 61 to 63° (20 mm.), was in accordance with this conclusion. The detection of unsaturated fragments in the mass spectrum was contradicted by the proton n.m.r. spectrum, which failed to show any olefinic C-H. The F^{19} n.m.r. spectrum included resonance peaks at -45.9, -42.5, -16.1, and 9.8 ppm from $CFCl_3$, attributable to N-F, and a weak triplet at +138.6 ppm, possibly due to C-F contamination.

TABLE I

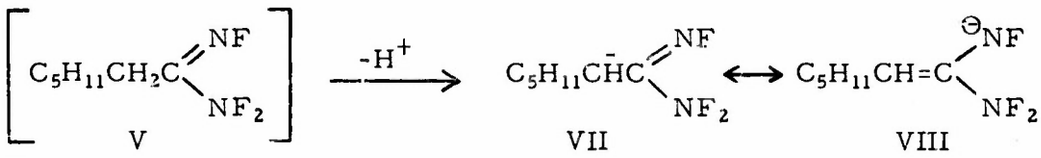
PARTIAL MASS SPECTRUM OF
DEHYDROFLUORINATION PRODUCT (VI)

m/e	Relative Intensity	Assignment
27	56.7	$C_2H_3^+$
29	80.7	$C_2H_5^+$
33	5.7	NF^+
39	33.2	$C_3H_3^+$
41	100.0	$C_2H_5^+$
42	40.7	$C_2H_6^+$
43	82.4	$C_3H_7^+$
55	38.5	$C_4H_7^+$
57	15.8	$C_4H_9^+$
69	11.1	$C_5H_9^+$
96	5.3	$C_6H_{10}N^+$
110	2.6	$C_7H_{12}N^+$
129	6.2	$C_7H_{12}NF^+$
162	2.2	$C_7H_{12}N_2F_2^+$

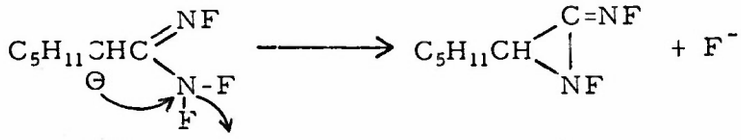
A careful weighing of all the evidence leads to the conclusion that the product has the fluoriminoazirane structure (VI). One may assume the initial formation of the amidine (V) by normal E_2 elimination, and subsequent removal of the proton on the α-carbon which would be expected to be activated by the electronegativity of the difluoramino and fluorimino groups. The carbanion (VII) can rearrange by an internal nucleophilic attack (S_Ni) on nitrogen (equation 7); subsequent elimination of fluoride ion would result in the formation of VI.



IV V (5)



V VII VIII (6)



VIII VI (7)

When the reaction described above was repeated, using a single equivalent of ion exchange resin and maintaining the reaction temperature at 16-20°, a different result was obtained. The liquid product contained N-F groups and unsaturation, but lacked the strong absorption at 1550 cm^{-1}. The presence of

water, presumably introduced into the system with the ion exchange resin, made more detailed interpretation of the spectrum impossible.

An attempt to repeat this 1:1 reaction on a larger scale, in order to obtain sufficient material for identification, produced an interesting result. Due to a mechanical failure, the reaction mixture was heated to 40° for a short period. Under these conditions, even though only one equivalent of the base was present, the product obtained was identical to VI.

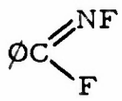
Another geminal bis(difluoramine) has been found to give anomalous results upon dehydrofluorination. In a preliminary experiment, a small quantity of α,α-bis(difluoramino)toluene (IX)[6] was dehydrofluorinated by refluxing in methylene chloride with a weakly basic ion-exchange resin. The infrared spectrum of the crude product, containing absorption peaks at 1642, 1568 and 1555 $cm.^{-1}$ and showing significant changes in the N-F region, 1040 to 800 $cm.^{-1}$, indicated that the expected benzamidine had been produced. When the reaction was repeated on

$$\underset{\text{IX}}{\text{ØCH(NF}_2)_2} \longrightarrow \underset{\text{X}}{\text{ØC}\begin{matrix}=\text{NF} \\ -\text{NF}_2\end{matrix}} \qquad (8)$$

a larger scale, distillation of the crude reaction mixture gave a 16% yield of pale yellow liquid, b.p. 54-57° (6 mm.). Elemental analysis did not agree with the composition of X, however, and v.p.c. revealed the presence of a second component. Two fractions were separated by preparative scale v.p.c., and the material having the longer retention time was identified by infrared and n.m.r.

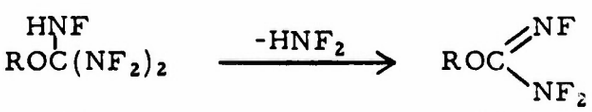
spectrometry as X. The proton n.m.r. spectrum showed a complex multiplet resonance centered at 448.2 c.p.s. (7.47 δ or 2.53 τ) from tetramethylsilane. In the F^{19} spectrum, single resonances were observed at -2558 c.p.s. (-45.35 Ø), -1144 c.p.s. (-20.80 Ø), and -387 c.p.s. (-6.86 Ø), with doublets (J=24 c.p.s.) at +2114 c.p.s. (+37.48 Ø) and +4438 c.p.s. (+78.69 Ø).

Unequivocal identification of the second component has not been possible. Its infrared spectrum contained absorptions at 1568 and 1555 $cm.^{-1}$ (C=N), at 1160 $cm.^{-1}$ (F>C=) and at 910 $cm.^{-1}$ (=NF). The structure XI is tentatively suggested as the most probable.



XI (9)

A major source of difficulty encountered in utilizing the addition reactions of perfluoroguanidine has been the tendency of the intermediate (XII) to eliminate the elements of HNF_2 to form an alkoxyformamidine (XIII):



XII XIII (10)

An investigation was initiated, therefore, to determine conditions which favor this decomposition reaction in order to provide information which will be valuable in avoiding it. The adduct used in this investigation was prepared from

pentanol and perfluoroguanidine (equation 11) using previously established procedures[7,8].

$$C_5H_{11}OH + FN{=}C(NF_2)_2 \xrightarrow{\text{urea}} C_5H_{11}O\overset{\overset{HNF}{|}}{C}(NF_2)_2 \qquad (11)$$

XIIa

---

(7) Minnesota Mining and Manufacturing Company, Report No. 11, Chemical Research as Related to Advanced Solid Propellants, 1961. (Confidential report).

(8) Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-64F, Advanced Oxidizer Research, Section II, "Synthesis of Compounds for Structure-Sensitivity Study," 31 December 1964 (Confidential report).

It has been shown that the crude product was principally XIIa and that it was stable to distillation under vacuum.

The conversion of the pentanol-PFG adduct, XIIa, to the corresponding

$$\underset{\text{XIIa}}{C_5H_{11}O\overset{\overset{HNF}{|}}{C}(NF_2)_2} \xrightarrow[\text{solvent}]{\text{NaF}} \underset{\text{XIII}}{C_5H_{11}OC\begin{matrix}=NF\\ \diagdown NF_2\end{matrix}} \qquad (12)$$

trifluoroformamidine (XIII) was found to depend strongly on the solvent or diluent used. No reaction occurred, for example, in Freon-113 at room temperature or in ethyl ether at 40°. In both experiments the adduct and the sodium fluoride were recovered unchanged. When acetonitrile was used as the solvent, however, the adduct lost the elements of HNF_2 to give 82-99% yields

of crude XIII. After distillation, b.p. 37-40° (5 mm.), 45-47° (9 mm.), the product was identified by its infrared spectrum.

Reaction of the adduct with sodium fluoride in ethanol gave anomalous results. The sodium fluoride was partially converted to bifluoride, and nitrogen was the only gaseous product evolved. The organic product contained CH, NF_2, and C=O groups, but no N-C=N unit, as shown by its infrared spectrum.

EXPERIMENTAL

1-Difluoramino-2-fluoriminocyclohexane - To 13.0 g. (0.0488 mole) of Amberlite IR-45 resin in 100 ml. CH_2Cl_2 was added dropwise 6.0 g. (0.0322 mole) of 1,2-bis(difluoramino)cyclohexane in 50 ml. CH_2Cl_2. The reaction mixture was refluxed for 6 hr., cooled, and filtered. The filtrate was then stripped of solvent to yield 4.3 g. of a crude liquid.

Distillation of the crude product yielded 3 fractions: (1) 2.99 g. boiling at 40-46° (3 mm.), (2) 0.050 g. boiling at 48-50° (3 mm.), and (3) 0.36 g. boiling at 54-56° (0.5 mm.). The first and third fractions were characterized by their infrared spectra as 1,2-bis(difluoramino)cyclohexane and 1,2-difluoriminocyclohexane, respectively. The middle fraction had an infrared spectrum which showed absorptions attributable to both $-NF_2$ and =NF groups.

1-Fluoro-2-fluorimino-3-pentylaziridine

1. A solution of 6.22 g. (0.031 mole) of 1,1-bis(difluoramino)heptane in 100 ml. of ether was added to 12.0 g. (0.060 eq.) of Amberlite IR-45 ion-exchange resin in a 300 ml. flask. The ether came to a boil and the mixture was stirred under reflux for about 15 min. The mixture gradually cooled to room temperature and stirring was continued for 24 hr. The resin was filtered off and the ether solution evaporated to dryness. The residue was distilled to yield 1.5 g. of colorless liquid, b.p. 35-38° (2.5 mm.).

Anal. Found: C, 49.97; H, 7.82; N, 16.51.

The -78° trap was found to contain an additional quantity of the product. This liquid was combined with the above product and distilled to yield 2.3 g. (46%) of colorless liquid, b.p. 61-63°(20 mm.).

Anal. Calcd. for $C_7H_{12}N_2F_2$: C, 51.84; H, 7.46; N, 17.27.

Found: C, 50.36/49.88; H, 7.55/7.64; N, 17.02/16.18.

2. A solution of 1.01 g. (5 mmoles) of 1,1-bis(difluoramino)heptane in 250 ml. ethyl ether was added 1.00 g. (5 meq.) of Amberlite IR-45 and the mixture was stirred for 64 hr. at 16-20° (water bath). The reaction mixture was worked up as described in (1) to give 0.75 g. of colorless liquid. The infrared spectrum was partially obscured by strong absorptions due to water, but the presence of bands due to C-H, N-F, and unsaturation were apparent. There was no significant absorption at 1550 $cm.^{-1}$.

N,N,N'-Trifluorobenzamidine - Refluxing 5.0 g. (25 mmoles) of α,α-bis-(difluoramino)toluene, b.p. 39° (2.2 mm.), with 7.0 g. (35 meq.) of Amberlite IR-45 in 200 ml. methylene chloride gave 3.50 g. (78%) of an orange liquid product. This material was chromatographed on a 12 ft. x 3/8 in. column of 20% Halocarbon oil on Fluoropak at 60°. The first fraction, representing 17% of the total and having a retention time of 12 min., gave an infrared spectrum containing absorptions at 1568 and 1555 cm.$^{-1}$ (C=N), 1160 cm.$^{-1}$ (=C$\diagdown\!\!\diagup_{F}$?), and 910 cm.$^{-1}$ (=NF?). The major fraction, retained for 49 min., was identified by infrared and n.m.r. spectra as N,N,N'-trifluorophenylformamidine.

Anal. Calcd. for $C_7H_5N_2F_3$: C, 48.28 H, 2.89; N, 16.09.

Found: C, 48.74 H, 2.83; N, 14.96.

N,N,N'-Trifluoropentoxyformamidine

(1) In Ethanol

To 0.57 g. (2.4 mmoles) of bis(difluoramino)fluoraminomethoxypentane (XII) in 20 ml. of absolute ethanol was added 0.109 g. (2.6 mmoles) of NaF with stirring. After several hours, the evolved gas was submitted for analysis and found to be N_2. The reaction mixture was filtered and the precipitate found by X-ray diffraction analysis to be a mixture of NaF and NaF·HF. Evaporation of the ethanol yielded 0.10 g. of a liquid whose infrared spectrum showed absorptions attributable to CH, NF_2, and C=O groups.

(2) In Freon-113

To 0.57 g. (2.4 mmoles) of XII in 15 ml. of Freon-113 was added 0.100 g. (2.6 mmoles) of NaF with stirring. After stirring the reaction mixture at ambient temperatures for several hours, the reaction mixture was filtered and the filtrate evaporated to yield 0.54 g. of unreacted XII.

(3) In Ethyl Ether

To a large excess of NaF in 10 ml. of Et_2O was added a solution of 1.37 g. (5.78 mmoles) of XII in 10 ml. of Et_2O. The reaction mixture was refluxed for 4 hr. and then filtered. Evaporation of the filtrate resulted in recovery of 1.32 g. of starting material.

(4) In Acetonitrile

To a large excess of NaF in 20 ml. of acetonitrile was added 1.1 g. (4.64 mmoles) of XII. Some fuming was observed as well as a slight exotherm. After the addition was complete, the reaction mixture was stirred at 40° for 3 hr. and then filtered. Upon evaporation of the filtrate, 0.70 g. (82%) of crude trifluoropentoxyformamidine was obtained. The crude product distilled at 37-40° (5 mm.) to give 0.59 g. (69%) of purified trifluoropentoxyformamidine.

Acknowledgements - The authors are indebted to Mr. Richard L. Hanson of the Office of Naval Research and to Dr. Murray S. Cohen of this laboratory for their interest in and encouragement of this work. We also wish to thank

John A. Creatura and Donald N. Pregler for analytical data, Raymond N. Storey and Daniel G. Chowanec for the infrared spectra, and David F. Kates for obtaining and interpreting the n.m.r. spectra. M. J. Socha and P. Shapiro also participated in the investigation.

III. APPENDIX — ORGANIC DIFLUORAMINE CHEMISTRY

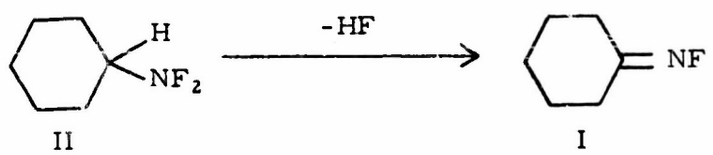
A. DISCUSSION

In this Appendix are presented the results of research efforts during 1965 which are not yet complete or which for other reasons do not lend themselves to publication at the present time. The subjects covered include a continuation of a study of the addition reactions of the ketofluorimine group and the attempted development of an efficient synthesis of cyclohexyldifluoramine. In addition, there are included some preliminary observations on the reactions of organic nitrogen-fluorine compounds with peroxides and with fluorine-abstracting Lewis acids.

Earlier studies (Ref 3) of the reactions of 1,2-difluoriminocyclohexane indicated the need for extension in two directions. First, a simpler model compound is required for a better understanding of some of the effects observed. Both electronic and steric factors introduced by the presence of two fluorimino groups on adjacent carbon atoms may complicate the system. Cyclohexylidenefluorimine (I) should serve admirably, avoiding these complications and having the added advantages of being non-shock sensitive and sufficiently high in molecular weight to facilitate handling of both reactant and potential products. Secondly, the original justification for initiating a study of alkylidenefluorimines rested, at least in part, upon analogy to known addition reactions of perfluoroguanidine. Since none of these reactions occurred with 1,2-difluoriminocyclohexane, our studies have been extended to include fluorimines which contain more strongly electronegative substituents, and, thus, are more closely analogous to perfluoroguanidine.

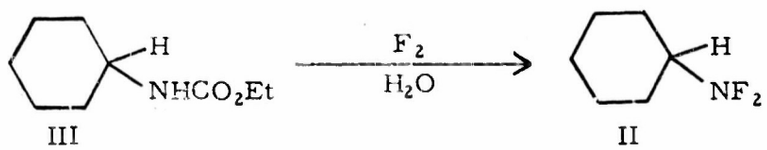
1. Synthesis of Cyclohexyldifluoramine (II)

The obvious synthetic approach to I involves the dehydrofluorination of difluoraminocyclohexane (II). The preparation of the required difluoramine



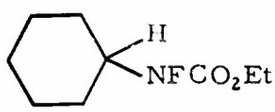
II I (1)

by aqueous fluorination of ethyl N-cyclohexylcarbamate (III) has been described (Ref 7). On duplicating this procedure, we obtained II in only 10-11% yield.



III II (2)

Attempts to improve the yield by modification of the quantity and rate of introduction of the fluorine were unsuccessful. Fluorination of emulsion systems, consisting of the carbamate, water, halogenated solvent, and an amphoteric surfactant gave equally poor yields (Ref 8). In each case, in addition to 5-10% of the desired product, small quantities of the intermediate (IV) were obtained, but the major constituent of the reaction mixture was unreacted III.



IV

The cessation of reaction at this point appeared to be unaffected by the continued introduction of additional fluorine. When the quantity of carbamate used was decreased by one-half without altering the remainder of the reaction mixture, the reaction proceeded until approximately the same quantity of II had been formed, effectively doubling the yield. This result suggested that a by-product was inhibiting the reaction after its concentration reached some critical level.

The most obvious of the possible interfering by-products is the hydrogen fluoride which is liberated during the reaction. An attempt to control this factor by including a stoichiometric quantity of calcium carbonate in the reaction mixture was unsuccessful. No significant quantity of II was obtained. In a related experiment, the pH of the aqueous system was determined at intervals, and was adjusted with sodium carbonate whenever it was found to have dropped to pH 3 or below. In this case also none of the desired product was obtained. A first attempt to obtain usable quantities by scaling up the system which had given 10% yields was also frustrated. Only traces of II were obtained in this experiment, and the principal product was IV. The III

used was from a different batch, and the fluorination appears to be sensitive to minor impurities in this starting material. This effect had not been noted before. The results of these carbamate fluorinations are summarized in Table I.

TABLE I

AQUEOUS FLUORINATION OF ETHYL N-CYCLOHEXYLCARBAMATE

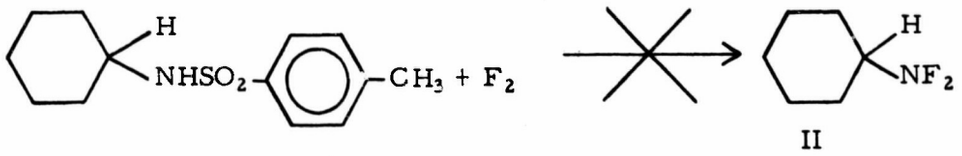
Exp. No.	Volume[a] (ml.)	Carbamate (moles)	F_2 (moles[c])	pH Control	$C_6H_{11}NF_2$ (moles)	Yield (%)
1	600	0.2	0.6	None	0.011[f]	5.5
2	600	0.1	0.4	None	0.010	10.3
3	600	0.2	0.5	$CaCO_3$[d]	0	0
4	600	0.2	0.5	Na_2CO_3[e]	0	0
5	1200	0.2[b]	1.0	None	0[g]	0

a. Proportions: 515 ml. H_2O, 85 ml. Freon-113, 0.5 g. "Deriphat 151-C" Emulsifier.
b. New batch, apparently less pure.
c. Diluted with N_2 to 20%.
d. Present during reaction 0.2 mole.
e. Added in increments to maintain pH > 3.
f. Approximate, corrected for gross impurity.
g. Ethyl N-fluoro-N-cyclohexylcarbamate was the principal product.

An effort was made to circumvent the possible difficulties arising from the insolubility of III in water, by fluorinating in a solvent system (Ref 9). Treatment of acetonitrile solutions of III with fluorine at 0-5° gave no isolable II. Considerable starting material was recovered, and a mixture of products exhibiting infrared absorptions indicative of fluorination on carbon was obtained.

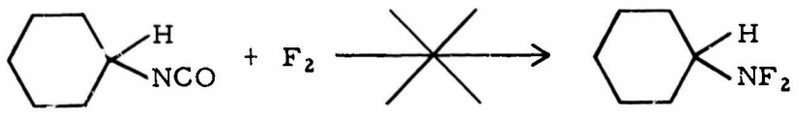
Several attempts were made to synthesize II by other routes. The fluorination of N-alkylsulfonamides has provided a route to alkyldifluoramines in some instances (Ref 10). N-cyclohexyl-p-toluenesulfonamide was prepared

by the reaction of p-toluenesulfonyl chloride with cyclohexylamine. The amide failed to react with 20% fluorine in aqueous suspension at 5-10°, and was recovered quantitatively (Ref 9).



II (3)

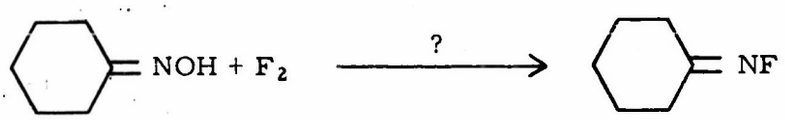
The reaction of cyclohexylisocyanate with 20% fluorine in Freon-113 solution produced a yellow liquid product (Ref 9). Its infrared spectrum indicated the presence of C-F bonds and no more than a trace of N-F. This approach was abandoned as a practical route to the desired intermediate.



II (4)

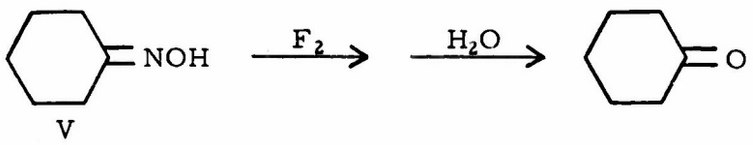
Another cyclohexylamine derivative, newly available commercially, is dicyclohexylcarbodiimide (V). When V was treated with fluorine in Freon solution, fluorine was slowly absorbed and a complex mixture of products was obtained. A very small amount of material boiling in the proper range for II (34°/24 mm.) was isolated by fractional distillation. The infrared spectrum of this fraction contained the expected absorptions for II, plus additional absorptions attributable to C=O and C-F bonds.

One other approach, not specificatlly directed toward the synthesis of cyclohexyldifluoramine, should be discussed here. Since the desired model compound is cyclohexylidenefluorimine (I), the fluorination of cyclohexane oxime (V) offers an intriguing possibility for the production of I in a single step. Such a direct route to other ketofluorimines would constitute a highly



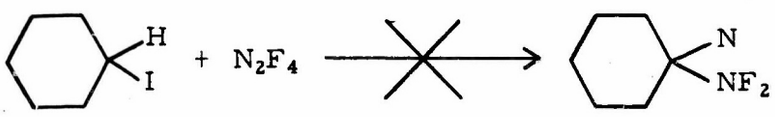
V I (5)

desirable adjunct to presently known nitrogen-fluorine chemistry. Accordingly, the fluorination of V was investigated in both aqueous suspension and acetonitrile solution. In both instances fluorine was slowly absorbed, but the only identifiable product isolated was cyclohexanone.



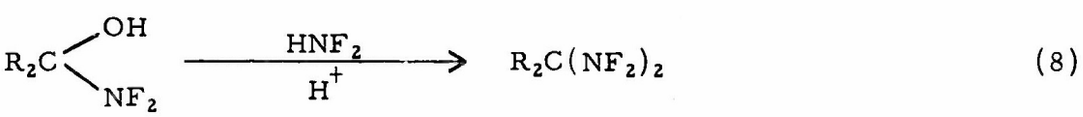
V (6)

Attempts to utilize NF_2 radicals from tetrafluorohydrazine in the synthesis of II were also unsuccessful (Ref 9). At 70°, N_2F_4 failed to react with cyclohexyl iodide in Freon-113 solution, and 82.5% of the iodide was recovered after 6 hr. Upon increasing the temperature to 110° and the reaction time to 15 hr., some decomposition occurred. Only 33% of the starting material could be recovered, but no N-F containing product was found.



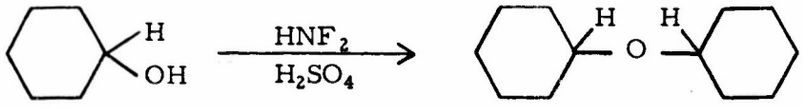
II (7)

In certain secondary alcohols having an electronegative substituent on the α-carbon (Ref 11, 12), the hydroxyl group has been replaced by NF_2 under strong acid conditions. One attempt has been made (Ref 9) to apply this procedure to the conversion of cyclohexanol to II. A Freon-113 solution of the



(8)

alcohol was added to difluoramine refluxing at 0 to 5° over fuming sulfuric acid. The oily product obtained was not characterized except to determine that it contained no N-F linkages; it was probably dicyclohexyl ether.



(?) (9)

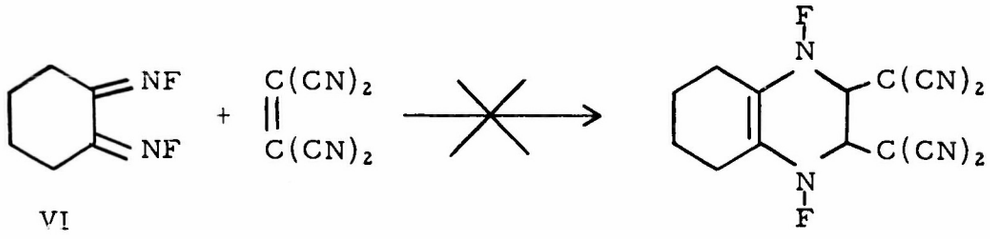
Despite the low yields obtained, the fluorination of ethyl N-cyclohexylcarbamate appears to be the best available route to cyclohexyldifluoramine.

2. Addition Reactions of Ketofluorimines

Since the addition reactions of the ketofluorimino grouping in perfluoroguanidine are important in the synthesis of new and useful propellant ingredients, efforts have been made to elucidate the chemistry of the ketofluorimino group, C=NF, and determine the scope of its usefulness.

The failure of 1,2-difluoriminocyclohexane (VI) to react with reagents appropriate for olefin or carbonyl groups has been documented in an earlier paper (Ref 13). Some supplementary observations on this point will be reported here.

One of the reactions examined in some detail was the Diels-Alder addition of typical dienophiles across the 1,4-positions of the conjugated unsaturated system. Neither maleic anhydride nor p-benzoquinone was found to react with VI under the usual Diels-Alder conditions. An additional attempt has been made using tetracyanoethylene, the most effective dienophile known. This too was unsuccessful. Since a Diels-Alder addition is generally believed (Ref 14)

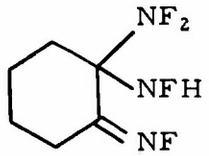


VI (10)

to be preceded by complex formation involving electron transfer from diene to dienophile, it is perhaps not too surprising that the difluorimine, with its strongly electronegative substitutents, does not behave as a typical diene. Following the hypothesis that it might be possible to effect a 1,4-addition by using an unsaturated reagent substituted with an electron-donating group, to

form a complex by the transfer of electrons in the opposite direction, we have attempted (Ref 8) the condensation of 1,2-difluoriminocyclohexane with a vinyl ether. Unfortunately, the results of this experiment were not conclusive. A cyclic product of the desired type was not obtained, but the fate of the fluorimine could not be determined. One of the products appeared to be a polymer of the vinyl ether.

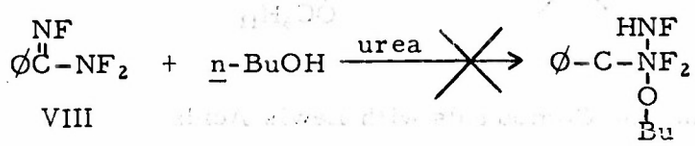
Yet another reaction system which was not included in the earlier series of experiments has now been examined (Ref 8). An indication of the degree to which the ketofluorimine function resembles the carbonyl function can be obtained by observing its behavior in the presence of difluoramine. Accordingly, 1,2-difluoriminocyclohexane was introduced into refluxing difluoramine in fuming sulfuric acid, under conditions which would lead to the conversion of a ketone to a gem-bis(difluoramine). Neither a geminal product nor the intermediate adduct (VII) was detected among the products. The difluorimine, on



VII

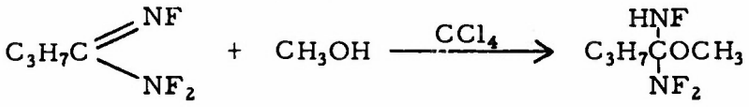
the other hand, was not recovered. This represents one more case where the presence of a second ketofluorimine group may be introducing unnecessary complications in the experimental results.

Simple (i.e., not electronegatively substituted) ketofluorimines are unreactive toward alcohols, as well as toward more effective active-hydrogen reagents. We therefore sought a new model compound for further investigation of this reaction. One attempt was made to carry out, with trifluorobenzamidine (VIII), (Ref 15, 16), an addition reaction analogous to that of PFG (equation 11). No reaction was found to occur and both compounds were



(11)

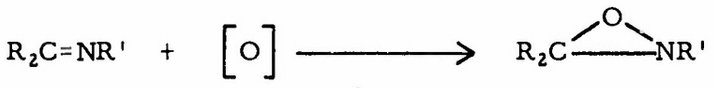
recovered (Ref 15). In contrast, an analogous addition reaction of methanol to N,N,N'-trifluorobutyramidine (equation 12) has been reported to occur (Ref 17).



(12)

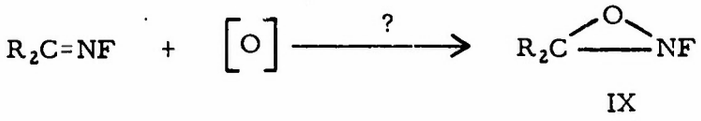
3. Peroxyacid Oxidation of Ketofluorimines

An interesting oxidation of alkylimines with peroxyacids to yield oxazirane derivatives (equation 13) has been reported (Ref 18, 19). Application of this



(13)

reaction to ketofluorimines would yield, according to equation 14, a new class

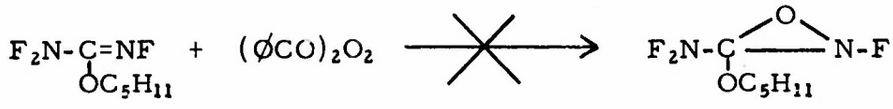


(14)

IX

of potentially energetic oxidizers, the N-fluorooxaziranes (IX). This area, which has not been explored, is currently under investigation in our laboratories.

In a preliminary experiment no reaction was found to occur between trifluoropentoxyformamidine and benzoyl peroxide in methylene chloride at 0^{o} or 25^{o}. Higher temperatures and other peroxides will be employed in future work.

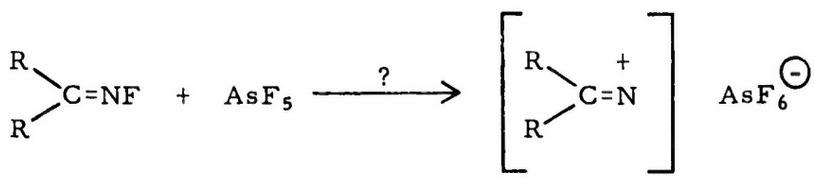


(15)

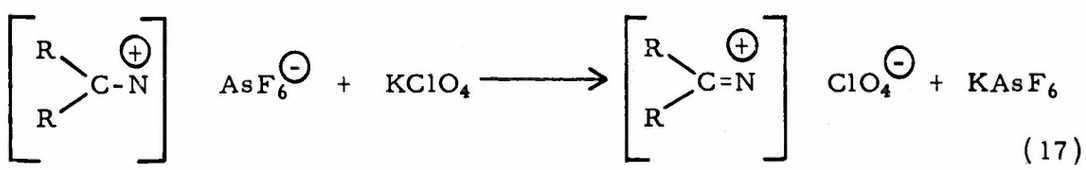
4. Reactions of Nitrogen-Fluorine Compounds with Lewis Acids

The ability of strong fluoride ion acceptors to abstract fluorine from inorganic compounds, such as N_2F_2 to give N_2F^+ salts (Ref 20, 21), has prompted

an investigation of the reaction of organic NF compounds with AsF_5. This could lead to new and potentially valuable oxidizer structures (equation 16, 17).

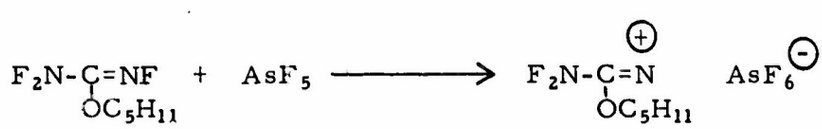


(16)



(17)

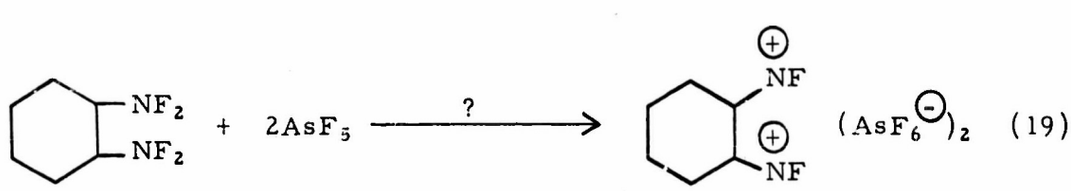
N,N,N'-Trifluoropentoxyformamidine (Ref 16) was found to react with AsF_5 in Freon-113 to yield an insoluble brown oil. Although the infrared



(18)

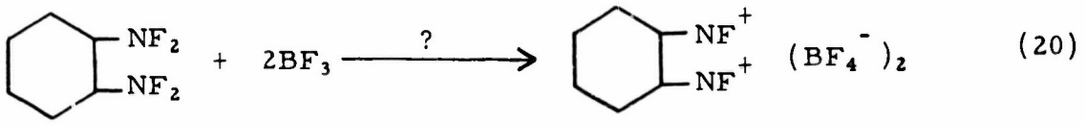
spectrum of this oil showed the characteristic AsF_6^- absorption, the remainder of the spectrum was not well defined, presumably because of decomposition.

A similar reaction was found to occur between AsF_5 and 1,2-bis(difluoramino)cyclohexane. In this instance, however, a white insoluble solid appeared first and subsequently decomposed.



(19)

Since BF_3 could be expected to react less vigorously than AsF_5 with N-F compounds, a preliminary experiment was conducted with BF_3 and 1,2-bis-(difluoramino)cyclohexane in the absence of a solvent. Although a solid product



(20)

was obtained, extensive decomposition occurred. When the reaction was repeated using methylene chloride as a solvent, a yellow tacky solid was obtained. This solid burned with a green flame indicating the presence of boron. It was storable for extended periods at refrigerator temperatures but decomposed slowly at ambient temperatures. The solid reacted vigorously with methanol, acetonitrile, and ethyl acetate, although it appeared to be stable in acetonitrile at temperatures below 0°. Further characterization of this interesting product is in progress.

B. EXPERIMENTAL

1. Attempted Reaction of Trifluoropentoxyformamidine with Benzoyl Peroxide

To 0.30 g. (1.6 mmoles) of trifluoropentoxyformamide in 25 ml. of CH_2Cl_2 at 0° was added 0.39 g. (1.6 mmoles) of benzoyl peroxide in 60 ml. of CH_2Cl_2. The reaction mixture was allowed to warm to room temperature and stirred overnight. It was then washed with Na_2CO_3 solution and the organic layer was dried over anhydrous Na_2CO_3. Evaporation of the CH_2Cl_2 yielded a pasty mass consisting of unreacted starting materials.

2. Reaction of Trifluoropentoxyformamidine with AsF_5

To a solution of 0.10 g. (0.54 mmole) of trifluoropentoxyformamidine in 5 ml. of Freon-113 at -196° was added 0.54 mmole of AsF_5. The reaction mixture was allowed to warm to room temperature. The insoluble brown oil which appeared was then separated. The infrared spectrum of the oil shows the characteristic absorption assigned to AsF_6^- but the remainder of the spectrum was not well defined.

3. Reaction of 1,2-Bis(difluoramino)cyclohexane with AsF_5

To a solution of 0.22 g. (1.18 mmoles) 1,2-bis(difluoramino)cyclohexane in 5 ml. of Freon-113 at -196° was added 2.20 mmoles of AsF_5. On warming slowly to room temperature a white precipitate appeared in the reaction mixture. The solid, however, decomposed yielding a dark brown pasty mass containing some unreacted 1,2-bis(difluoramino)cyclohexane.

4. Reaction of 1,2-Bis(difluoramino)cyclohexane with BF_3

To a solution of 0.52 g. (2.79 mmoles) of 1,2-bis(difluoramino)cyclohexane in 12 ml. of CH_2Cl_2 at -196° was added 2.79 mmoles of BF_3. The reaction mixture was warmed to 0°, stirred for 1.5 hr. and tested for unreacted BF_3. No evidence of unreacted BF_3 was obtained and an additional 2.79 mmoles of BF_3 was added as before; again no unreacted BF_3 was detected. A third addition of 1.10 mmoles of BF_3 was recovered. The reaction mixture was subsequently filtered and 0.50 g. of a yellow pasty solid was obtained.

IV. REFERENCES

1. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 076-S-62, Difluoramine Chemistry (U), 31 December 1962

2. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD-AOR-ATS-63, Advanced Oxidizer Research (U), Section I, "Difluoramine Chemistry," 31 December 1963

3. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD-5043-64F, Advanced Oxidizer Research (U), Section I, "Difluoramine Chemistry," 31 December 1964.

4. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5007-F-62, Synthesis of Compounds for Structure-Sensitivity Study (U), 14 November 1962

5. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD-AOR-ATS-63, Advanced Oxidizer Research (U), Section II, "Synthesis of Compounds for Structure-Sensitivity Study," 31 December 1963

6. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-64F, Advanced Oxidizer Research (U), Section II, "Synthesis of Compounds for Structure-Sensitivity Study," 31 December 1964

7. Aerojet-General Corporation, Report 0235-01-15, Research in Fluoro-Nitro Compounds (U), January 1963

8. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q1-65, Advanced Oxidizer Research (U), Section I, "Organic Difluoramine Chemistry," 31 March 1965

9. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q2-65, Advanced Oxidizer Research (U), Section I, "Organic Difluoramine Chemistry," 30 June 1965

10. Rohm and Haas Company, Report AF-14, Quarterly Progress Report on Air Force High Energy Solid Propellant Program (U), 3 August 1962

11. Rohm and Haas Company, Report P-59-10, Quarterly Progress Report on Synthetic Chemistry (U), Part 2, "Organic Chemistry," 21 October 1959

12. Stauffer Chemical Company, Report SCC-824-Q3, High Energy Storable Liquid Monopropellant Synthesis and Development (U), 15 April 1961

13. H. F. Smith, J. A. Castellano, and D. D. Perry, The Chemistry of Alkyldifluoramines. III. The Synthesis and Some Reactions of 1,4-Bis-(difluoramino)cyclohexene-2 and 1,2-Difluoriminocyclohexane, incorporated in Reference 3

14. M. C. Kloetzel, Organic Reactions, Vol. IV, R. Adams, Ed., John Wiley and Sons, Inc., New York, New York, 1948, p. 8

15. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q3-65, Advanced Oxidizer Research (U), Section I, "Organic Difluoramine Chemistry," 30 September 1965

16. H. F. Smith, J. J. Dvorak, and D. D. Perry, Some Elimination Reactions of Organic Difluoramines, Preprint D, above

17. Stanford Research Institute, Report TPR-9, Synthesis of High Energy Oxidizers (U), 31 January 1965

18. U. S. Patent 2,784,182, March 1957

19. W. D. Emmons, J. Am. Chem. Soc., 78, 6208 (1956)

20. D. Moy and A. R. Young II, ibid., 87, 1889 (1965)

21. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-64F, Advanced Oxidizer Research (U), Section VI, "Chemistry of Difluorodiazine and of Nitrosyl Fluoride," 31 December 1964

SECTION II

TASK 53

INORGANIC OXIDIZER SYNTHESIS

Section II

INORGANIC OXIDIZER SYNTHESIS

A. R. Young, II
S. I. Morrow
D. Moy

Contributors

R. Crooker B. Fagan
D. Kates

CONTENTS

		Page
I.	INTRODUCTION	1
II.	MANUSCRIPTS OF PAPERS FOR PUBLICATION	2
	A. The Reaction of Tetrafluorohydrazine with Arsenic Pentafluoride. Evidence for the Existence of $N_2F_3^+$ Salts	3
	B. On the Nature of Nitrogen (IV) Oxide Adducts with Group VA Pentafluorides	17
III.	APPENDIX	21
	A. Chemistry of N_2F_4	21
	1. Reaction of N_2F_4 with $HClO_4$ in HF	21
	2. Attempted Reaction of N_2F_4 with XeF_6 in HF	22
	B. Chemistry of $N_2F_3AsF_6$	22
	1. Hydrolysis	22
	2. Reaction of $N_2F_3AsF_6$ with NaF in IF_5	23
	3. Reactions of $N_2F_3AsF_6$ with ClO_4^- and SO_3F^-	24
	4. Attempted Preparation of $N_2F_3ClO_4$ in HF	24
	C. Chemistry of Oxygen Subfluorides	25
	1. Reaction of O_2AsF_6 with NO_2ClO_4	26
	2. Reaction of $CsClO_4$ with O_2AsF_6 in IF_5	27
	D. Reactions of Tetrafluorohalate Salts	27
	1. Preparation of Tetrafluorhalate Salts	28
	2. Reaction of $CsClF_4$ with N_2FAsF_6	30
	3. Reaction of $CsClF_4$ and O_2AsF_6	30
	4. Reaction of $CsBrF_4$ with O_2AsF_6	31
	E. Attempted Preparation of $NONFAsF_6$	31
IV.	REFERENCES	33

ILLUSTRATIONS

MANUSCRIPT A

Figure		Page
1.	Infrared Spectrum of Tetrafluorohydrazine-Arsenic Pentafluoride Adduct	10
2.	F^{19} N.M.R. Spectrum of Tetrafluorohydrazine-Arsenic Pentafluoride Adduct in Hydrazine Fluoride	10

TABLES

MANUSCRIPT A

Table		Page
I	Reaction of N_2F_4 with AsF_5	8
II	Diffraction Pattern of N_2F_4-AsF_5 Adduct	11

APPENDIX

I	Hydrolysis of $N_2F_3AsF_6$	23
II	Diffraction Patterns of Cesium Tetrafluororochlorate Samples	29

I. INTRODUCTION

The objective of this phase of the advanced oxidizer program is to discover routes to new inorganic oxidizers through a study of the chemistry of inorganic NF and OF compounds. During the past year our main concern has been with the characterization of N_2F_4-AsF_5 adducts. A great weight of evidence has been compiled in support of the hypothesis that such adducts are ionic and contain the interesting new oxidizer cation, $N_2F_3^+$. The manuscript of a paper on this phase of our study is presented in Section II and will be submitted for publication in the Journal of the American Chemical Society. A second paper on the nature of the reaction of AsF_5 with NO_2 is the result of studies undertaken in attempting to elucidate the solid state reaction of NO_2ClO_4 with O_2AsF_6.

Section III (Appendix) contains a description of work performed during the year which is either incomplete or not of sufficient general interest to be presented in the form of a publication.

II. MANUSCRIPTS OF PAPERS FOR PUBLICATION

A. The Reaction of Tetrafluorohydrazine with Arsenic Pentafluoride. Evidence for the Existence of $N_2F_3^+$ Salts

Prepared for submission to the Journal of the American Chemical Society

B. On the Constitution of Nitrogen (IV) Oxide Adducts with Group VA Pentafluorides

Correspondence prepared for submission to Inorganic Chemistry

[Contribution from the Reaction Motors
Division of Thiokol Chemical Corporation
Denville, N. J.]

Archie R. Young, II and David Moy (1)

(1) Present address: Esso Research and Engineering Co., Linden, New Jersey

Tetrafluorohydrazine reacts slowly with arsenic pentafluoride at -78° to yield a solid adduct of composition approaching $N_2F_4 \cdot 2AsF_5$. On warming to room temperature, the adduct gives off AsF_5 and its composition approaches $N_2F_4 \cdot AsF_5$. Since an identical product is obtained by the reaction of N_2F_4 with $H_2F^+ AsF_6^-$ in anhydrous HF, it was postulated that the adduct contains $N_2F_3^+$ ions. The infrared spectrum of the solid and the F^{19} n.m.r. spectrum of a solution of the solid in HF are consistent with the presence of $N_2F_3^+$ ions.

INTRODUCTION

The preparation of a stable adduct of tetrafluorohydrazine and antimony pentafluoride, $N_2F_4 \cdot 2SbF_5$, has recently been reported by Ruff.(2) Ruff suggests the

(2) John K. Ruff, J. Am. Chem. Soc., 87, 1140 (1965).

possibility that tetrafluorohydrazine acts as a fluoride ion donor in forming this adduct and, in support of this, indicates the presence of an absorption at 666 cm^{-1} in the infrared spectrum of the adduct which can be attributed to the hexafluoroantimonate ion. We have prepared a similar adduct of tetrafluorohydrazine with arsenic pentafluoride. The results of our studies of this material provide additional evidence that tetrafluorohydrazine acts as a fluoride ion donor.

In speculating about the nature of the N-F species present in the antimony pentafluoride adduct, Ruff [2] concludes that either the nitrogen-nitrogen bond is not broken or heterolytic cleavage occurs upon adduct formation, since the adduct is not paramagnetic. We conclude that F^{19} n.m.r. and infrared spectra of tetrafluorohydrazine adducts with arsenic pentafluoride and antimony pentafluoride are consistent with the presence of $N_2F_3^+$ cations.

EXPERIMENTAL

Materials. Tetrafluorohydrazine (95%) was obtained from Air Products Inc. The principal impurities are CF_4 and C_2F_6. Arsenic pentafluoride (>95%) was obtained from Peninsular ChemResearch (impurities are BF_3 and SiF_4). These two reagents were used without further purification. Anhydrous hydrogen fluoride was obtained from the Matheson Co. and treated with the tetrafluorohydrazine adduct prior to its use as a solvent.

Preparation of Adduct. Two methods of adduct preparation were employed. The principal one was the direct combination of N_2F_4 with liquid AsF_5 at -78°.

In a typical run, N_2F_4 and AsF_5 were successively expanded from storage tanks to an evacuated Monel flask of known volume to the desired pressure, and then condensed into a 95 ml. Pyrex pressure reactor (obtained from Fischer and Porter Co., Warminster, Pa.) at -196°. The reactor was fitted with a pressure gauge and could be isolated from the gas measuring system by a Monel valve. The valve was closed and the reactor warmed to -78° and maintained there for 18-24 hours. The valve was then opened to admit the residual gases to the gas measuring system. These gases (volatile at -78°) were collected in a Kel-F U-trap at -196°. After closing the reactor valve, the material in the U-trap was measured by allowing it to expand into a known volume at ambient temperature and recording the pressure. It was identified by infrared spectroscopy. The reactor was then allowed to warm to room temperature where additional volatile material was released. This was measured and then identified by infrared spectroscopy. The residual solid adduct was removed from the Pyrex reactor in a dry nitrogen atmosphere and stored in a Kel-F sample vial. (Storage for periods of 1-2 days in Pyrex at room temperature resulted in the conversion of the solid to $NOAsF_6$ and the liberation of decomposition gases containing trans-N_2F_2 and NF_3.) Samples of the solid adduct prepared in this manner were examined by infrared, X-ray, F^{19} n.m.r. (HF solution), and wet chemical analysis. The composition of the adduct corresponds to the formula, $N_2F_4 \cdot 1.33\ AsF_5$.

Anal. Calcd. for $N_2F_4 \cdot 1.33\ AsF_5$: N, 8.37; F, 61.31; As, 30.22

Found: N, 8.39; F, 62.15; As, 30.56.

In the second method of preparation, anhydrous HF was used as a solvent for the reaction. Arsenic pentafluoride (12.5 mmoles) was condensed at -196° into a 75 ml. Kel-F tube through a Teflon valve. Anhydrous liquid HF (25 ml.) was distilled into the tube, the valve was closed, and the tube was warmed to -78° in order to form a homogeneous solution of arsenic pentafluoride in the HF. The solution was then frozen and cooled to -196°, and 9.6 mmoles of N_2F_4 were condensed into the reaction tube. The valve was again closed and the reactor was warmed to -78° (slightly below the boiling point of N_2F_4), where it was maintained for 20 hours. The valve was opened and unreacted N_2F_4 was removed by pumping the volatiles in the reaction tube at -78° into a series of three Kel-F traps at -196°. In this manner, 1.3 mmoles N_2F_4 were recovered from the solution at -78°. The Dry Ice bath was removed from the reaction tube, and the HF was distilled into a Kel-F storage trap, leaving a white solid residue. The latter was pumped for 30 hours at room temperature and then removed from the reactor in a dry nitrogen box. The X-ray pattern and infrared spectrum of this solid were identical to those of products obtained by the reaction of N_2F_4 with AsF_5 in the absence of HF.

Infrared Spectrum. Infrared spectra were obtained by pressing powder samples between AgCl optical plates. The samples were examined from 2-20 μ with a Perkin-Elmer Model 521 grating spectrometer.

X-ray Diffraction Pattern. Powder diffraction patterns of adduct samples sealed under nitrogen in Pyrex capillaries, were photographed using CuKα radiation from a Ni filter.

F^{19} N.M.R.Spectrum. The F^{19} n.m.r. spectrum of the adduct was obtained on a Varian HR-60 spectrometer at ambient temperature using 25-30% solutions in anhydrous HF. Kel-F tubes were used as sample holders. The chemical shifts of the N-F fluorines were observed relative to the HF fluorine and then referred to $CFCl_3$ by a substitution technique.

RESULTS AND DISCUSSION

Stoichiometry. P-V-T measurements were made on initial reagents and volatile materials recovered at -78° and at ambient temperatures after approximately 20 hours reaction time. These enabled us to estimate the compositions of adducts stable at low temperatures (-78° → -45°) and at ambient, respectively. These data are presented in Table I. They indicate compositions approaching $N_2F_4 \cdot 2AsF_5$ at -78° and $N_2F_4 \cdot AsF_5$ at ambient. The overall reaction may be approximately represented by equation 1. It should be noted (runs 6 and 7, Table I) that the tetrafluorohydrazine was completely complexed at -78° only in those runs in which arsenic pentafluoride was in large excess (at least 4:1).

$$N_2F_4 + 2AsF_5 \xrightarrow{-78^\circ} N_2F_4 \cdot 2AsF_5 \xrightarrow{\text{ambient}} N_2F_4 \cdot AsF_5 + AsF_5 \qquad (1)$$

TABLE I
REACTION OF N_2F_4 with AsF_5

Run No.	Initial N_2F_4 (mmoles)	Initial AsF_5 (mmoles)	Recovered at -78° N_2F_4 (mmoles)	Recovered at -78° AsF_5 (mmoles)	AsF_5/N_2F_4 Consumed at -78°	Recovered at Ambient N_2F_4 (mmoles)	Recovered at Ambient AsF_5 (mmoles)	AsF_5/N_2F_4 Consumed at Ambient
1	12.0	4.8	9.6	0.0	2.0	---	---	---
2	6.5	13.1	1.5	0.0	2.6	---	---	---
3	11.0	11.0	5.4	0.0	2.0	0.0	5.1	1.1
4	10.5	21.0	0.9	0.0	2.2	0.0	6.9	1.5
5	13.8	27.6	2.9	0.0	2.5	0.0	10.6	1.6
6	5.9	23.6	0.0	10.4	2.3	0.0	7.8	0.92
7	1.4	5.6	0.0	2.4	2.3	0.0	1.6	1.14
				Ave.	2.3 ± 0.2			Ave. 1.3 ± 0.2

Complete elemental analysis on one sample of the adduct stable at ambient temperatures gave a composition, $N_2F_4 \cdot 1.33\ AsF_5$.

Infrared Spectrum. The infrared spectrum (Figure 1) of the solid adduct shows a very strong, broad absorption centered at 695 cm^{-1}, which suggests the presence of hexafluoroarsenate ion.[3] In addition, there are three strong

(3) R. Peacock and D. W. A. Sharp, J. Chem. Soc., 2762 (1959).

peaks at 922 cm^{-1}, 1110 cm^{-1}, and 1295 cm^{-1} which are comparable to absorptions reported by Ruff[2] for the adduct of tetrafluorohydrazine with antimony pentafluoride. There is also a sharp peak of medium intensity at 1500 cm^{-1}.

F^{19}N.M.R. Spectrum. The F^{19} nuclear magnetic resonance spectrum of an HF solution of the adduct is shown in Figure 2. There are three very broad absorptions at -122 Ø, -146 Ø, and -180 Ø, respectively. These are comparable to the bands reported for $N_2F_4 \cdot 2SbF_5$ in liquid sulfur dioxide.[2] The areas under the peaks are virtually identical (1.09:1.09:1.04).

X-ray Diffraction Pattern. The X-ray diffraction pattern of the adduct was indexed on a cubic unit cell, $a_0 = 7.60 \pm 0.3$ Å (Table II). The pattern serves to distinguish the adduct from another possible reaction product of N_2F_4 with arsenic pentafluoride namely, N_2FAsF_6.[4] Similarly, the

(4) D. Moy and A. R. Young, II, J. Am. Chem. Soc., 87, 1889 (1965).

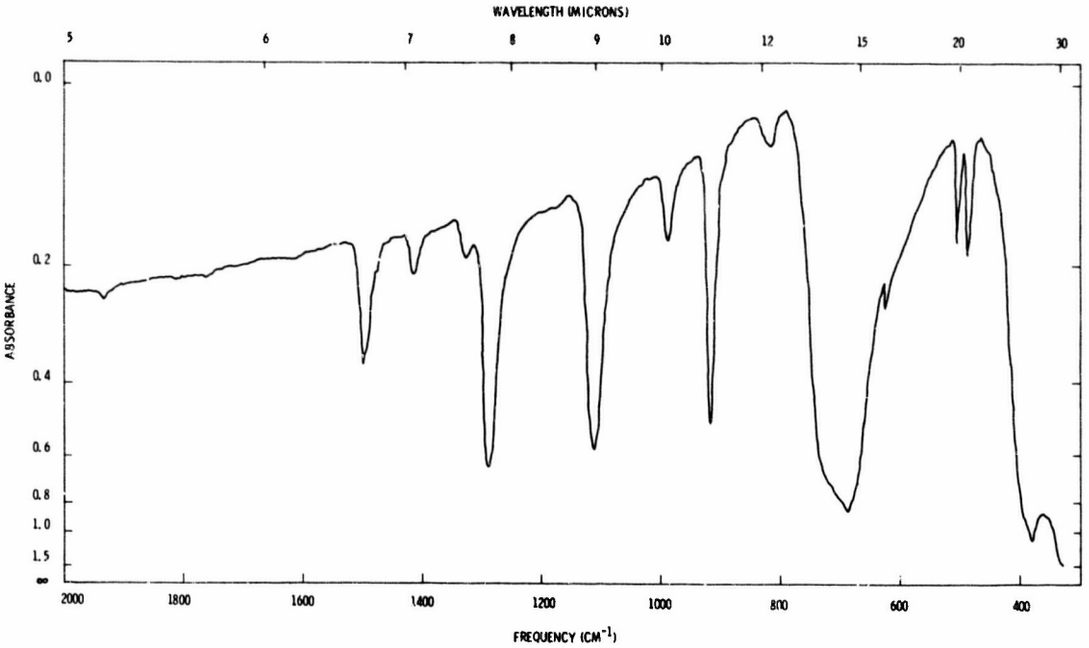


Figure 1. Infrared Spectrum of Tetrafluorohydrazine-Arsenic Pentafluoride Adduct

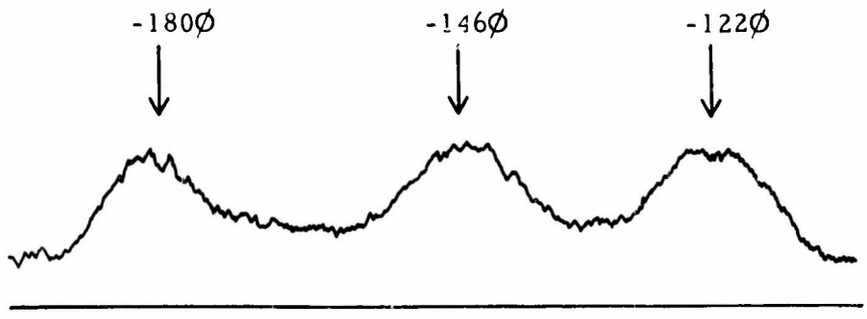


Figure 2. F^{19} N. M. R. Spectrum of Tetrafluorohydrazine-Arsenic Pentafluoride Adduct in Hydrazine Fluoride

pattern clearly shows no indication of the presence of oxygen-containing impurities such as NO_2AsF_6 [4] and $NOAsF_6$. [5]

(5) A. R. Young, II, T. Hirata, and S. I. Morrow, J. Am. Chem. Soc., 86, 20 (1964).

TABLE II

DIFFRACTION PATTERN OF N_2F_4-AsF_5 ADDUCT

Cubic Unit Cell
$a_0 = 7.60 \pm 0.03$ Å

$N_2F_4 \cdot AsF_5$

h, k, l	d, Å (calcd.)	d, Å (obs.)	I/I_0 (rel.)
110	5.37	5.37	40
111	4.39	4.46	100
200	3.80	3.75	1
210	3.40	3.41	80
220	2.69	2.69	15
221, 300	2.53	2.51	1
311	2.29	2.30	12
222	2.19	2.19	1
321	2.03	2.06	8
322	1.84	1.86	2
330	1.79	1.80	5
331	1.74	1.72	2
420	1.70	1.70	2
421	1.66	1.67	3
332	1.62	1.60	1
520	1.41	1.40	2

Constitution of the Adduct. The observation of a strong absorption at 695 cm^{-1} in the infrared spectrum of the adduct (Figure 1) initiated speculation that the adduct might be ionic. Since this absorption has the shape and frequency

characteristic of the ν_3 fundamental of the octahedral AsF_6^- ion, it seemed very likely that the adduct formed as a result of fluoride ion transfer from N_2F_4 (or $\cdot NF_2$) to AsF_5. It was believed that a critical test of this hypothesis would be to determine whether the adduct could be prepared in anhydrous hydrogen fluoride. Hyman et al. [6] report that below a concentration

(6) H. Hyman, L. Quarterman, M. Kilpatrick, and J. Katz, Abstracts, 136th Metting Amer. Chem. Soc., Atlantic City, 1959.

of 20 mole %, antimony pentafluoride is completely converted to SbF_6^- in anhydrous HF. Similarly Clifford [7], as evidence that PF_5 and SbF_5 are

(7) A. Clifford and S. Kongpricha, J. Inorg. and Nucl. Chem., 20, 147, (1961).

strong acids in HF, reports that PF_6^- and SbF_6^- do not undergo solvolysis ($MF_6^- + HF \not\rightleftharpoons HF_2^- + MF_5$). Since the acid strength of AsF_5 lies between that of PF_5 and SbF_5 in HF [8], it seems reasonable to assume that in dilute

(8) A. Clifford, Ph. D. Thesis, Univ. of Delaware, 1949.

solution in anhydrous HF (~1 mole %), AsF_5 is completely converted to AsF_6^- (equation 2). It is unlikely that N_2F_4 could displace fluoride ions from AsF_6^- species to form molecular adducts, $N_2F_4 \cdot (AsF_5)_x$.

$$AsF_5 + 2HF \xrightarrow[HF]{-78^\circ} H_2F^+ + AsF_6^- \qquad (2)$$

When we added N_2F_4 to a dilute solution of hexafluoroarsenic acid, 86% of the reagent was consumed after 20 hours at -78°C. Furthermore the solid product of the reaction of N_2F_4 with $HAsF_6$ gave the same infrared spectrum and X-ray pattern as the product of the reaction of N_2F_4 with AsF_5. We therefore became convinced that the adduct was of ionic constitution and were led to examine its infrared and F^{19} n.m.r. spectra for evidence of the structure of the cationic N-F species present.

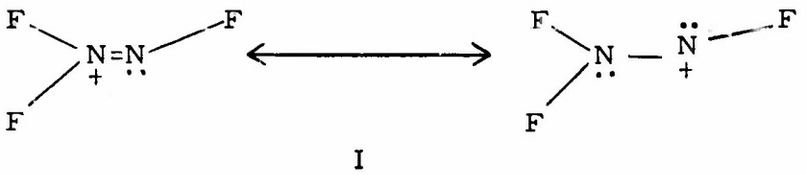
There are three possible NF cations obtainable from N_2F_4 or NF_2 by a single fluoride ion transfer to AsF_5 or $H_2F^+AsF_6^-$, namely, $N_2F_3^+$, $\dot{N}F^+$ and NF_2^+ (equations 3, 4, 5). Of these, only an $N_2F_3^+$ cation in which there is restricted rotation about the N-N bond (Structure I) is consistent with the

$$2HF + N_2F_3^+ \xleftarrow{H_2F^+} N_2F_4 \xrightarrow{AsF_5} N_2F_3^+ + AsF_6^- \qquad (3)$$

$$HF + HNF_2 + NF_2^+ \xleftarrow{H_2F^+} N_2F_4 \xrightarrow{AsF_5} NF_2^+ + AsF_6^- + 1/2\ N_2F_2 \qquad (4)$$

$$2HF + \dot{N}F^+ \xleftarrow{H_2F^+} \dot{N}F_2 \xrightarrow{AsF_5} \dot{N}F^+ + AsF_6^- \qquad (5)$$

observed infrared spectrum of the solid (Figure 1) and the F^{19} n.m.r. spectrum of its HF solution (Figure 2).



I

The F^{19} n.m.r. spectrum indicates the presence of three nonequivalent N-F fluorines, as one would predict for an $N_2F_3^+$ species having restricted rotation, in which one of the "NF_2" fluorines is cis and the other trans with respect to the "NF" fluorine. The broadness of the peaks (Figure 2) is also reasonable, since the spectrum of I would be expected to exhibit peak splittings due to cis, trans, and gem fluorine-fluorine couplings, on which the effect of fluorine-nitrogen coupling would also be superimposed, thus giving three broad, unresolvable sets of lines.

Similarly, the infrared spectrum of the solid (Figure 1) is readily interpreted in terms of Structure I. There are three strong, sharp absorptions at 922 cm^{-1}, 1100 cm^{-1}, and 1295 cm^{-1}, respectively, that may reasonably be assigned to NF stretching vibrations of an $N_2F_3^+$ cation. In addition, the medium intensity peak at 1500 cm^{-1} is located in the region of N=N stretching vibrations. For example, in N_2F_2 [9], the N=N stretching frequency has been assigned at 1524 cm^{-1}, and in $CF_3N{=}NCF_3$ [10], at 1570 cm^{-1}.

---

(9) R. H. Sanborn, J. Chem. Phys., 33, 1855 (1960).

(10) J. Jander and R. N. Hazeldine, J. Chem. Soc., 919 (1954).

Finally, we should reiterate the fact that the data are in excellent agreement with the infrared and F^{19} n.m.r. data reported by Ruff [2] for

the "NF" species in $N_2F_4 \cdot 2SbF_5$. It seems very probable, therefore, that both the antimony pentafluoride and arsenic pentafluoride adducts are examples of $N_2F_3^+$ salts.

ACKNOWLEDGEMENT

This work was supported by the Advanced Research Projects Agency and monitored by the Office of Naval Research under Contract NOnr 4364(00).

On the Nature of Nitrogen (IV) Oxide Adducts with Group VA Pentafluorides[1]

---

(1) This work was supported by the Advanced Research Projects Agency and monitored by the Office of Naval Research under Contract NOnr 4364(00).

Sir:

Various investigators[2, 3, 4] have reported the existence of adducts of

---

(2) E. Aynsley, et al., Chem. and Ind. (London), 1117 (1951).

(3) M. Schmeisser, et al., Angew. Chem., 69, 780 (1957).

(4) E. Muetterties, et al., J. Inorg. Nucl. Chem., 16, 52 (1960).

---

nitrogen (IV) oxides that may be represented by the formula, $NO_2 \cdot MF_5$, where M is P, As, or Sb. Although the formula implies that these are 1:1 molecular adducts, no data have been presented in support of such a characterization.

We recently prepared "$NO_2 \cdot AsF_5$"[2, 3] in order to obtain a reference X-ray diffraction pattern. We found that the powder diffraction pattern of the adduct was virtually identical to that of $NO^+ AsF_6^-$[5], and that the few weak lines not belonging

---

(5) A. Young, T. Hirata, S. Morrow, J. Am. Chem. Soc., 86, 20 (1964).

---

to $NO^+ AsF_6^-$ could readily be attributed to the presence of $NO_2^+ AsF_6^-$[6].

(6) D. Moy and A. Young, J. Am. Chem. Soc., 87, 1889 (1965).

This led us to examine the infrared spectra of "$NO_2 \cdot AsF_5$" samples. These were obtained on powder samples pressed between silver chloride windows, as well as on fluorocarbon oil mulls. The spectra show absorptions in the range from 2350 cm^{-1} to 2370 cm^{-1} where NO^+ and NO_2^+ have been reported to absorb [7],

(7) J. Evans et al., Inorg. Chem., 3, 857 (1964).

and a strong, broad absorption at 695-700 cm^{-1}. The latter absorption has been assigned [8] to the ν_3 fundamental of the AsF_6^- ion.

(8) R. Peacock and D. Sharp, J. Chem. Soc., 2762 (1959).

These observations definitely point to an ionic constitution for the "adduct". In addition, they raise some doubt about the elemental composition implicit in the formula, $NO_2 \cdot AsF_6$. Perhaps the reaction of nitrogen(IV) oxide with arsenic(V) fluoride parallels that of nitrogen(IV)oxide with boron(III)fluoride, reported by Evans [7] (equation 1)

$$5N_2O_4 + 12AsF_5 \longrightarrow 5NOAsF_6 + 5NO_2AsF_6 + As_2O_5 \qquad (1)$$

However, reactions such as those shown in equations 2 and 3 cannot be ruled out,

$$N_2O_4 + 2AsF_5 \longrightarrow NO_2AsF_4 + NO_2AsF_6 \qquad (2)$$

$$NONO_3 + NO_2AsF_{4,6} \longrightarrow NOAsF_{4,6} + [NO_2NO_3] \qquad (3)$$

$$[NO_2NO_3] \longrightarrow NONO_3 + 1/2\ O_2$$

since the X-ray and infrared spectra of AsF_4^- may be indistinguishable from those of corresponding AsF_6^-. That is, AsF_4^- ions may form octahedra by sharing corners [8]. Careful analytical studies of the reaction products of nitrogen (IV) oxide with AsF_5, PF_5 and SbF_5 are in progress at this laboratory. Results of these, together with the results of further spectral studies (particularly Raman spectra)[7], should resolve the questions of the compositions and constitutions of nitrogen (IV) oxide-Group VA pentafluoride reaction products.

Chemistry Department
Reaction Motors Division
Thiokol Chemical Corporation
Denville, New Jersey

Scott I. Morrow
Archie R. Young, II

III. APPENDIX

A. CHEMISTRY OF N_2F_4

1. Reaction of N_2F_4 with $HClO_4$ in HF

In the paper entitled The Reaction of N_2F_4 with AsF_5. Evidence for the Existence of $N_2F_3^+$ Salts (Section I), we point out that $N_2F_3AsF_6$ can be prepared by the reaction of N_2F_4 with H_2FAsF_6 (equation 1) as well as by reaction with AsF_5.

$$N_2F_4 + H_2F^+ + AsF_6^- \longrightarrow N_2F_3^+ + AsF_6^- + 2HF \qquad (1)$$

It should be possible, therefore, to prepare $N_2F_3^+$ salts of any strong acid in hydrogen fluoride. Unfortunately, the only verified cases of substances behaving as strong acids in HF are those that act as fluoride ion acceptors (PF_5, AsF_5, and SbF_5) rather than acids in the Bronsted sense (proton donors). For example, nitric acid (Ref 1), behaves as a base in HF (equation 2).

$$2HF + HNO_3 \longrightarrow H_2NO_3^+ + HF_2^- \qquad (2)$$

In 1954 Brauer and Distler (Ref 2) refuted an earlier claim (1930) by Hantzsch (Ref 3) that one could isolate a stable solid, $H_2F^+ ClO_4^-$, from solutions of $HClO_4$ in HF. However, Brauer's study did not address itself to the question of whether $H_2F^+ClO_4^-$ exists in solution. We decided, therefore, to examine the reaction of N_2F_4 with a solution of anhydrous perchloric acid in HF in the hope that perchloric acid would be acidic enough to protonate HF (equation 3). Under the same conditions as were used to prepare $N_2F_3AsF_6$ in HF (20 hours at -78°), all of the N_2F_4 was recovered (Ref 4).

$$N_2F_4 + H_2F^+ + ClO_4^- \xrightarrow{HF} 2HF + N_2F_3^+ + ClO_4^- \qquad (3)$$

It would appear then, that $HClO_4$ ionizes in HF (equation 4) in a manner analogous to HNO_3.

$$2HF + HClO_4 \longrightarrow H_2ClO_4^+ + HF_2^- \quad (4)$$

2. Attempted Reaction of N_2F_4 with XeF_6 in HF

XeF_6 gives conducting solutions in HF (Ref 5) and has been reported to form XeF_7^- and $XeF_8^=$ salts (Ref 6) with alkali metal fluorides. We thought it likely, therefore, that an ionic adduct of N_2F_4 ai l XeF_6 could be synthesized in HF (equation 5).

$$N_2F_4 + H_2F^+ + XeF_7^- \xrightarrow{?} N_2F_3^+ + XeF_7^- + 2HF \quad (5)$$

Unfortunately, the Kel-F reactor in which we attempted this reaction developed a massive leak, and further evaluation of the feasibility of this reaction is therefore required.

B. CHEMISTRY OF $N_2F_3AsF_6$

1. Hydrolysis

Initially, the hydrolysis of $N_2F_3AsF_6$ (Ref 7) was examined as a method of analysis, but the reaction proved to be too complex for this purpose. Under mild conditions (ca. 0^o), the primary gaseous hydrolysis product was nitric oxide (equation 6), in which the oxidation state of nitrogen is the same as that in $N_2F_3^+$.

$$N_2F_3AsF_6 + 2H_2O \longrightarrow 2NO + 3HF + HAsF_6 \quad (6)$$

However, in the absence of a bath to absorb the heat of reaction, a high percentage of nitrogen was observed in the product gases. In both cases significant quantities of nitrogen fluorides were produced. The results of two typical hydrolysis runs are presented in Table I. In the case of sample 1, no effort was made to cool the hydrolysis flask and roughly 50% of the gaseous products was nitrogen.

TABLE I

HYDROLYSIS OF $N_2F_3AsF_6$

Sample No.	Sample Weight (g.)	Gas Evolved (mmoles)	Composition (mole %)
1	0.254	0.940	N_2(46.8), NO(44.2), NF_3(7.9), N_2F_2(1.1)
2	0.200	0.893	N_2(3.7), NO(68.4), NF_3(11.6), N_2F_2(16.3)

It is clear from the "typical" results shown in Table I that the reaction of $N_2F_3AsF_6$ with water is a good deal more complex than indicated by equation 6. Unfortunately, time did not permit more than a cursory study of this reaction.

2. Reaction of $N_2F_3AsF_6$ with NaF in IF_5

The reaction of sodium fluoride with $N_2F_3AsF_6$ should proceed as shown in equation 7, assuming that $N_2F_3IF_6$ is unstable. When the reaction was attempted

$$NaIF_6 + N_2F_3AsF_6 \xrightarrow{IF_5} NaAsF_6 + \left[N_2F_3IF_6\right] \longrightarrow N_2F_4 + IF_5 \qquad (7)$$

N_2F_4 was indeed obtained as the predominant gaseous product (Ref 7), but there were also significant amounts of NF_3 (28%) and trans- N_2F_2(4%) present. It is felt that this result at least qualitatively supports the structure we have proposed for the $N_2F_3^+$ ion (Ref 8). This structure could undergo attack by fluoride ion on either nitrogen atom (equations 8 and 9).

$$IF_6^- \longrightarrow IF_5 + F^- \qquad (8)$$

$$\left[\begin{array}{c} F \\ F \end{array}\!\!>\!\overset{+}{N}\!=\!N\!-\!F \right] \longleftrightarrow \left[F\!-\!N\!-\!\overset{+}{N}\!<\!\begin{array}{c} F \\ F \end{array}\right] \xrightarrow{F^-} N_2F_4,\ NF_3,\ \cdot NF \qquad (9)$$

However, the ratio of NF_3 to N_2F_2 in the products should be 2/1 rather than 7/1, as observed. As in the case of the water reaction, we feel that a more careful study of the reaction of $N_2F_3AsF_6$ with NaF is required.

3. Reactions of $N_2F_3AsF_6$ with ClO_4^- and SO_3F^-

We have reported (Ref 9) that the N_2F^+ cation reacts rapidly with oxygen-containing anions to yield N_2O. In order to test the stability of the $N_2F_3^+$ in the presence of such anions, roughly equimolar quantities of $N_2F_3AsF_6$ and the potassium salts of ClO_4^- and SO_3F^-, respectively, were mixed under dry nitrogen in an agate mortar. In the case of the $KClO_4$-$N_2F_3AsF_6$ mixture, there was no visible sign of reaction during 10-15 minutes of vigorous mixing and grinding. An infrared spectrum of the resulting mixture showed strong absorptions due to $N_2F_3^+$, as well as ClO_4^- and AsF_6^-. The X-ray pattern was hopelessly complex as expected for a four component mixture. The KSO_3F-$N_2F_3AsF_6$ composition reacted visibly when treated in the same manner. The infrared spectrum of the residual mixture showed no N-F absorptions and the X-ray pattern indicated virtually pure $KAsF_6$.

It was concluded that $N_2F_3^+$ is stable in the presence of ClO_4^-. Therefore the existence of a stable perchlorate of the $N_2F_3^+$ is a definite possibility.

4. Attempted Preparation of $N_2F_3ClO_4$ in HF

a. From $AgClO_4$

An HF solution containing 0.7 mmole $N_2F_3ClO_4$ was added to an equimolar quantity of dry $AgClO_4$. No gas evolution or color change was noted. The solution was separated from undissolved material and stripped of solvent. The soluble residue was predominantly $N_2F_3AsF_6$, although a positive test for ClO_4^- (methylene blue) was obtained on a hydrolysate of the soluble fraction. The insoluble fraction was predominantly $AgClO_4$, containing a small amount of $AgAsF_6$. It was concluded that insufficient time had been allowed for the exchange reaction to proceed to any appreciable extent. $AgClO_4$ is apparently only sparingly soluble in anhydrous HF.

b. From $KClO_4$

Unlike the case of $AgClO_4$, an equimolar mixture (1 mmole each) of $KClO_4$ and $N_2F_3ClO_4$ produced an immediate color (yellow-brown) when HF was

added at -80°. Approximately 0.8 mmole N_2F_4 was recovered from the mixture between -80° and room temperature. A small amount of Cl_2 was also detected in the gaseous products by mass spectroscopy. Upon removal of all volatiles the solid residue was examined by infrared, showing AsF_6^- and ClO_4^- absorptions. Although the results of this experiment were not as clear cut as one would desire, it appears that the predominant reaction is the solvolysis of ClO_4^- (equation 10) producing fluoride ions. For this reason,

$$ClO_4^- + HF \rightleftharpoons HClO_4 + F^- \qquad (10)$$

$$N_2F_3^+ + F^- \longrightarrow N_2F_4 \qquad (11)$$

most of the $N_2F_3^+$ was recovered as N_2F_4 (equation 11). It is likely that a similar result was not obtained in the case of $AgClO_4$ because of its low solubility in HF. It would appear then, that we must examine a different solvent (perhaps IF_5 or SO_2) as a reaction medium for the combination of $N_2F_3^+$ with perchlorate ions.

C. CHEMISTRY OF OXYGEN SUBFLUORIDES

Previous studies of the chemistry of dioxygen difluoride demonstrated that it may act as a source of the dioxygenyl (O_2^+) cation (Ref 10 and 11). The synthesis of a salt of this cation containing an anion, such as ClO_4^-, NO_3^-, or ClF_4^-, subsequently became one of the primary goals of this program. Unfortunately, the synthesis of dioxygenyl salts directly from O_2F_2 is apparently limited to such complex fluoroanions as BF_4^-, PF_6^- AsF_6^-, and SbF_6^-. The ease of formation of salts of these anions may be understood in terms of their large negative heats of formation. The BF_4^- ion, which forms one of the least stable dioxygenyl salts, has a heat of formation of -406 kcal/mole, for example. This may be compared with values for ClO_4^-, NO_3^-, and ClF_4^-, of -80.5, -81, and -156 kcal/mole, respectively (Ref 12, 13, 14).

By making reasonable assumptions about the magnitudes of the lattice energies of dioxygenyl salts (Ref 7) the following estimates of heats of formation were obtained:

$\Delta H_f\ O_2\ BF_4 = -273$ kcal/mole $\qquad \Delta H_f\ O_2\ ClO_4 = +6.4$ kcal/mole

$\Delta H_f\ O_2\ ClF_4 = -21$ kcal/mole $\qquad \Delta H_f\ O_2\ NO_3 = +44$ kcal/mole

The small endothermic (+6.4 kcal/mole) heat of formation estimated for the hypothetical salt, O_2ClO_4, in view of the relatively large endothermic heat of formation of known binary compounds of chlorine and oxygen, seemed sufficient reason to seek synthetic routes to this oxidizer. Accordingly, we began an investigation (Ref 6) of the synthesis of O_2ClO_4 by the solid state reaction of O_2AsF_6 with NO_2ClO_4 (equation 12). Studies of this reaction, as

$$O_2AsF_6 + NO_2ClO_4 \dashrightarrow NO_2AsF_6 + O_2ClO_4 \qquad (12)$$

well as the related reaction of $CsClO_4$ with O_2AsF_6 in IF_5, were continued during the current program.

1. Reaction of O_2AsF_6 with NO_2ClO_4

The initial investigation of this reaction during the preceding year resulted in the following observations:

(1). Substantial amounts of O_2 and ClO_3F were given off during the reaction.

(2). The color of the reactants changed from white to yellow or orange-brown during mixing in a vacuum.

(3). Debye-Scherrer X-ray powder photographs of the products contained several major lines that did not appear to belong to NO_2AsF_6, the predominant phase present.

We continued this investigation to determine whether O_2ClO_4 could be identified in the solid products. The hoped-for reaction was:

$$O_2AsF_6 + NO_2ClO_4 \longrightarrow O_2ClO_4 + NO_2AsF_6 \qquad (13)$$

Due to the fact that substantial amounts of ClO_3F were evolved during the reaction, it was reasoned that a species, such as an AsF_5 adduct or AsF_3, must have also been formed. We were led to speculate that the following reactions might be involved:

$$NO_2ClO_4 + O_2AsF_6 \longrightarrow NO_2AsF_6 + \left[O_2ClO_4\right] \longrightarrow ClO_3 + 3/2\ O_2 \qquad (14)$$

$$NO_2AsF_6 + ClO_3 \xrightarrow{?} ClO_3F + NO_2 \cdot AsF_5 \qquad (15)$$

Upon further investigation it was established that two previously unexplained major "d" lines in the product, 4.91 and 4.53 Å, actually belong to the pattern of NO_2AsF_6. As is described in section I, we made a determined effort to prepare Aynsley's $NO_2 \cdot AsF_5$ adduct (Ref 15), in order to obtain its X-ray powder pattern. In the course of this work, we came to the conclusion, on the basis of X-ray and I.R. data, that Aynsley's adduct was actually a mixture of $NOAsF_6$ and NO_2AsF_6. It is possible, however, that a compound, such as $NO_2^+ AsF_4^-$, could be present without affecting the X-ray pattern significantly. The AsF_4^- could become octahedral in a lattice structure by means of fluorine bridge bonding. Equation 15 might, therefore, better be written as shown in equation 16.

$$NO_2AsF_6 + 2 \cdot ClO_3 \longrightarrow 2ClO_3F + NO_2AsF_4 \qquad (16)$$

We concluded that a brownish oil, formed during the solid state reaction, was in all probability Cl_2O_6 (m.p. 3° , b.p. 200°), formed by coupling of two ClO_3 radicals (equation 14). Cl_2O_6 normally decomposes slowly at room temperature, releasing Cl_2, ClO_2, and O_2, all of which were observed products. It was apparent as a result of the study of the NO_2ClO_4-O_2AsF_6 system that the ionic solid, O_2ClO_4, could not be isolated at ambient temperatures.

2. Reaction of $CsClO_4$ with O_2AsF_6 in IF_5

Concurrently with studies of the solid state reaction of O_2AsF_6 with NO_2ClO_4, we investigated the metathetical formation of O_2ClO_4 in solution. We had observed (Ref 7) that O_2AsF_6 may be recovered from solution in IF_5 at room temperature and, consequently, hoped that a perchlorate could be found that would react with O_2AsF_6 in IF_5 to produce an insoluble hexafluoroarsenate salt. $CsClO_4$ was selected for an initial test of the feasibility of this approach. Although some difficulty was encountered in duplicating our earlier preparations of a stable O_2AsF_6-IF_5 solution, we were finally successful in carrying out a reaction of O_2AsF_6 with $CsClO_4$ in IF_5. The results were quite similar to those obtained with NO_2ClO_4 in the solid state. Oxygen was rapidly liberated from solution, and an orange oil (Cl_2O_6) was observed to form and float to the surface of the IF_5.

D. REACTIONS OF TETRAFLUOROHALATE SALTS

Theoretically, it should be possible to prepare new oxidizers from tetrafluorohalate salts by metathetical reactions such as the following.

$$CsClF_4 + O_2AsF_6 \longrightarrow O_2ClF_4 + CsAsF_6 \qquad (17)$$

$$CsClF_4 + N_2FAsF_6 \longrightarrow N_2FClF_4 + CsAsF_6 \qquad (18)$$

Lattice energy calculations gave a heat of formation value of -21 kcal/mole (Ref 8) for the hypothetical salt O_2ClF_4. In view of this encouraging result, we investigated the preparation of this salt and the hypothetical salt, N_2FClF_4, from $CsClF_4$. We also attempted to prepare O_2BrF_4 from $CsBrF_4$.

1. Preparation of Tetrafluorhalate Salts

Our first concern was to prepare $CsClF_4$ for use as a reagent and we found that it is quite difficult to prepare this material in a high degree of purity. According to the method of Whitney et al. (equation 19, Ref 15), CsF and ClF_3 were heated in a stainless steel bomb with shaking at 100°. It became evident that a Monel or nickel bomb was required to avoid contamination of the

$$CsF + ClF_3 \longrightarrow CsClF_4 \qquad (19)$$

product with heavy metal fluorides. Furthermore, the ClF_3 used in the preparation had to be purified before use by passing it over a bed of NaF pellets to remove HF. $CsClF_4$ is a highly active and corrosive material and in the presence of excess ClF_3, readily dissolves metals such as stainless steel. It has a pink to lavender color, exhibits strong oxidizer activity with acidic KI, and reacts violently with water.

Despite many attempts, we were unable to obtain a satisfactory infrared spectrum of $CsClF_4$ as a smear on AgCl plates. X-ray powder data on two of the products are given in Table I. Chemical analysis of one sample indicated the presence of 25-30% unreacted CsF, which may have had considerable influence on the negative results we obtained in trying to prepare O_2ClF_4 and N_2FClF_4. For example, CsF could react to displace the weaker bases, O_2F and N_2F_2 from their AsF_6^- salts (equation 20), although one would not expect this reaction to proceed extensively at reduced or ambient temperatures.

$$CsF + O_2AsF_6(N_2FAsF_6) \longrightarrow O_2F(N_2F_2) + CsAsF_6 \qquad (20)$$

TABLE II

DIFFRACTION PATTERNS OF CESIUM TETRAFLUOROCHLORATE SAMPLES

Sample 1 (Note 1)		Sample 2 (Note 2)	
d	I/I	d	I/I
3.626	75	3.62	50
3.456	100*	3.58	15
3.342	50	3.45	100*
3.175	50*	3.40	10
3.032	25*	3.32	15
2.759	13	3.19	10
2.682	5	3.13	10*
2.597	13	3.03	15*
2.576	5	2.67	15
2.329	37	2.59	5
2.252	13	2.49	10
		2.465	10
		2.44	5
		2.33	20
		2.30	< 3
		2.26	< 3
		2.20	5
		2.14	3
		2.08	3
		2.06	10
		1.92	3
		1.88	3
		1.77	10

* Part of the intensity of these reflections is probably due to unreacted CsF.

1. Emmission spectroscopy showed that this product was badly contaminated with heavy metals from the stainless steel bomb.

2. Emissions spectroscopy indicated this sample prepared in a Monel bomb contained only traces of heavy metal impurities.

2. Reaction of $CsClF_4$ with N_2FAsF_6

Considerable effort was made to synthesize the hypothetical salt, N_2FClF_4, by mixing N_2FAsF_6 and $CsClF_4$ in an evacuated apparatus. Most of the experiments were carried out in a metal-Kel-F reactor, which was attached to directly to a mass spectrometer. Gases from the reactor were monitored before and after mixing the reagents at -78°, and while warming the mixture room temperature.

Results of the experiments could not be interpreted unambiguously. In several experiments a band of orange material was detected on the wall of the reactor when the reagents were mixed at -78°. At the same time, the mass spectrometer showed the presence of Cl_2 (65%), O_2 (28%), CO_2 (3%), and ClO_3F (4%). The total quantity of gases given off at -78° was, however, negligible. The reactor was then warmed to 0°, whereupon a large amount of gas, composed primarily of N_2 and O_2, was evolved. As the temperature of the reactor was raised to ambient, in some runs the mass spectrometer detected N_2F^+ and NF^+ peaks, as well as HF and N_2O. X-ray analysis of the solid products from two different runs showed the presence of $CsAsF_6$ and a material that had a significant number of unidentified "d" spacings.

At first glance it would appear that the presence of O_2 and N_2 in the gases from these reactions was probably due to a leak in the apparatus. In one experiment, however, it was conclusively proved that there was no leak by permitting the system to stand for a week before opening it. The pressure in the system did not increase during this period. The appearance of O_2^+ and ClO_x^+ fragments could have been due to wall reactions of F_2 or ClF_3 occurring in the mass spectrometer.

It is evident from these ambiguous results that more work must be done on the preparation of a pure ClF_4^- salt for use as a reagent in the attempted preparation of N_2FClF_4.

3. Reaction of $CsClF_4$ and O_2AsF_6

A series of experiments was carried out in a metal-Kel-F reactor to determine whether O_2ClF_4 could be made by the solid state reaction of $CsClF_4$ with O_2AsF_6. In most cases, the reactor was attached to a mass spectrometer and the off-gases were analyzed immediately. The reaction was examined from -78° to ambient temperature. It was found that when the two materials were mixed in vacuo, some oxygen was evolved, even at -78°.

When the system was allowed to stand overnight at -78°, Cl_2 and O_2 were liberated in a ratio of 3:1. As the system was warmed to 0°, the amount of gases given off increased to the point where it was obvious that major decomposition of the reagents was occurring. As in the case of N_2FClF_4, it would be advisable to reinvestigate the preparation of O_2ClF_4 when we have obtained a very pure ClF_4^- reagent.

4. Reaction of $CsBrF_4$ with O_2AsF_6

The reaction of O_2AsF_6 with $CsBrF_4$ could lead to the formation of O_2BrF_4, as shown in equation 21. This transformation was attempted at room

$$O_2AsF_6 + CsBrF_4 \xrightarrow{?} O_2BrF_4 + CsAsF_6 \qquad (21)$$

temperature in a glass apparatus and in the absence of solvent. Shortly after mixing the two solid reagents, a color change occurred, giving evidence of the occurrence of a reaction. The gases evolved during a 45-minute mixing period were F_2, O_2, SiF_4, and Br_2. The presence of SiF_4 and Br_2 suggests that either O_2BrF_4, or its decomposition products, reacts with glass at room temperature. The solid residue was identified as predominantly $CsAsF_6$ by X-ray analysis.

E. ATTEMPTED PREPARATION OF $NONFAsF_6$

Discovery of the low temperature-stable compound $NONF_2$ by Colburn and Johnson (Ref 17 and 18) led us to speculate on the possible preparation of $NONF^+AsF_6^-$ by reaction of $NONF_2$ with AsF_5. Consequently, we initiated a study of the reaction shown in equation 22:

$$NONF_2 + AsF_5 \longrightarrow \left[NONF^+\right]\left[AsF_6^-\right] \qquad (22)$$

We first examined the reaction of $NONF_2$ and AsF_5 over the temperature range of -162 to -65°. When the freshly generated $NONF_2$ and AsF_5 were allowed to come in contact with each other at -163° in a glass apparatus, the color of the resultant solid was much darker than that of either reagent by itself at this temperature. The dark color gradually changed to brick red near -90°. At -80°, the solid had become pure white. Although the X-ray pattern of the product showed it was composed primarily of $NOAsF_6$, some weaker, unexplained lines were also present.

Since $NONF_2$ can be stabilized at higher temperatures by the use of pressure, we examined the reaction in a 5.2 cc thick-walled glass ampoule. The quantities of $NONF_2$ and AsF_5 were adjusted so as to keep the pressure at about 15 atmospheres. After sealing off the capillary, it was kept at -115 to -95° for about 7 hours, during which time the color of the contents remained a purplish red. The temperature was then raised to -78° and kept there for one week. After the gases were removed from the reactor at -78°, the color of the solid was brick red, with whitish spots. This red color persisted as the temperature was raised, but finally changed to white at room temperature. X-ray analysis showed that the product isolated at room temperature was $NOAsF_6$. We plan to continue this study, using low temperature infrared spectroscopy to follow the course of the reaction.

IV. REFERENCES

1. L. Audrieth and J. Kleinberg, Non-aqueous Solvents, John Wiley and Sons, New York (1953).

2. G. Brauer and H. Distler, Z. Anorg. u.Allgem. Chemie, 275, 157 (1954).

3. A. Hantzsch, Ber. 63, 1789 (1930).

4. Thiokol Chemical Corporation, Reaction Motors Division, Advanced Oxidizer Research, Report RMD-Q3-65, 1 July 1965 to 30 1965.

5. Noble Gas Compounds, H. Hyman, Ed., Univ. of Chicago Press (1963).

6. H. Hyman, Science, 145, 773 (1964).

7. Thiokol Chemical Corporation, Reaction Motors Division, Advanced Oxidizer Research, Report RMD-Q1-65, 1 January 1965 to 31 March 1965.

8. Ibid., Report RMD-Q2-65, 1 April 1965 to 30 June 1965.

9. D. Moy and A. R. Young, II, J. Am. Chem. Soc., 87, 1889 (1965).

10. I. Solomon,et al., Inorg. Chem., 3, 457 (1964).

11. A. R. Young, II, T. Hirata, S. Morrow, J. Am. Chem. Soc., 86, 20 (1964).

12. H. Halliwell and S. Nyburg, J. Chem. Soc., 4603 (1960).

13. T. Waddington, Adv. in Inorg. Chem. and Radiochem., VI, Academic Press, New York (1959), p. 204.

14. E. Whitney,et al., J. Am. Chem. Soc., 86, 4340 (1964).

15. E. Aynsley,et al., Chem. and Ind., 1117, 1951.

16. E. Whitney, et al.,J. Am. Chem. Soc., 86, 2583 (1964).

17. C. Colburn and F. Johnson, Inorg. Chem., 1, 715 (1962).

18. F. Johnson and C. Colburn, J. Am. Chem. Soc., 83, 3043 (1961).

SECTION III

TASK 55

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

Thiokol
REACTION MOTORS DIVISION

SECTION III

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

C. J. Grelecki
and
W. J. Cruice

CONTENTS

		Page
I	INTRODUCTION	2
II	MANUSCRIPT OF PAPER FOR PUBLICATION	3
	The Thermal Decomposition Reactions of Hydroxylammonium Perchlorate and Hydroxylammonium Chloride	4
III	APPENDIX	30
	A Introduction	30
	B Notes on the Thermal Decomposition of Hydrazinium Diperchlorate	30
	C Comparative Stabilities of Hydroxylammonium Perchlorate and Hydrazinium Diperchlorate at 70°C	33
	D Oxidation of Ammonium Perchlorate with Anhydrous Perchloric Acid	33

ILLUSTRATIONS

MANUSCRIPT

Figure		Page
1	Sickle Gauge Apparatus	9
2	Destructive Distillation Apparatus	11
3	Rate of Decomposition of Hydroxylammonium Chloride as a Function of Temperature	12
4	Temperature Coefficients for the Thermal Decomposition of Hydroxylammonium Chloride	15
5	Rate of Decomposition of Hydroxylammonium Perchlorate as a Function of Temperature	18
6	Arrhenius Plot: Coefficient of Linear Portion of Curve vs $\frac{1}{T^{\circ}K} \times 10^3$, Hydroxylammonium Perchlorate	19

APPENDIX

1	Thermal Decomposition of Hydrazinium Diperchlorate at 140°C. Under Varied Sample Size and Geometry	31

TABLES

MANUSCRIPT

		Page
I	Mass Spectrometric Analyses of Residual Vapors, $HONH_3Cl$ Decomposition	13
II	Values of K_{HONH_2} for Two Reaction Paths, $HONH_3Cl$ Decomposition	16
III	Coefficients of Linear Portion of Curve as a Function of Temperature-Hydroxylammonium Perchlorate Decomposition	20
IV	Stoichiometric Relationships, $HONH_3ClO_4$ Decomposition	21
V	Relative Reaction Rates for $HONH_3ClO_4$ Under Continuous Pumping-Disproportionation and Oxidation at 180°C	23

I. INTRODUCTION

A number of advanced solid oxidizers are in various stages of research or development and complete characterization of their properties is required before their role in solid propellants can be determined. One of the most important properties is the thermal stability of the oxidizer because this limits the storage life and operational temperature limits of the propellant. In addition, propellant combustion characteristics are often intimately related to the decomposition of the oxidizer.

High-energy oxidizers of current interest include hydrazinium diperchlorate, nitronium perchlorate, and hydroxylammonium perchlorate. From an overall point of view, including performance and handling, hydrazinium diperchlorate appears to be the most feasible new oxidizer. As an example, because of its increased energy and density, substitution of hydrazinium diperchlorate for ammonium perchlorate can increase the range of the current Minuteman missile by 70 percent. Nitronium perchlorate gives slightly higher performance under analogous conditions; however, the problems associated with its stability and handling are more severe. In general, the higher the energy the more unstable the oxidizer, and the future high energy oxidizers can be expected to be accompanied by thermal stability problems. An understanding of the mechanism by which oxidizers decompose is important in defining conditions under which they can be prepared and handled. In addition, such an understanding could conceivably result in modifications which may improve their properties.

Thiokol Chemical Corporation, Reaction Motors Division, had conducted a quantitative study of the thermal decomposition of hydrazinium diperchlorate in 1962-1963. Many of the features of its thermal decomposition have been defined, but a considerable amount of additional work is required to adequately describe its reaction mechanism.

The objective of Task 55 was to study the kinetics of the thermal decomposition reactions of high-energy solid oxidizers in order to obtain a thorough understanding of the mechanism by which they decompose. A thorough examination of the literature, correlation of existing information, and supplementary

laboratory work to render as complete an understanding as possible of the field have been the three primary approaches employed.

Although hydrazinium diperchlorate is the most likely candidate for use as an improvement over presently used oxidizers, the reaction is so complex that this study began with perchloric acid, hydrazinium monoperchlorate, and hydroxylammonium perchlorate, inasmuch as these compounds were expected to undergo more elementary processes, relatively speaking. The information obtained, on the acid and the monoperchlorate in particular, as well as the experimental techniques developed, could then be used as a firm base for elucidation of the decomposition mechanism for the diperchlorate.

Experimental work on anhydrous perchloric acid and hydrazinium monoperchlorate was presented in the form of articles for submission to the Journal of Physical Chemistry in RMD 5043-64F; portions of the work on the monoperchlorate, combined with previously performed work on hydrazinium diperchlorate, were presented in a paper at the 149th National Convention of the American Chemical Society (1). This paper has been accepted for publication in a forthcoming volume of Advances in Chemistry. Results of a literature survey on perchlorate oxidizers performed at the beginning of the program were included in RMD 5043-64F.

In this report results of experimental work on hydroxylammonium perchlorate and hydroxylammonium chloride are presented in the form of an article for submission to the Journal of Physical Chemistry. Results of exploratory studies on hydrazinium diperchlorate and comparative stability studies on hydrazinium diperchlorate and hydroxylammonium perchlorate are presented in an appendix.

---

(1) C. J. Grelecki and W. Cruice, "The Thermal Reactions of Some Advanced Solid Oxidizers," American Chemical Society, Division of Fuel Chemistry, Vol. 9, No. 1, Preprints of Papers Presented at Detroit, Michigan, April 4-9, 1965. (Symposium on Advanced Propellant Chemistry in Cooperation with AIAA.)

II. MANUSCRIPT OF PAPER FOR PUBLICATION

The Thermal Decomposition Reactions fo Hydroxylammonium Perchlorate and Hydroxylammonium Chloride.

Prepared for submission to the Journal of Physical Chemistry.

[Contribution from the Chemistry Department, Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey]

The Thermal Decomposition Reactions of Hydroxylammonium Perchlorate and Hydroxylammonium Chloride (1)

Chester J. Grelecki and William J. Cruice

---

(1) This work was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research, under Contract NOnr 4364(00).

INTRODUCTION

Hydroxylammonium perchlorate was first reported by J. H. Robson, III in a U. S. patent in 1956 (2,3). The preparation according to the reaction

---

(2) J. H. Robson, III, Chem Abstr 51, P3146G (1957), U S Patent 2,768,874, 30 October 1956.

(3) Dow Chemical Co. Annual Report AR-4Q-60, Contract AF33(616)-6149, 30 January 1961.

$$2HOHN_3Cl + Ba(ClO_4)_2 \xrightarrow{EtOH} 2HONH_3ClO_4 + \underline{\underline{BaCl_2}}$$

is described, and the melting point, drop weight sensitivity value, and initial decomposition temperature are given as 87.5-90 °C., 15 cm. and 120 °C., respectively.

More recently Zinov'ev and Zakharova issued a paper [4] claiming to have carried out preliminary studies on the compound in 1954. A preparation

(4) A. A. Zinov'ev and I. A. Zakharova, Zhur. Neorg Khim, 5, 775 (1960).

from hydroxylammonium sulfate and barium perchlorate in aqueous solution is described, as well as an unsuccessful attempt to prepare the material from perchloric acid dihydrate and hydroxylammonium chloride. Qualitative solubility studies in organic solvents are described, and a rather approximate guess at the stoichiometry of reaction is made on the basis of comparison of DTA experiments with others performed on ammonium perchlorate. The product gases, evolving first at 180°C., are said to be neutral and mainly oxygen, leading to the proposition of the expression

$$HONH_3ClO_4 \longrightarrow NH_4ClO_4 + 0.5\ O_2$$

Rocchiccioli in 1961 [5] reported that the salt is ionic in character on the basis of an infrared spectrophotometric study in which characteristic

(5) C. Rocchiccioli, Compt Rend. 253, 838 (1961).

$HONH_3^+$ and ClO_4^- bands were obtained.

Research on hydroxylammonium perchlorate carried out at Thiokol's Elkton Division [6] in 1963 indicated that the method of preparation patentedby Robson is best. Vapor pressure studies by the Langmuir technique

---

(6) C. W. Vriesen, et al., Thiokol Chemical Corp., Elkton Division, Final Report G154-63 on Contract NOw 63-0284-c, 30 September 1963.

---

and the Knudsen technique indicate vapor pressures ranging from 10^{-2} μ, to 10 μ. Hg. between 95° and 160°C., with a variance of a factor of 10 between the two techniques. The heats of vaporization from the two techniques are 32.3 and 33.5 kcal/mole, in excellent agreement. Mass spectrometer studies of the thermal decomposition have shown "no significant decomposition" at 150° C. for one hour. At temperatures in excess of 200°C., a complex mixture of gases was detected above the sample; the simple decomposition to ammonium perchlorate and oxygen reported by Zinov'ev and Zakharova was not detected, but ammonium perchlorate was found as a residue of DTA studies. A rather good set of DTA thermograms is reproduced, each showing a melting endotherm, solvent impurity endotherm, and a deflagration exotherm. The precise location of these peaks depends on the heating rate and, to some slight extent, the concentration of impurity; at 4.5°C./min. the impurity peak occurs at 65°C., the melting peak at 88°C., and the deflagration from 190° to 206°C.

This work was performed to further elucidate the kinetic parameters, stoichiometry and decomposition mechanism of hydroxylammonium perchlorate as part of a general study of the thermal decomposition of ammoniacal salts of perchloric acid. A brief study of the thermal decomposition of hydroxylammonium chloride was performed to obtain information on the thermal reactions of the hydroxylamine moiety independent of external oxidizing agents. Results of these experiments have been included here as they are of considerable interest and importance in understanding the reactions of the perchlorate.

EXPERIMENTAL

Preparation

The preparation of hydroxylammonium perchlorate used in these experiments was performed by a method based on that patented by Robson in 1956. Stoichiometric amounts of barium perchlorate and hydroxylammonium chloride in absolute ethanol react when mixed according to the expression

$$Ba(ClO_4)_2 + 2HONH_3Cl \xrightarrow{EtOH} 2HONH_3ClO_4 + \underline{BaCl_2}$$

The insoluble barium chloride is removed by filtration and the filtrate taken to dryness in a flash evaporator. Excess reactants are removed by dissolving the dry product in dry diethyl ether and filtering; this process is repeated until no insoluble materials remain. To this solution, anhydrous benzene is added to precipitate the hydroxylammonium perchlorate, which is then dried

at ambient temperature and stored in a sealed vessel in a dry box. Samples are taken as required, dried for one hour at 70°C., and assayed immediately before use. Typical assays are in the 99.3-99.6% pure range (by potentiometric titration with ~0.05 N sodium hydroxide); no sample is used that does not assay over 99.0% pure. The hydroxylammonium chloride used in this work was Matheson, Coleman and Bell, ACS Reagent Grade, assayed here at 98.9% by titration with sodium hydroxide solution.

Apparatus

The system employed in most of these experiments is the modified all-glass Sickle gauge as illustrated in Figure 1. The apparatus consists of a pressure sensitive glass diaphragm, a spherical reactor, a glass seal-off arm for introduction of sample, and a glass break-seal for sampling gaseous products into the Bendix mass spectrometer. Sample sizes varied from 0.090 g. to 0.150 g. for the perchlorate, but were kept at 0.110 g. for the chloride. The spherical sample chamber was 16-18 cc. in most cases. The mass balance runs on the perchlorate were performed in Sickle gauges of 68-71 cc. volume containing over 0.500 g. of sample to facilitate analytical procedures. After loading the gauge in a dry box, the assembly is evacuated to 0.005 mm. Hg. for 30 min. at ambient temperature and sealed. Runs were performed in thermostated baths of silicone oil controlled to ±0.05°C. and checked with ASTM thermometers. The gauge assembly acts as a null device

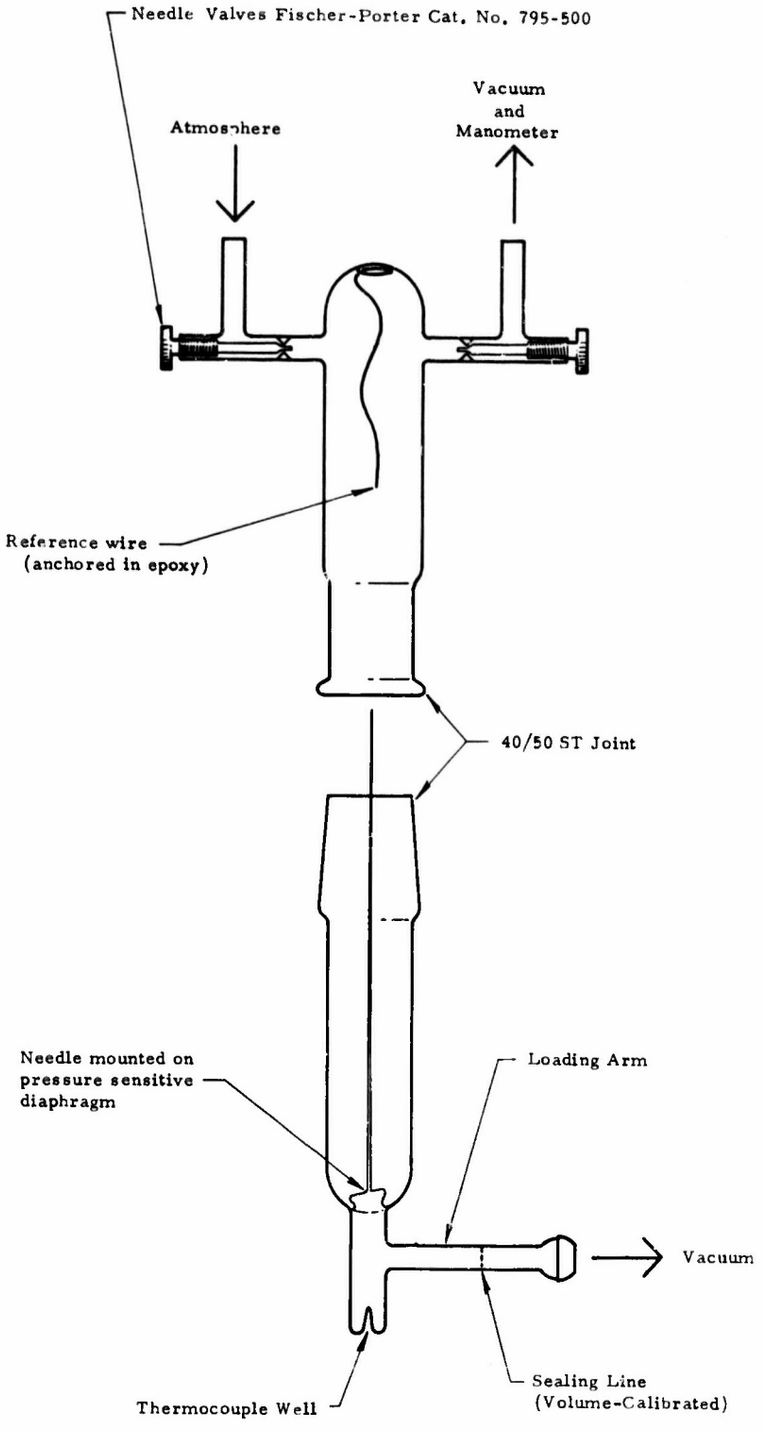


Figure 1. Sickle Gauge Apparatus

and is sensitive to pressure differentials of less than 0.5 mm. Hg. between the reactor and reference sides of the diaphragm. The reference side is backpressured to restore the null point and the pressure measured with a mercury manometer.

Other experiments were performed in which the sample was subjected to high temperature under constant vacuum (destructive distillation). The apparatus is illustrated in Figure 2. The volume of the reaction vessel is generally of the order of 150 cc. and the sample size is generally about 1.30 g. Procedures are as above excepting the seal-off step.

RESULTS

Hydroxylammonium Chloride

Pressure versus time data were collected at temperatures from 130° to 160°C. For convenience in comparing different systems, all data were reduced to n/N_o versus time, where n = moles of gaseous product (PV/RT) and N_o = moles of sample initially present. Average plots at various temperatures are shown in Figure 3. Mass spectrometric analyses of the vapors uncondensed at ambient temperature are tabulated in Table I. Perhaps the most significant point illustrated is the gradual reversal of the ratio N_2O/N_2; the N_2O is the predominant product at 130°C., whereas at 160°C., the N_2 is strongly predominant. The trend is apparent despite the anomalous results at 150°C.

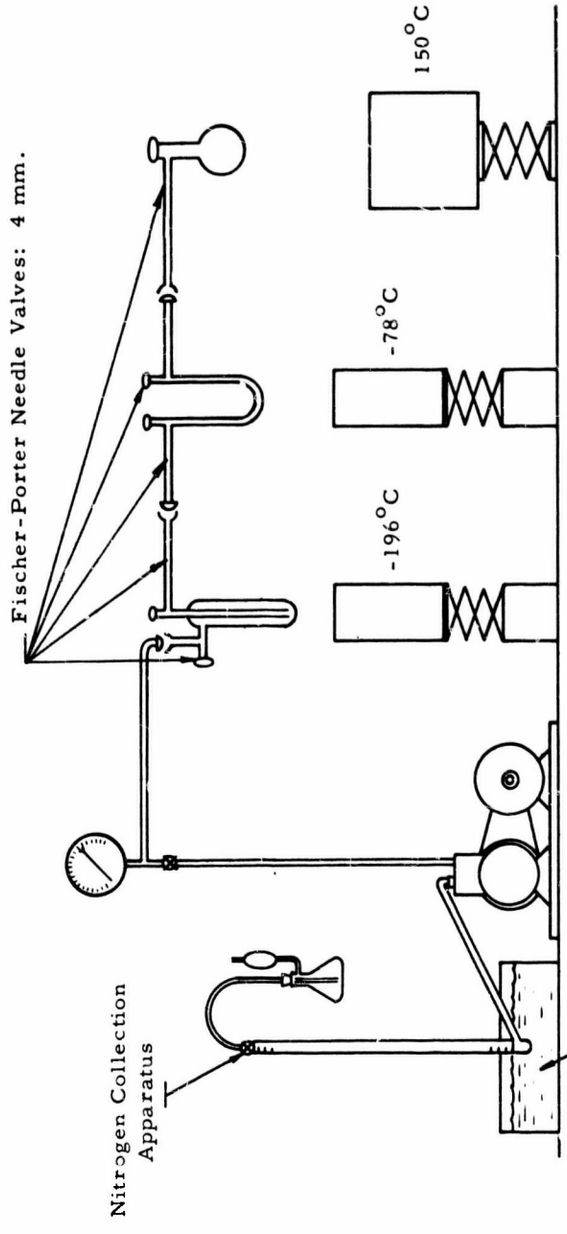


Figure 2. Destructive Distillation Apparatus

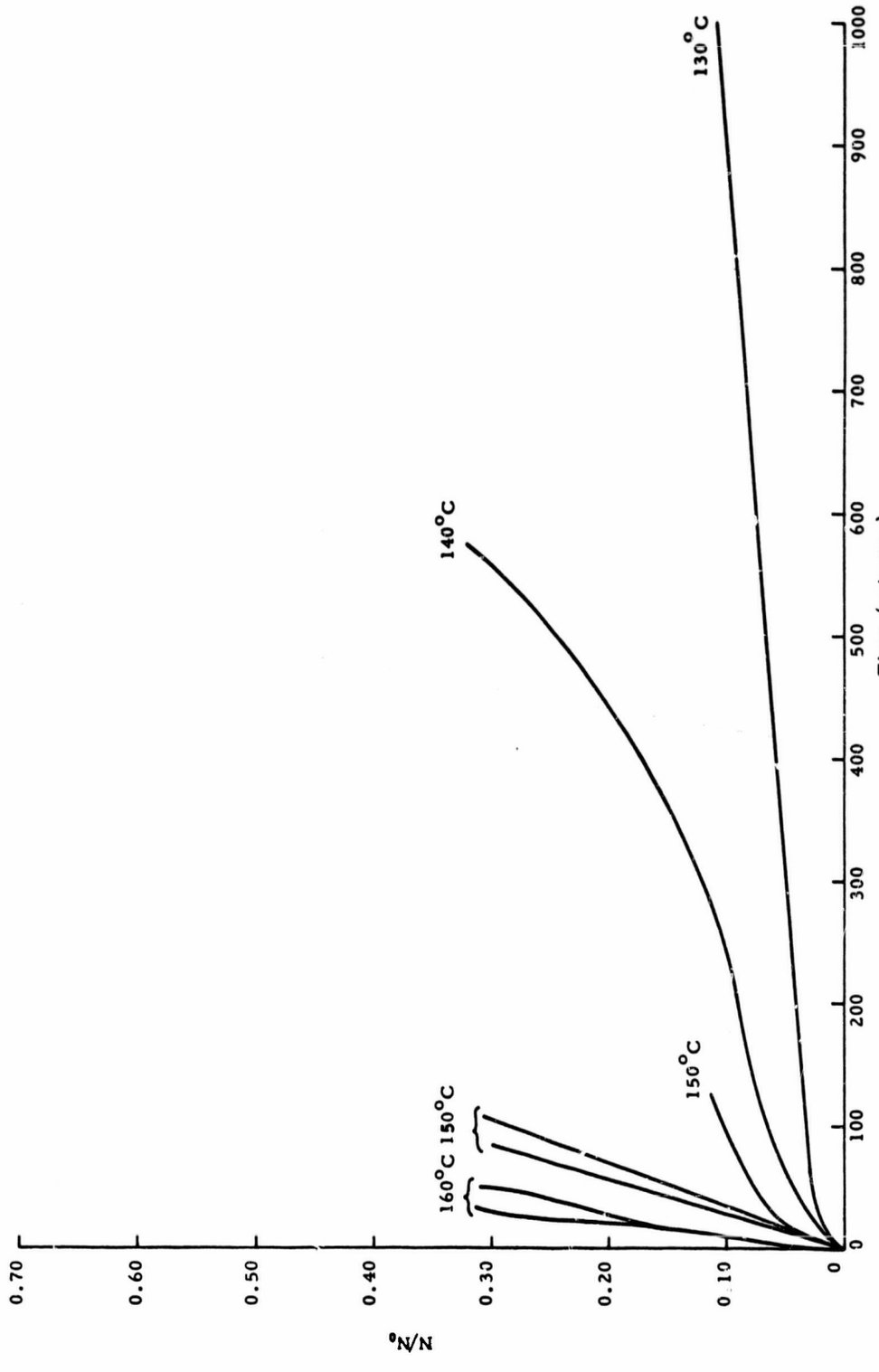


Figure 3. Rate of Decomposition of Hydroxylammonium Chloride as a Function of Temperature

TABLE I

MASS SPECTROMETRIC ANALYSES OF
RESIDUAL VAPORS, $HONH_3Cl$ DECOMPOSITION

Temp. (°C)	Pf (mm. Hg.)	Pr (mm. Hg.)	Mole Percent N_2	Mole Percent N_2O	HCl	H_2O/N_2
130	893	430	21	52	27	2.5
130	953	448	7	48	43	6.8
140	400	154	38	41	21	1.1
140	780	366	39	46	15	1.2
150	748	320	23	27	48	1.2
150	752	309	20	51	23	2.5
160	748	255	71.5	14.9	13.5	0.21
160	750	260	45	12	43	0.27

Pf = Final pressure at run temperature.

Pr = Residual pressure at ambient temperature.

Although the autocatalytic nature of the reaction is apparent in the curve at 140°C., and that at 130°C. exhibits similar curvature above 1600 min. (not shown), the earlier portions of the curves are very nearly linear, suggesting a steady-state condition. Attempts to plot the coefficient of the linear portion of the curve versus reciprocal absolute temperature yielded a curve characteristic of competing reactions, however.

The thermal decomposition of hydroxylammonium chloride in aqueous solution was investigated by Hofmann and Kroll [7] in 1924. These investigators suggested a dual reaction path corresponding to the expressions

(7) K. A. Hofmann and F. Kroll, BER 57B, 937 (1924).

$$4HONH_2 \longrightarrow 2NH_3 + N_2O + 3H_2O \qquad (1)$$

$$3HONH_2 \longrightarrow NH_3 + N_2 + 3H_2O \qquad (2)$$

in a 2:5 ratio, respectively, the ratio independent of temperature and dilution. On the assumption that these expressions are also valid for the molten salt and that the proportions of N_2O and N_2 remain constant throughout the reaction, the extent of reaction may be calculated for each path. The correct reduction formula is

$$\left(\frac{n_G}{N_o}\right)_t = \frac{Pr}{Pf} \cdot \frac{Tf}{Tr} \cdot \frac{\%\,G}{100} \cdot \left(\frac{n}{N_o}\right)_t$$

The rates of N_2 and N_2O evolution may then be obtained for the linear portions of the curves by

$$\frac{\left(\frac{n_G}{N_o}\right)_{t_2} - \left(\frac{n_G}{N_o}\right)_t}{t_2 - t_1} = \Delta \frac{n_G}{N_o} \Big/ \Delta t = K_G$$

The values of K_G were then converted to K_{HONH_2} by the appropriate factors obtained from the stoichiometry. These converted values are shown in Table II and presented versus $1/T^{o}x\ 10^3$ in Figure 4.

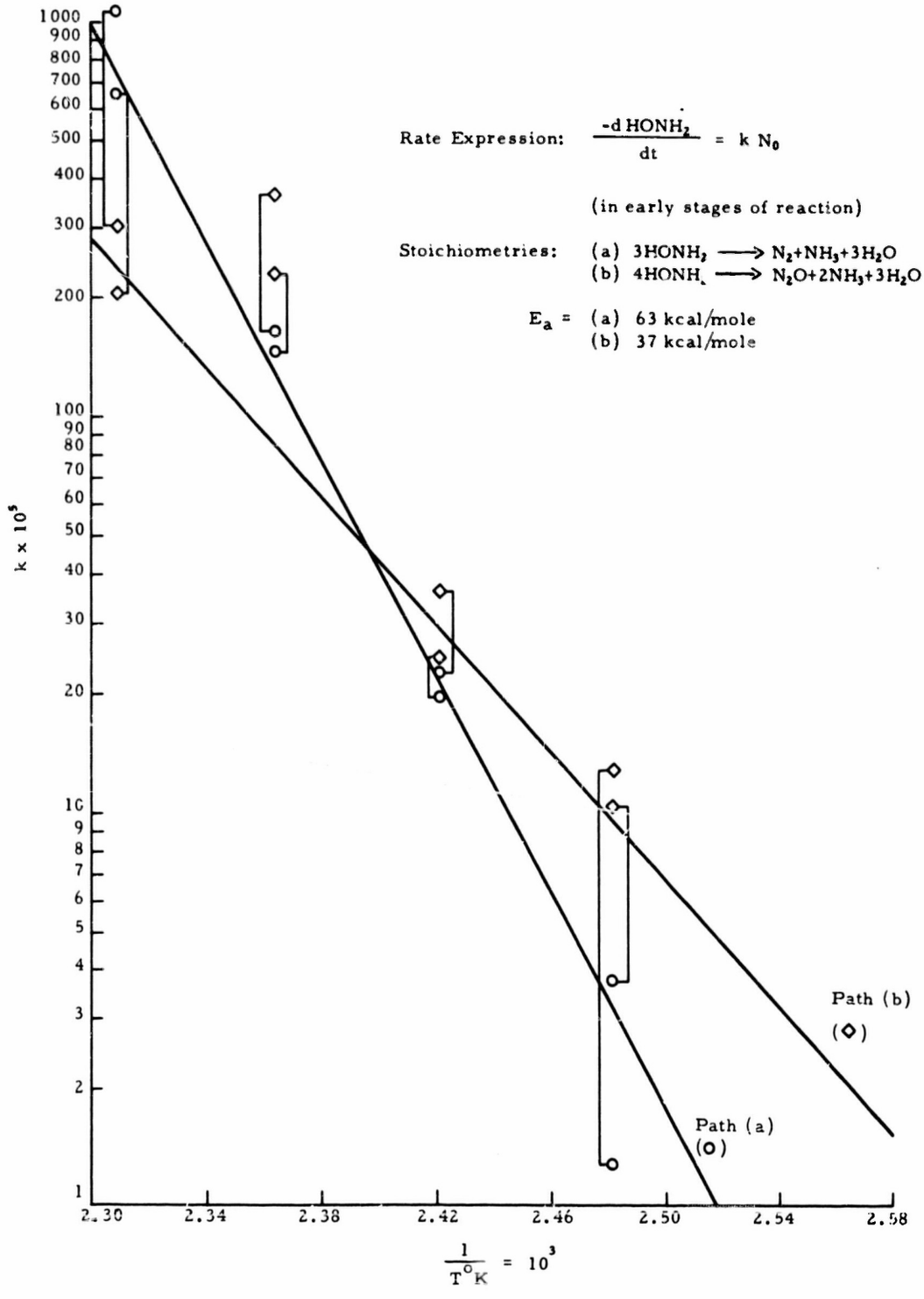


Figure 4. Temperature Coefficients for the Thermal Decomposition of Hydroxylammonium Chloride

TABLE II

VALUES OF K_{HONH_2} FOR TWO REACTION PATHS,

$HONH_3Cl$ DECOMPOSITION

Temp. (°C)	Temp. (°K)	$K^{I} \times 10^{5}$*	$K^{II} \times 10^{5}$*
130	403	3.75	10.12
130	403	1.26	12.64
140	413	19.65	24.20
140	413	22.65	35.60
150	423	144	226
150	423	166	358
160	433	1077	300
160	433	650	202

* K^{I} applies to N_2-producing path; K^{II} applies to N_2O-producing path.

The activation energy for the nitrogen-producing path is 63 kcal/mole; that for the path producing nitrous oxide is 37 kcal/mole. Apparently the proportional influence of these two paths is a function of temperature in the decomposition of the molten salt, as opposed to decomposition in aqueous solution.

Hydroxylammonium Perchlorate

Pressure versus time data were collected at temperatures from 120° to 150°C. ,above 150°C. the rate of gas evolution exceeded the capacity of

our monitoring equipment. Point-for-point reproducibility of curves at the same temperature leaves much to be desired, but the general characteristics of the curves are the same. A slight "bump" is generally observed in the early stage of the reaction; this may be a manifestation of the vaporization of the impurities. A linear relationship then prevails, followed by an autoacceleratory phase. Average plots are illustrated in Figure 5, and observed values of the coefficient of the linear phase are presented in Table III. A plot of the average of the coefficients observed for each temperature versus reciprocal absolute temperature (Figure 6) yields a value of 44.3 kcal/mole for the activation energy of the reaction.

Vapors remaining uncondensed at ambient temperature were analyzed for all runs. The products were nitrous oxide and chlorine, although large quantities of hydrogen chloride were frequently detected. Analysis of the residues proved impractical, as the residual mass was so slight that experimental errors were greatly magnified. Larger Sickle gauges were employed to contain larger samples which were then run to completion at 140°C. overnight. The vapors were found to be exclusively nitrous oxide and chlorine; analysis of the residues detected very slight quantities of ammonia in solution in aqueous perchloric acid. The stoichiometry for such a reaction should be

$$14\ HONH_3ClO_4 \longrightarrow 7N_2O + 2Cl_2 + 10\ HClO_4 + 23\ H_2O$$

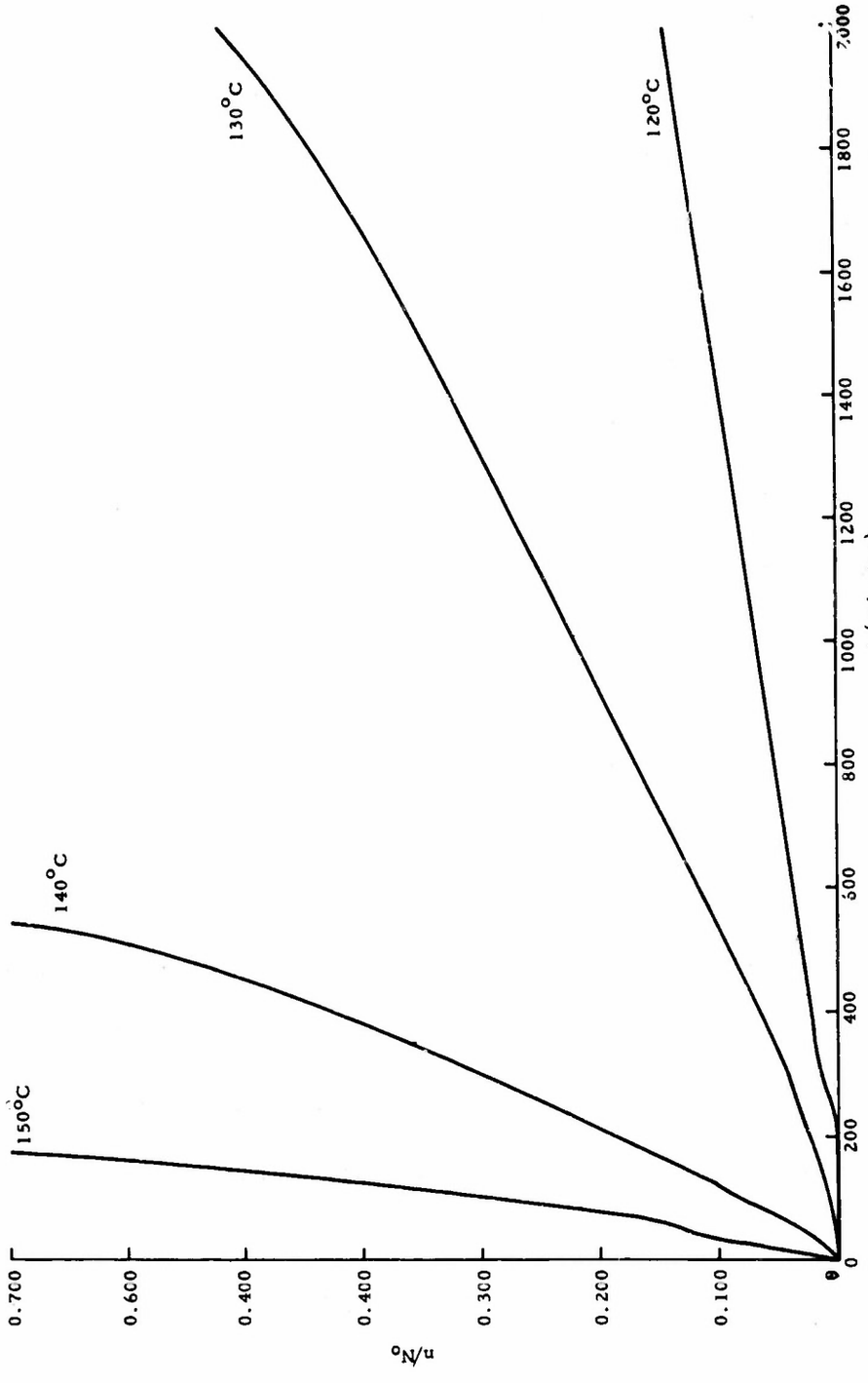


Figure 5. Rate of Decomposition of Hydroxylammonium Perchlorate as a Function of Temperature

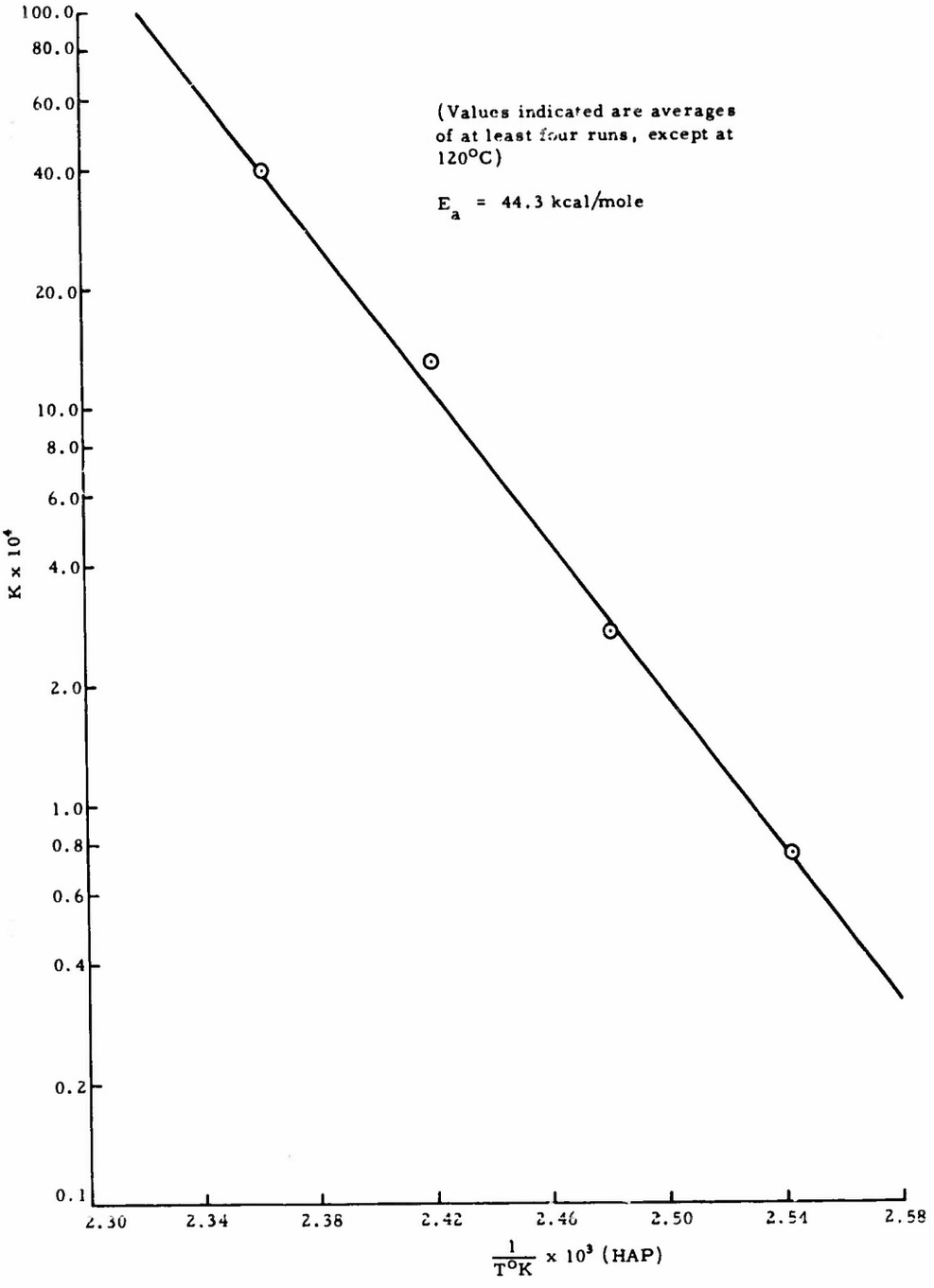


Figure 6. Arrhenius Plot: Coefficient of Linear Portion of Curve vs $\frac{1}{T^{\circ}K} \times 10^{3}$; Hydroxylammonium Perchlorate

TABLE III

COEFFICIENTS OF LINEAR PORTION OF CURVE AS A FUNCTION OF TEMPERATURE-HYDROXYLAMMONIUM PERCHLORATE DECOMPOSITION

Temp. (^{o}K)	K x 10^{4}	Temp. (^{o}K)	K x 10^{4}
393	0.74	413	14.6
403	3.43	413	11.4
403	2.67	413	15.1
403	2.90	423	43.8
403	1.73	423	31.4
413	11.1	423	48.3
413	11.9	423	31.3

Average Values: 393^{o}K 0.74×10^{-4} 413^{o}K 12.8×10^{-4}

403^{o}K 2.68×10^{-4} 423^{o}K 38.7×10^{-4}

On this basis, certain product ratios were predicted and confirmed by the analyses. Comparisons of predicted and observed values are presented in Table IV.

TABLE IV

STOICHIOMETRIC RELATIONSHIPS,
$HONH_3ClO_4$ DECOMPOSITION

	Run A	Run B
Milligram-atoms, Nitrogen		
Initial	4.766	4.283
Final	4.799	4.726
Percent Recovered	100.7	110.3
*Milligram-atoms, Hydrogen		
Initial	19.706	17.710
Final	19.813	18.230
Percent Recovered	100.5	102.9
*Milligram-atoms, Oxygen		
Initial	19.385	17.421
Final	22.836	21.451
Percent Recovered	117.8	123.1
Milligram-atoms, Chlorine		
Initial	4.766	4.283
Final	4.484	3.680
Percent Recovered	94.1	85.9
Final Pressure, 140°C Observed	1255 mm. Hg.	1260 mm. Hg.
(N_2O, Cl_2) Predicted	1120	1124
Vapor Press Residue	135	136
Final Pressure, Ambient Observed	826	833
(N_2O, Cl_2) Predicted	807	817
Vapor Press Residue	19	16
*N_2O/Cl_2 Observed	3.35	6.53
Predicted	3.60	3.60
*$HClO_4/H_2O$ Observed	0.36	0.37
Predicted	0.42	0.36

*Values adjusted to include 0.9% H_2O initial impurity and/or slight degradation to ammonia.

The relationships calculated from the analytical results are as follows (not balanced):

$$14\ HONH_3ClO_4 \longrightarrow 7.0\ N_2O + 2.2\ Cl_2 + 9.3\ HClO_4 + 23.8\ H_2O \quad \text{(Run A)}$$

$$14\ HONH_3ClO_4 \longrightarrow 7.0\ N_2O + 1.2\ Cl_2 + 9.7\ HClO_4 + 24.2\ H_2O \quad \text{(Run B)}$$

Destructive distillation experiments were performed on hydroxylammonium perchlorate to determine the course of the reaction under constant vacuum. Under these conditions, the molten salt gradually changes to a solid, and bright red substances condense in the liquid nitrogen trap. The condensate in the Dry Ice trap is a small quantity of colorless liquid, highly acidic. Satisfactory analyses of the trap contents have not been obtained as of this writing, but the brightly-colored condensate from the liquid nitrogen trap decomposes on warming and cannot be recondensed; the products of this reaction are N_2O, HCl and Cl_2. The solid residue in the reaction vessel is found to be a mixture of unreacted hydroxylammonium perchlorate, ammonium perchlorate and perchloric acid. Pertinent data for one such destructive distillation are tabulated in Table V.

TABLE V

RELATIVE REACTION RATES FOR $HONH_3ClO_4$ UNDER CONTINUOUS PUMPING DISPROPORTIONATION AND OXIDATION AT 180°C

Hydroxylammonium Perchlorate, initial	9.041 millimoles
Hydroxylammonium Perchlorate, recovered	0.800 millimole
Hydroxylammonium Perchlorate, reacted	8.241 millimoles
Ammonium Perchlorate, recovered	0.658 millimole
$HONH_3ClO_4$ disproportionated (2 x NH_3 recovered)	1.316 millimoles
$HONH_3ClO_4$ oxidized	6.925 millimoles
Relative reaction rates, disproportionation/oxidation	0.19

DISCUSSION

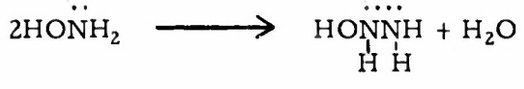
Hydroxylammonium Chloride

Hofmann and Kroll, in the source referenced above, propose a complex reaction path in which three moles of hydroxylamine combine to form the reactive species $HON(NH_2)_2$, eliminating two moles of water. This species may then decompose spontaneously to nitrogen, ammonia and water, or may recombine with one mole of water forming nitrous acid and two moles of ammonia. The nitrous acid then oxidizes a fourth mole of hydroxylamine, producing nitrous oxide and two moles of water.

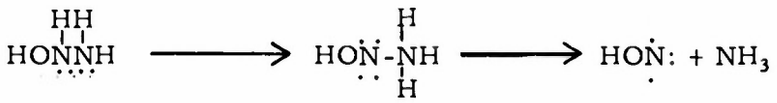
Kurtenacker and Werner [8] in 1927 proposed a somewhat simpler scheme.

(8) A. Kurtenacker and F. Werner, Z. anorg. allgem. chem., 160, 333 (1927).

The first step is a condensation reaction, followed by a tautomerization and the production of ammonia and a diradical species as shown below.



(1)

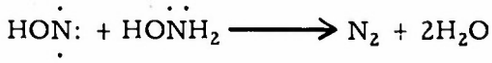


(2)

The diradical can then dimerize to produce hyponitrous acid, which decomposes to nitrous oxide and water [9], or may attack a third mole of hydroxylamine to yield nitrogen and two moles of water.

(9) L. F. Audrieth, J. Phys. Chem., 34, 538 (1930).

(3)



(3a)

The oxidation of hydroxylamine to HON: and H_2O was confirmed by Bodenstein [10] in studying the decomposition of solid $HONH_2$ at -25°C.

(10) M. Bodenstein, Z. Elektrochem, 47, 501 (1941).

The relative activation energies for the two reactions (i.e., 37 kcal/mole for N_2O path, 63 kcal/mole for N_2 path) are in agreement with the reaction

scheme show above. The reaction shown in (3a) should require a relatively large energy of activation, whereas the dimerization ought to have a lower energy of activation. As is apparent, all reaction schemes presuppose the dissociation of the salt to acid and base:

$$HONH_3^+ + Cl^- \rightleftharpoons HONH_2 + HCl$$

as the first step of the reaction.

Hydroxylammonium Perchlorate

Although the absence of ammonium perchlorate among the decomposition products of hydroxylammonium perchlorate in sealed systems would lead one to suspect that the reaction mechanism is radically different from that proposed for the chloride, such is probably not the case. The presence of ammonium perchlorate as a decomposition product in constantly evacuated systems is noted above and has also been reported by Cordes [11].

---

(11) H. F. Cordes, U. S. Naval Ordnance Test Station (China Lake, Calif.,) Quart Prog Rpt Rsch in Chem NOTS TP 3823., p, 11, March 1965 (Confidential).

Apparently the production of ammonium perchlorate occurs only if the oxidizing species (i.e., $HClO_4$) is removed. The initial steps in the reaction

are most probably identical to those proposed in the decomposition of the chloride:

$$HONH_3^+ + ClO_4^- \rightleftharpoons HONH_2 + HClO_4 \qquad (1)$$

$$2HONH_2 \longrightarrow \overset{HH}{HONNH} + H_2O \qquad (2)$$

The perchloric acid formed in (1) decomposes virtually instantaneously in the temperature range studied. The fragments, however, are all strong oxidants, and, if not removed from the reaction will oxidize the intermediate formed in reaction (2) to nitrous oxide and water, thus preventing the formation of ammonia in the sealed systems.

$$\overset{HH}{HONNH} + 2\ [O] \longrightarrow N_2O + 2H_2O \qquad (3)$$

In constantly evacuated systems, the concentration of oxidizing species in the melt is considerably lower; the perchloric acid is removed almost as rapidly as it is formed in reaction (1). In the report referenced above, Cordes derives the expression based on mass spectrograph studies at

$$NH_3OHClO_4 \longrightarrow 3a\ H_2O + aN_2O + (a-1/4)\ HCl + (a + 1/4)\ HClO_4 + (1-2a)\ NH_4ClO_4$$

79.5°C. The value of "a" obtained from the proportions of N_2O and HCl is 0.35. Substituting this value for "a" and clearing fractions yields

$$20\ HONH_3ClO_4 \longrightarrow 21\ H_2O + 7\ N_2O + 2\ HCl + 12\ HClO_4 + 6\ NH_4ClO_4. \qquad (4)$$

If one writes the expression for simple disproportionation of the hydroxylamine moiety:

$$4HONH_3ClO_4 \longrightarrow N_2O + 2NH_4ClO_4 + 2HClO_4 + 3H_2O \qquad (5)$$

and an expression for oxidation of the hydroxylamine by the perchloric acid:

$$4HONH_3ClO_4 \longrightarrow 2N_2O + HCl + 3HClO_4 + 6H_2O \qquad (6)$$

and combines these in a three-to-two ratio, respectively, one reproduces equation (4) precisely. This ratio should be directly related to the relative reaction rates at 79.5°C., i.e., $\frac{k\ (\text{disproportionation})}{k\ (\text{oxidation})} = 3{:}2$. From Table V, the relative rates at 180°C. under roughly similar conditions were found to be $\frac{k\ (\text{disproportionation})}{k\ (\text{oxidation})} = 0.19{:}1$. The values of k (disproportionation) between 130°C and 160°C, are recorded in the study on hydroxylammonium chloride (Table II); by extending the Arrhenius plot (Figure 6) downward to 79.5°C. and upwards to 180°C., one can calculate the values of k (disp) at these temperatures and then calculate the values of k (ox) from the ratios given above. Using these values of k (ox), one can calculate the E_A for the oxidation reaction and predict the values of k (ox) in the 140°C. region. These values of E_A (ox) and k (ox) correspond to those obtained for the decomposition of the perchlorate in closed systems. The calculated values are compared to those observed in Table VI.

TABLE VI

CALCULATION OF k (ox) AND E_A (ox) FROM REACTION RATE RATIOS AND k (disp), COMPARISON OF CALCULATED AND OBSERVED VALUES

	Calculated Values	Observed Values
k (disp) at 140°C.:	----------	2.99×10^{-4}
k (disp) at 80°C.:	1.45×10^{-7}	----------
k (disp) at 180°C.:	154×10^{-4}	----------
k (ox) at 80°C.:	9.67×10^{-8}	----------
k (ox) at 180°C.:	810×10^{-4}	----------
E_A (ox):	43.6 kcal/mole	44.3 kcal/mole
k (ox) at 140°C.:	7.75×10^{-4}	12.8×10^{-4}

As is apparent, the values of the activation energy are in excellent agreement. The disparity in the rate constant values is attributed to the fact that the calculated value is based on the value of k ($HONH_3Cl$) for the disappearance of $HONH_2$, whereas the "observed" value is representative of the rate of pressure buildup due to product formation in the decomposition of the perchlorate. The ratio of k ($HONH_3ClO_4$; pressure buildup) to k ($HONH_3ClO_4$; disappearance of starting material) is not independently established at the early stages of the reaction, where the observed value of k ($HONH_3ClO_4$; pressure buildup) was obtained. The close agreement

of the activation energy values and the close "order-of-magnitude" correlation of the values of the rate constants form strong evidence for the accuracy of the assumptions on which the calculations are based, i.e., that the reactions in the open system are identical with those in the sealed systems, and that the variation in products is a function solely of the differences in concentration of oxidizing species. The production of HCl rather than Cl_2 in open systems is attributed to the relative excess of reducing agent in such systems.

III. APPENDIX

A. INTRODUCTION

The main course of research performed on this program during 1965 was the study of the thermal decomposition reactions of hydroxylammonium perchlorate and hydroxylammonium chloride discussed above. In addition to this, three considerably smaller studies were conducted concurrently with the principal investigation, all of which yielded information of potential value to future investigators. These are: (1) a very brief study of the decomposition of hydrazinium diperchlorate employing a new approach, (2) comparative thermal stability studies on hydrazinium diperchlorate and hydroxylammonium perchlorate at 70°C. and (3) the oxidation of ammonium perchlorate by anhydrous perchloric acid. None of these secondary efforts represents a conclusive study, but rather each constitutes a "note" which may afford a clue useful in obtaining a solution to a related problem.

B. NOTES ON THE THERMAL DECOMPOSITION OF HYDRAZINIUM DIPERCHLORATE

A modest effort extended over approximately a two year period under other programs (since terminated) has resulted in definition of many characteristics of the HP-2 decomposition reaction. The results of rate studies, however, have not exhibited satisfactory repeatability, generally speaking. Among the problems encountered in the past are the catalytic effects of a large variety of potential impurities, the difficulty of drying the salt without removing some of the loosely-held perchloric acid (producing HP) and the relatively undefined variations due to packing, self-heating, intra- and intergranular stresses, particle sizes, etc. Experiments in the past were performed on quantities varying from 0.6 to 1.2 g. in reactors of total volume of from 8 to 14 cc. Two experiments performed on ~1.00 g. samples in ~85 cc. reactors seemed to indicate no volume effect, but more recent experiments on this project lead to the suspicion that the governing factor in these two experiments was the tendency of the material to undergo self-heating.

Some experiments have been performed on HP-2 during this program, the objective being to determine the effect of hydrazinium monoperchlorate on the decomposition rate of HP-2. It has previously been established that the presence of excess perchloric acid accelerates the reaction, whereas exposure of the salt to NH_3 vapor stabilizes it. The addition of other basic materials to the system ought to stabilize the material also. Rather than add basic impurities, the known equilibrium dissociation of the reaction

$$N_2H_6\ (ClO_4)_2 \rightleftharpoons N_2H_5ClO_4 + HClO_4\ (v)$$

was employed to adjust the HP to HP-2 ratio in the condensed phase. This was accomplished by conducting the experiments in reactors of varying total volume. The pertinent data are recorded in Table I, and illustrated in Figure 1.

TABLE I

THERMAL DECOMPOSITION EXPERIMENTS ON HP-2
AT 140°C

		Percent by Weight*		
Mass	Volume	HP-2	HP	t acceleration
0.649	9.5	98.8	1.2	23
0.913	11.5	99.5	0.5	6.6
1.360	11.0	99.5	0.5	41
0.120	7.0	94.9	5.1	did
0.100	17.0	85.6	14.4	not
0.100	17.0	85.6	14.1	accelerate

* Refers to composition of the condensed phase adjusted for dissociation to equilibrium.

The "time to acceleration" is defined as the time when dp/dt is so large that the apparatus ruptures. Such a condition was never attained in experiments performed with small samples. The remarkable increase in duration of the run is attributed primarily to the lack of self-heating; the depression of the initial slope of the reaction is attributed to the presence of a large quantity of HP intimately mixed with the HP-2, which eliminates the presence of free $HClO_4$ at the surface. On the other hand, the presence of HP-2 effectively suppresses the following reaction proposed as the initial step in decomposition of HP:

$$N_2H_5ClO_4 \longrightarrow N_2H_4 + HClO_4$$

Thus, it appears that mixtures of HP + HP-2 may be more stable than either of the pure materials.

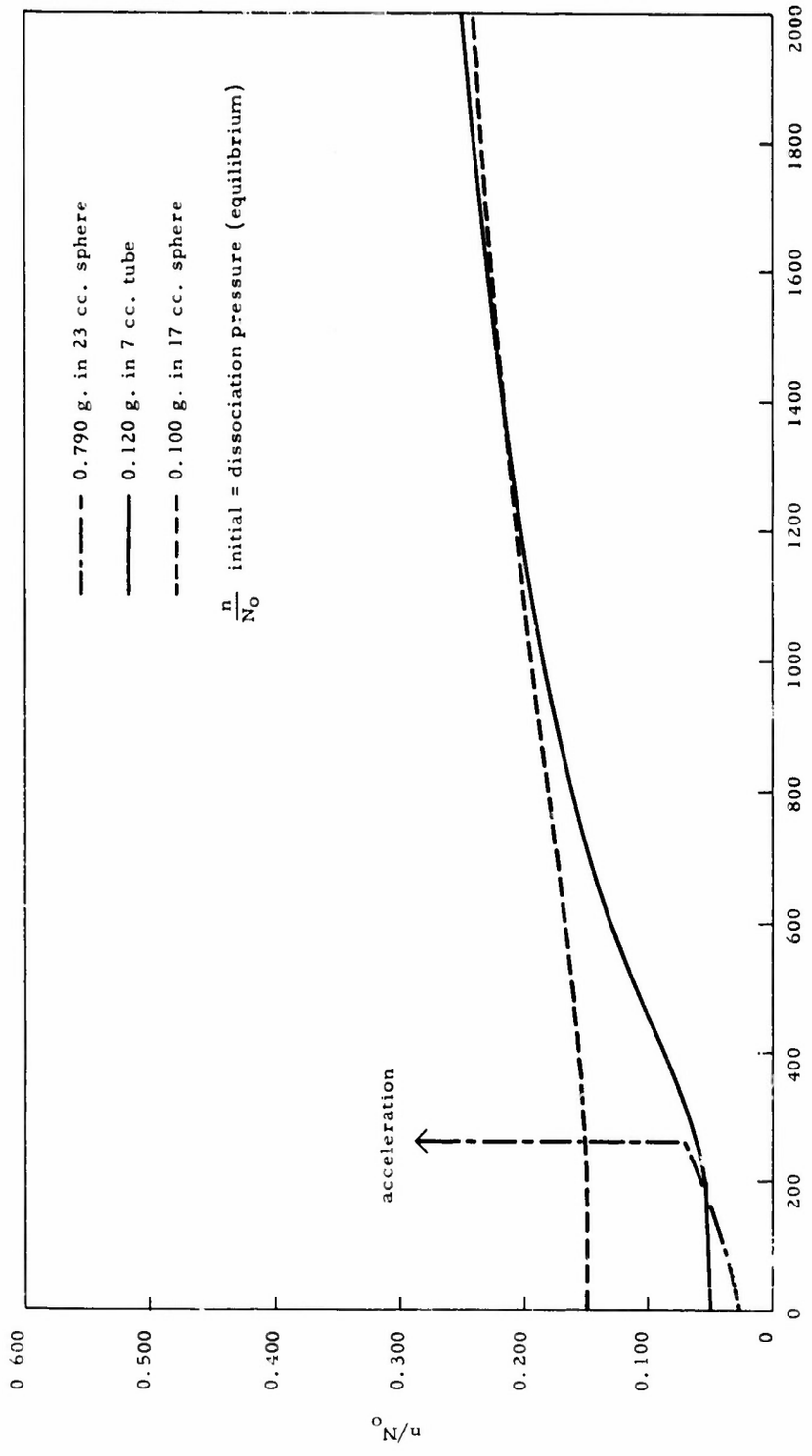


Figure 1. Thermal Decomposition of Hydrazinium Diperchlorate at 140°C. Under Varied Sample Size and Geometry

C. COMPARATIVE STABILITY STUDIES ON HYDRAZINIUM DIPERCHLORATE AND HYDROXYLAMMONIUM PERCHLORATE AT 70°C.

A sample of hydrazinium diperchlorate was maintained in a sealed Sickle gauge for over 23 months at 70°C.; the pressure in the reactor did not attain one atmosphere. A comparable sample of hydroxlammonium perchlorate in a comparable reactor exceeded atmospheric pressure in approximately 7 months time. These samples were destroyed due to mechanical failure in the thermostat system which raised the bath temperature to over 200°C.

A second set of samples of approximately the same mass were placed in identical reactors three months ago. The sample of hydroxylammonium perchlorate generates pressure at approximately ten times the generation rate for the hydrazinium diperchlorate sample. This relationship is comparable to that obtained with the earlier experiment described above.

Comparison of the pressure vs time curves for hydrazinium diperchlorate in section B with the pressure vs time curves for hydroxylammonium perchlorate presented in the publication manuscript affords a measure of the relative stabilities at 140°C. The hydrazinium diperchlorate is considerably more stable at 140°C. also.

D. OXIDATION OF AMMONIUM PERCHLORATE WITH ANHYDROUS PERCHLORIC ACID

Ammonium perchlorate mixed with 72% perchloric acid in equimolar proportion was maintained at 150°C. for 72 hours with no evidence of reaction. Ammonium perchlorate mixed with anhydrous perchloric acid at 55°C. yields gaseous decomposition products characteristic of the decomposition of anhydrous perchloric acid. Traces of N_2O were detected in the residual gaseous products of an experiment at 70°C. and 2% N_2O was detected in the products of an experiment at 100°C. The favored reaction is the decomposition of the anhydrous acid, at higher temperatures however, the acid or its decomposition fragments can oxidize ammonium perchlorate to nitrous oxide.

Confidential
Security Classification

DOCUMENT CONTROL DATA - R&D
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Thiokol Chemical Corporation Reaction Motors Division Denville, New Jersey	2a. REPORT SECURITY CLASSIFICATION Confidential 2b. GROUP Group IV

3. REPORT TITLE

Advanced Oxidizer Research (U)

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report

5. AUTHOR(S) (Last name, first name, initial)

Smith, H. F.; Dvorak, J. J.; Young, A. R., III; Morrow, S. J.; Grelecki, C. J.; Cruice, W. J.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
31 December 1965		

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
NOnr 4364(00) b. PROJECT NO. ARPA Order No. 417, Amendment No. 2 c. Tasks 51, 53, 55 d. Code 0810	RMD 5043-65F 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. AVAILABILITY/LIMITATION NOTICES

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Advanced Research Projects Agency (Office of Naval Research)

13. ABSTRACT

Task 51 - Tertiary alkyl- and arylalkyldifluoramines are reduced by organolithium reagents to give products derived from free radical and nitrene intermediates. Syntheses and gas chromatographic purification of 1,1-bis(difluoramino)hexane and -heptane, 1,2-bis(difluoramino)cyclohexane, 2,3-bis(difluoramino)-2,3-dimethylbutane; 2,3-bis(difluoramino)pentane isomers, and 1,1-, 1,2-, and 2,2-bis(difluoramino)phenylethane are described. Elimination of HF or HNF_2 from certain organic difluoramines yielded ketofluorimines or trifluoroformamidines; chemical reactions of these compounds are discussed.

Task 53 - Evidence for the existence of stable salts of the $N_2F_3^+$ cation is presented. A salt having a composition approaching $N_2F_3AsF_6$ can be prepared by the reaction of N_2F_4 with AsF_5 or $HAsF_6$. Infrared and F^{19} n.m.r. data support an ion structure. Unsuccessful attempts to prepare O_2ClO_4, O_2ClF_4, and N_2FClF_4 are described.

Task 55 - The thermal decomposition reactions of hydroxylammonium perchlorate have been studied between 120°C and 150°C in sealed systems and at 180°C in an open system. The thermal decomposition reactions of hydroxylammonium chloride were studied in the temperature range 130°C-160°C to obtain an understanding of the decomposition reactions of hydroxylamine free from external oxidants. The chloride was found to decompose by two mechanisms, and the reaction of the perchlorate was found to undergo similar initiating steps, but the presentce of excess oxidant increases the reaction rate and leads to a different stoichiometry. The results obtained in the open system were correlated to work reported at NOTS.

DD FORM 1 JAN 64 1473

Confidential
Security Classification

Confidential

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Difluoramines and Bis(difluoramines)						
Dehydrofluorination						
Ketofluorimines and Fluorimines						
Trifluoroformamidines						
Chromatography						
Solid Oxidizers						
NF Chemistry						
OF Chemistry						
N_2F_4 Adducts						
Inorganic Synthesis						
Ammoniacal and Hydroxylammonium Perchlorates						
Ammonium Perchlorate Oxidation						
Hydrazinium Diperchlorate						
Hydroxylammonium Chloride						
Thermal Decomposition						
Bis(difluoramino)fluoraminomethoxypentane						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

_____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

_____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through

_____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS), (S), (C), or (U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

Confidential

Security Classification