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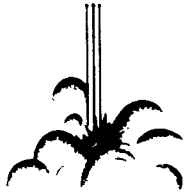
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Report RMD 5043-Q2-64

Contract No. NONr 4364(00)

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ADVANCED OXIDIZER RESEARCH

Report Period: 1 April 1964 to 30 June 1964

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

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Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVER, NEW JERSEY

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ADVANCED OXIDIZER RESEARCH

Report Period: 1 April 1964 to 30 June 1964

Contract No. NONr 4364(00), ARPA Order No. 417

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30 June 1964 shall be used for
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GENERAL FOREWORD

This quarterly 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. The work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer, and includes the following tasks:

Section	Task No.	Title
I	51	Difluoramine Chemistry
II	52	Synthesis of Compounds for Structure-Sensitivity Study
III	53	Chemistry of the Oxygen Subfluorides
IV	54	Stabilization of Nitronium Perchlorate by Complexation
V	55	Thermal Stability of Advanced Solid Oxidizers
VI	56	Chemistry of Difluorodiazine and Nitrosyl Fluoride

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ABSTRACT

This report describes research conducted at Thiokol Chemical Corporation, Reaction Motors Division directed toward the development of advanced solid oxidizers. The six major tasks on which work has been performed are listed below, together with an abstract of each task, and are included as six separate sections of this report.

SECTION I - DIFLUORAMINE CHEMISTRY

Neither perfluoroguanidine nor isocyanic acid could be induced to add to the double bonds of 1,2-bis(fluorimino)cyclohexane. This compound was degraded by aqueous sodium hydroxide to give a quantitative yield of fluoride ion and unidentified water-soluble organic products; a possible reaction sequence is suggested.

The photolysis of 1,4-bis(fluorimino)cyclohexene-2 in cyclohexane solution resulted in rapid reaction, accompanied by darkening and precipitation. The products have not yet been identified.

The acid-catalyzed reaction of *n*-heptanal with difluoramine has been studied and the conditions favoring the formation of gem-bis(difluoramine) or the symmetrical ether have been defined. A mechanism for the reaction is postulated.

The dehydrofluorination of 1,1-bis(difluoramino)heptane did not yield the corresponding trifluoroamidine in a straightforward manner. Some properties of the product derived by the loss of two equivalents of hydrogen fluoride are described. Ethyldiisopropylamine, a new dehydrofluorinating agent has been successfully applied in the synthesis of 1,2-bis(fluorimino)-cyclohexane.

Additional quantities of 1,2-bis(fluorimino)cyclohexene-2 and 1,2-bis(fluorimino)cyclohexene-3 have been synthesized for use in reaction studies.

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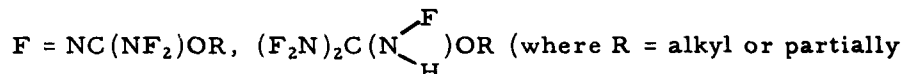
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SECTION II - SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

Work is reported on the synthesis and gas chromatographic purification of aliphatic difluoramines for evaluation of the relationship between structure and sensitivity. A series of tris(difluoramino)methoxyalkanes has been synthesized by reacting C₄-C₉ alcohols with perfluoroguanidine followed by fluorination. An investigation was made of the chromatographic conditions required for obtaining adducts that are >99% pure. The main impurities in these compounds were of the following types:



fluorinated alkyl group). In addition, 23.0 gm of 1,2-bis(difluoramino)-cyclohexane and 6.3 gm of 1,1-bis(difluoramino)propane were synthesized, and after chromatographic purification, were submitted to the Naval Ordnance Laboratory for sensitivity measurements.

SECTION III - CHEMISTRY OF THE OXYGEN SUBFLUORIDES

The major stable reaction product of the O₂F₂-Xe reaction was identified as XeF₂ by single crystal x-ray analysis. Evidence was obtained that unstable O-Xe-F materials are also formed in the reaction but these remain unidentified.

Unsuccessful attempts were made to prepare BrF₇ by reactions of O₂F₂ with BrF₅ and with CsBrF₆. O₂F₂ reacts with CsBrF₄ to give CsBrF₆ and some BrF₅. The presence of CsF had no effect on the nature of reaction products obtained from the reaction of Cl₂ with O₂F₂.

Samples of O₃F₂ were prepared and analyzed in preparation for a study of chemical properties.

SECTION IV - STABILIZATION OF NITRONIUM PERCHLORATE BY COMPLEXATION

Attempts were made to prepare NO₂(C₅H₅N)ClO₄ by (a) direct reaction of NO₂ClO₄ with pyridine, and (b) reaction of I(C₅H₅N)₂ClO₄ with NO₂. The reaction of NO₂ClO₄ with pyridine in Freon 113 gave a product which analysis showed to be 80% NO₂ClO₄·C₅H₅N; its x-ray pattern, however,

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was almost identical to that of pure NO_2ClO_4 . This product darkens slowly on standing at room temperature, and it is believed that this is due to a slow nitration of the pyridine. In the reaction of $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ with NO_2 , iodine was liberated as expected, but analysis of the residual solid has not yet been completed.

The reaction of NOCl with $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ in chloroform gave a product which is predominantly a mixture of pyridinium perchlorate and pyridinium nitrate.

Nitronium perchlorate reacted with PCl_3 to give NOClO_4 and POCl_3 . There was no reaction between NO_2ClO_4 and PF_3 .

SECTION V - THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

Additional experiments on the vapor pressure and thermal decomposition of anhydrous perchloric acid were carried out and evaluated in the light of recent reports from other sources.

Thermal decomposition work on hydrazine-perchlorate indicates no detectable vapor pressure for this compound below its decomposition threshold. It was discovered that the transition from solid phase to liquid phase is accompanied by an increase in thermal stability. An explanation of this phenomenon has been proposed, as well as a comparison of other reported results in the literature.

SECTION VI - CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE

cis-Difluorodiazine forms a stable 1:1 solid adduct with arsenic pentafluoride. On the basis of its infrared spectrum, F^{19}NMR spectrum, and x-ray diffraction pattern, this adduct has been characterized as the fluorodiazonium salt $\text{N}_2\text{F}^+\text{AsF}_6^-$.

Several attempts were made to synthesize new derivatives containing the $-\text{N}_2\text{F}$ group by the reduction of the N_2F^+ cation. However, cis- N_2F_2 was the only N-F containing product observed in the reactions studied. The reagents used in these studies were: NO , NO_2 , CF_3NO , CF_3I , CF_3H , CF_3Cl , NOCl , HCl , N_2F_4 , and trans- N_2F_2 .

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Section I

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DIFLUORAMINE CHEMISTRY

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Section I

DIFLUORAMINE CHEMISTRY

Harry F. Smith

Report RMD 5043-Q2-64

RMD Project 5043, Task 51
Report Period: 1 April 1964
to 30 June 1964

Contract No. NONr 4364(00)
ARPA Order No. 417
Project Code 4910

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FOREWORD

This section of the quarterly project report describes research conducted from 1 April to 30 June 1964 on the synthesis and chemical reactions of organic fluoronitrogen compounds.

Technical personnel contributing to this effort were: H. F. Smith (Project Scientist), J. A. Castellano and C. B. Parisek (Synthesis), J. Creatura and A. Fremmer (Chemical Analysis) and R. Storey and D. Kates (Instrumental Analysis).

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I. INTRODUCTION

The objective of this research program is the investigation of the chemical reactions of difluoramino alkanes and related organic fluoronitrogen compounds. It is expected that information developed in the course of these studies will serve the propellant industry in several ways. Many of the known organic NF compounds promise satisfactory energy levels when incorporated into propellant compositions, but their utilization has been inhibited by sensitivity to thermal or mechanical shock. Research by a number of organizations is currently directed toward discovering means of decreasing this sensitivity; an exploration of the chemistry of organic NF compounds will assist in this effort. In addition, the utilization of NF materials in practical propellant formulations involves questions of mutual compatibility. A systematized knowledge of the chemistry of this relatively new functional group should simplify this problem. It is likely that our investigations of chemical reactions will in some cases lead to products of new structural types, some examples of which may possess an appropriate balance between stability and available energy.

During the present report period emphasis has been placed upon the definition and elucidation of the chemical reactivity of >C=NF group, primarily because of the interesting and useful reactions which have been discovered involving the >C=NF of PFG. Experiments with a number of model difluoramines aimed at determining the extent to which >C=NF resembles olefinic or carbonyl linkages are described.

The analogy to perfluoroguanidine can be carried one step closer by the use of trifluoroguanidines as model compounds. The initial steps in the synthesis of a model compound of this type via the dehydrofluorination of a 1,1-bis(difluoramino)alkane have been undertaken.

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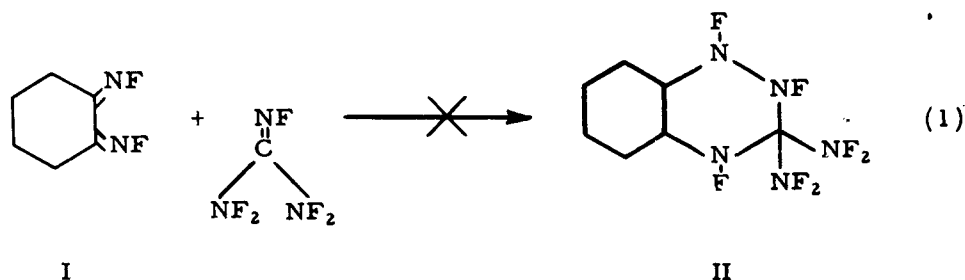
II. DISCUSSION

A. REACTIONS OF 1,2-BIS(FLUORIMINO)CYCLOHEXANE

A number of unsuccessful attempts to bring about additions to the double bond of a fluorimino compound were described in our previous report (Ref 1). Several of these attempts have been repeated under increased forcing conditions, and some new potential addends have been investigated.

1. Diels-Alder Reactions

The conjugated unsaturated system of 1,2-bis(fluorimino)cyclohexane (I) resembles that of a 1,3-diene, and so might possibly serve as a diene in the Diels-Alder reaction. Perfluoroguanidine has been reported (Ref 2) to function as a dienophile in certain instances and the reaction of these two compounds would be expected to give a product (II) with desirable energy and stability. Initial efforts to effect this reaction have not been successful:



Reaction conditions are limited by the thermal instability of perfluoroguanidine, and typical temperatures for the Diels-Alder reaction could not be used.

In order to determine whether the bis(fluorimine) is capable of undergoing a 1,4-addition, reactions with two typical dienophiles have been attempted. Neither maleic anhydride nor *p*-benzoquinone was found to add to I in refluxing xylene; decomposition occurred on heating to 200° in the absence of solvent.

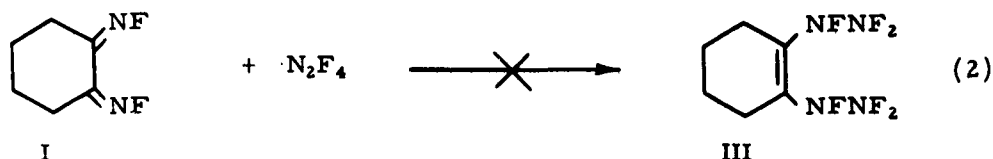
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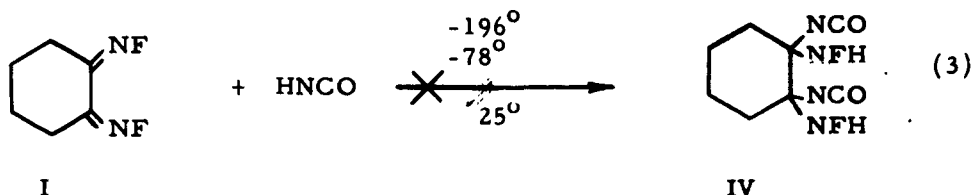
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2. Other Addition Reactions

An initial unsuccessful attempt to bring about the addition of tetrafluorohydrazine to 1,2-bis(fluorimino)cyclohexane at 100° and subatmospheric pressure was reported earlier (Ref 1). During the current quarter this experiment was repeated in a metal bomb at elevated pressure. A solution of the reactants in Freon-113 in a 75 ml reactor was heated to 60-80° for 12 hours (calculated pressure = 310 psi). No reaction occurred, and 92% of the starting materials was recovered.



The addition of isocyanic acid to perfluoroguanidine has provided an intermediate which has made available a number of desirable compounds (Ref 3). The application to other $\text{C}=\text{NF}$ compounds would be a logical extension of this reaction and might provide a route to new structural types such as combination vic-gem compounds. The possibility that such a reaction can be achieved is strengthened by the reported additions of isocyanic acid to carbonyl groups (Ref 4) and to olefinic linkages (Ref 5). An available Sargent Micro Combustion Unit was modified to provide a convenient apparatus for the preparation of isocyanic acid by the pyrolysis of cyanuric acid (Ref 6). The depolymerized acid was condensed with 1,2-bis(fluorimino)cyclohexane (I) in a bulb at -196°. The temperature was increased in stages, culminating in a 16-hour period at 25-28°. The acid was found to have reverted to the trimer; I was recovered unchanged.



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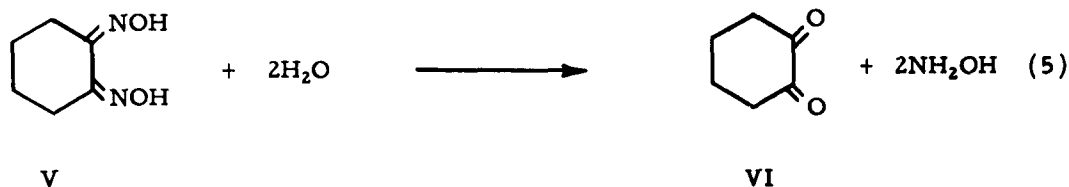
3. Reaction With Base

The stability of secondary fluorimines toward base is an important consideration in the synthesis of N,N,N'-trifluoroamidines, as well as of the fluorimines themselves. The observation that aqueous sodium hydroxide was consumed by 1,2-bis(fluorimino)cyclohexane was included in our previous report (Ref 1). This experiment has been repeated on a larger scale. The fluorimino compound appeared to react rapidly with 0.5 N aqueous sodium hydroxide solution at room temperature with the system forming a single phase. After 48 hours the reaction mixture was titrated potentiometrically with standard acid; inflections occurred at pH 7.25 and 5.30 (Figure 1). The first break was probably due to unreacted sodium hydroxide and the second may be attributed to a carboxylic acid salt. According to this interpretation 85% hydrolysis occurred producing a 30% yield of carboxylate. The color of the solution interfered with the colorimetric analysis for fluoride ion so that little significance may be attached to the value obtained (113% of theory). Any organic products formed were sufficiently hydrophilic to prevent extraction with ether.

One possible interpretation of the observed results involves nucleophilic attack on nitrogen with simultaneous elimination of fluoride ion:



A base-catalyzed hydrolysis of the dioxime would probably ensue, giving cyclohexandione (VI). The diketone is subject (Ref 7) to further nucleophilic



attack, undergoing a benzilic type rearrangement with ring contraction to give a hydroxyacid salt (VII) as the final product. It is also possible that some of

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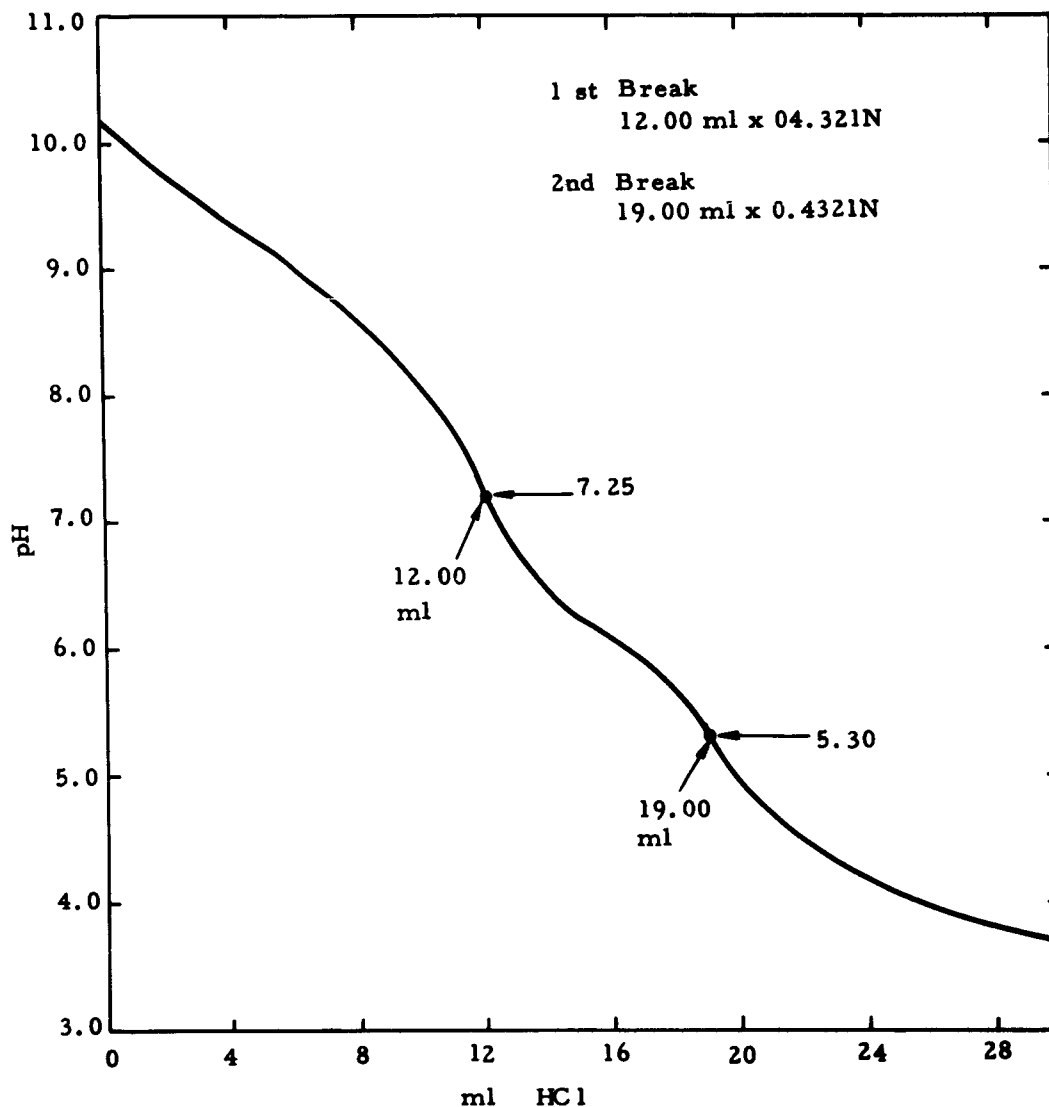


Figure 1. Titration Curve, Reaction of 1,2-Bis(difluoramino)cyclohexane With Sodium Hydroxide

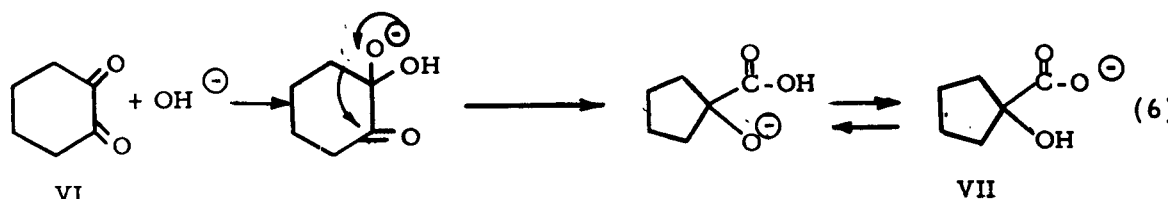
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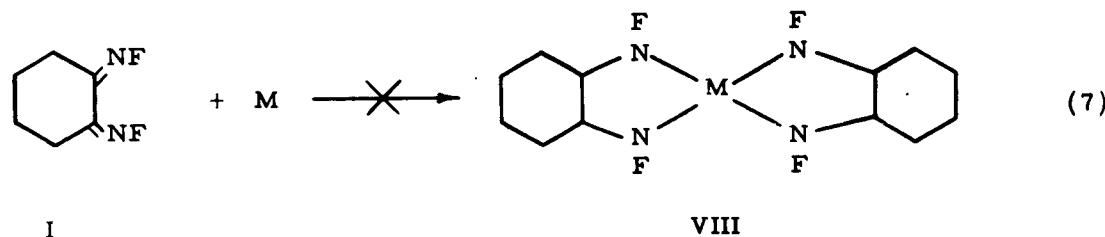
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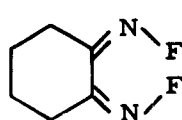
the sensitive diketone was oxidized by air to adipic acid. Other possible reaction courses, involving initial nucleophilic attack on carbon, cannot be ruled out at this point.

4. Metal Complexes

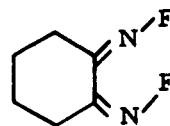
Considering the favorable geometry of 1,2-bis(fluorimino)cyclohexane (I), the formation of coordination complexes such as VIII with metal ions provides a significant test of the extent to which the C=NF group resembles carbonyl. Such complexes, furthermore, might serve as reactive intermediates for the synthesis of new NF compounds useful in the propellant field. In addition to the attempted preparation of a nickel complex already reported (Ref 1), we have found that no complex is formed between I and copper, cobalt, or ferric ions in alcohol/water solution. This observation may be interpreted



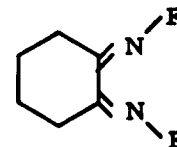
as an indication that substantial differences exist in the electron distributions of C=O and C=NF. The situation is further complicated by steric considerations which do not apply in the case of α -diketones. Each of the C=NF groups can theoretically exist in either syn or anti configuration, and the relative stability and rate of interconversion of the three possible forms are not yet known.



Ia
syn, syn



Ib
syn, anti



Ic
anti, anti

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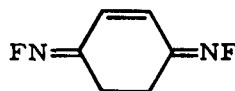
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Steric interactions between fluorine atoms may restrict bidentate coordination to the anti,anti isomer, and may in fact prevent formation of the syn,syn form.

B. PHOTOLYSIS OF 1,4-BIS(FLUORIMINO)CYCLOHEXENE-2

The photochemical reaction of 1,4-bis(fluorimino)cyclohexene-2 (IX)



IX

described previously (Ref 1) has been explored further on a preparative scale. A solution of IX in cyclohexane, approximately 0.08 molar, was exposed in a thin film at room temperature to the radiation from an immersed quartz-filtered high-pressure mercury-vapor lamp. Visible changes occurred within ten minutes. The colorless solution became yellow and an insoluble brown solid was deposited on the wall of the quartz well. Since only a small fraction of the solution was in the illuminated zone and the rate of diffusion was very low as compared to the rate of reaction, uniform exposure of the entire solution was not possible. As a consequence the final products obtained represent the results of high conversion and possible subsequent activation of primary products, even though the overall conversion of the bulk of the fluorimine was probably low. The products obtained in this experiment are being examined but greater emphasis will be placed on future experiments which will incorporate the necessary refinements to compensate for the unexpectedly rapid reaction.

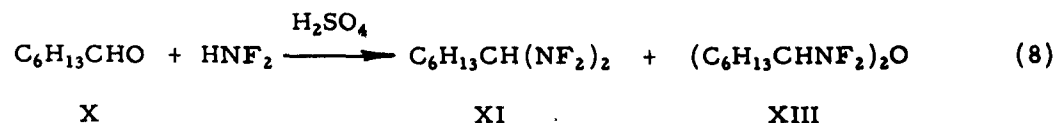
C. REACTION OF HEPTANAL WITH DIFLUORAMINE

A planned extension of our study of the chemistry of the fluorimino group called for the synthesis of an N,N,N'-trifluoroamidine. The n-heptyl derivative was chosen as a suitable model compound because of its low sensitivity and the ready availability of the corresponding aldehyde.

The reaction of n-heptanal (X) with difluoramine has been found to give varying yields of 1,1-bis(difluoramino)heptane (XI) and bis(1-difluor-aminoheptyl) ether (XII), depending upon the relative concentrations of

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reactants and the rate of addition of the aldehyde. The results of four experiments are summarized in Table I.

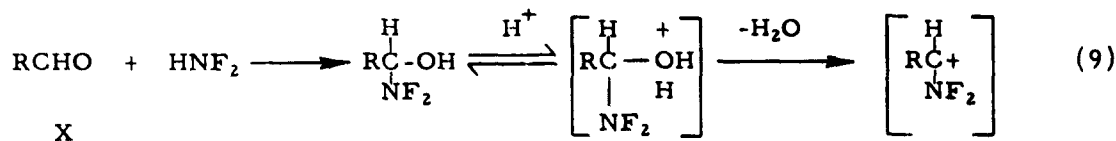
TABLE I

REACTION OF N-HEPTANAL WITH DIFLUORAMINE

Expt. No.	HNF ₂ mmoles	RCHO mmoles	Con- ditions ^a	Products			
				gem-cpd		Ether	
				mmoles	(%)	mmoles X2	(%)
1	253	50	b	0	0	11	22
2	275	50	c	17.5	35	4	8
3	320	53	d	20	38	5	20
4	320	26	d	12.5	47	0.5	3.6

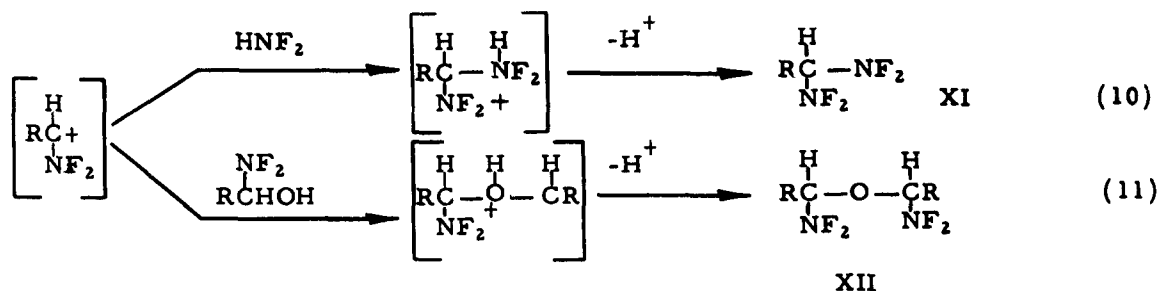
- All expts at 0° in 5.0 ml 105% fuming H_2SO_4
- RCHO added while HNF_2 was being generated
- RCHO added during 105 min after all HNF_2 was present; refluxed 105 min
- RCHO added after all HNF_2 was present, refluxed 4 hours.

The products were isolated by vacuum distillation and characterized by elemental analyses, infrared spectra, proton and F^{19} NMR spectra; and in the case of XI, by comparison of physical properties with reported values (Ref 8).



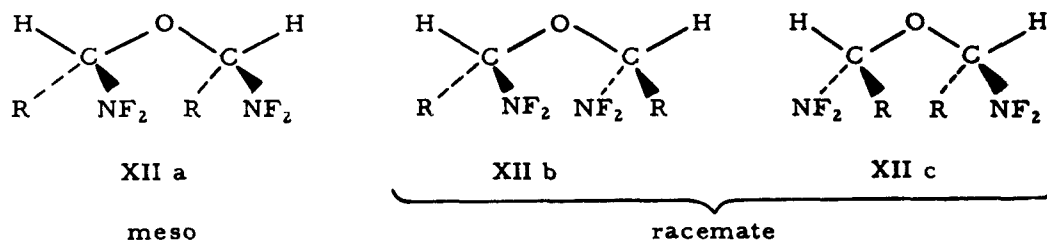
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A large excess of difluoramine and/or the slow introduction of aldehyde would favor the reaction shown in equation 10, producing the desired gem-compound, XI. If the local concentration of aldehyde is permitted to build up, on the other hand, formation of the ether (XII) via equation 11 becomes more probable.

The F^{19}NMR spectrum of XII (Figure 2) consisted of an extraordinary AB quartet with J greater than $\Delta \nu$. The smaller splittings are due to coupling with hydrogen atoms gem to difluoramino groups. The observed resonances indicate that both difluoramino groups are identical, but that the two fluorine atoms in each group differ from each other in their environments. Such a situation requires that rotation about the carbon-nitrogen bonds be restricted, although such restriction is not clearly evident from examination of Fisher-Hirschfelder models. The problem is further complicated by the asymmetry of carbon atoms carrying the difluoramino groups; it is not known whether the compound at hand is the racemate or the meso isomer. Similar F^{19}NMR spectra were observed for cis (meso)- and trans (dl)-1,2-bis(difluoramino)-cyclohexane (Figures 3, 4). The infrared spectra of these two compounds have been published previously (Ref 9). The infrared spectrum of XII



is presented in Figure 5.

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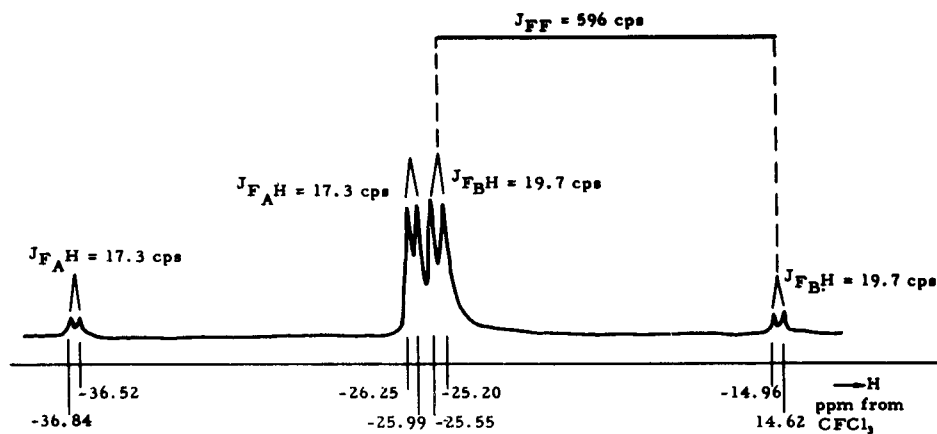


Figure 2. F^{19} NMR Spectrum of Bis(1-difluoraminoheptyl) ether

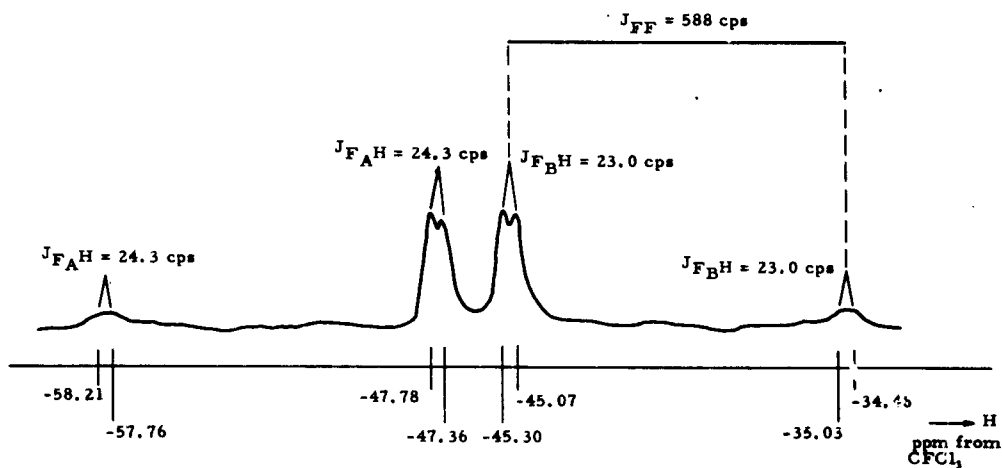
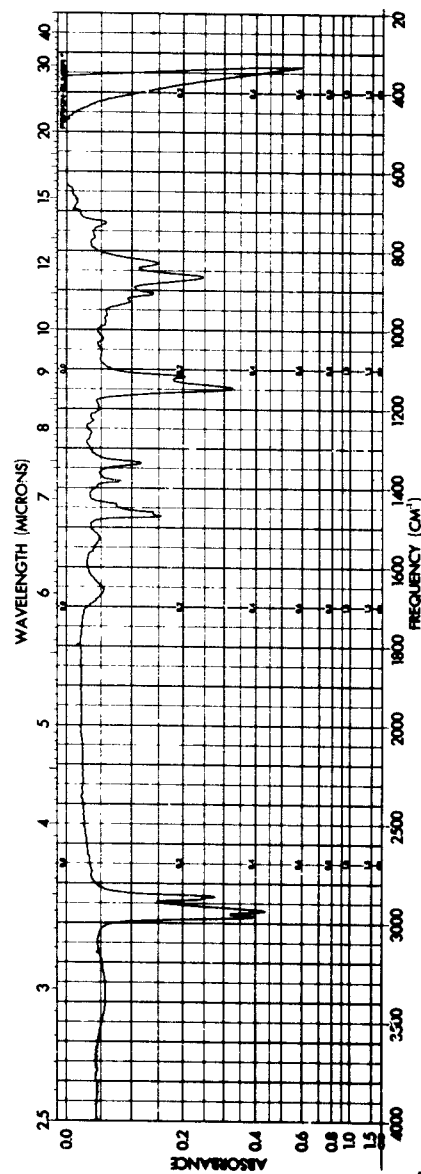
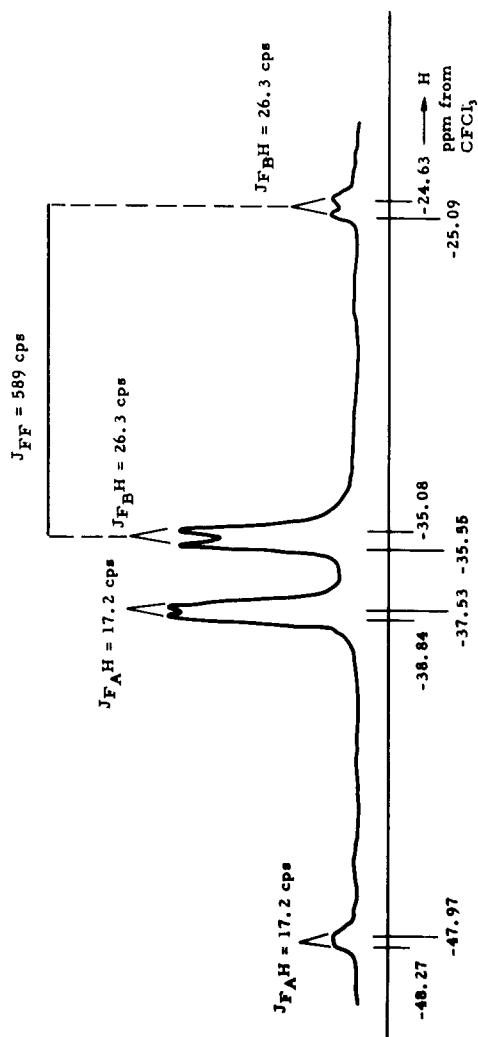


Figure 3. F^{19} NMR Spectrum of cis-1,2-Bis(difluoramino)cyclohexane

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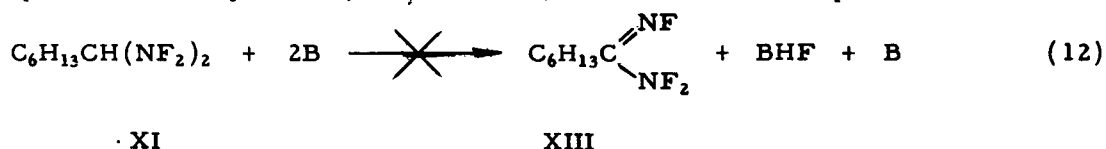
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D. DEHYDROFLUORINATION REACTIONS

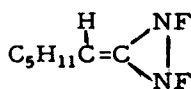
1. 1,1-Bis(difluoramino)heptane

The basic ion-exchange resin (weak base type) which has proven to be an effective reagent for the dehydrofluorination of 1,2-bis(difluoramino)cyclohexane and 1,2- and 1,4-bis(difluoramino)cyclohexenes (Ref 10) was applied in the dehydrofluorination of 1,1-bis(difluoramino)heptane (XI). Using the customary two-fold excess of resin, a liquid compound 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 (XIV) included, in addition to the expected C-H

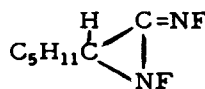


and N-F absorptions, a band at 1642 cm^{-1} indicating unsaturation ($\text{C}=\text{C}$ or $\text{C}=\text{N}$) and a strong sharp band at 1550 cm^{-1} , probably due to a ring vibration (Figure 6).

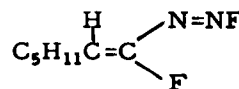
Several plausible structures can be postulated for a compound having these features and the empirical formula $\text{C}_7\text{H}_{12}\text{N}_2\text{F}_2$. Mass spectral evidence



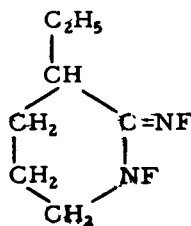
XIV a



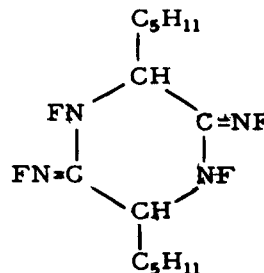
XIV b



XIV c



XIV d



XIV e

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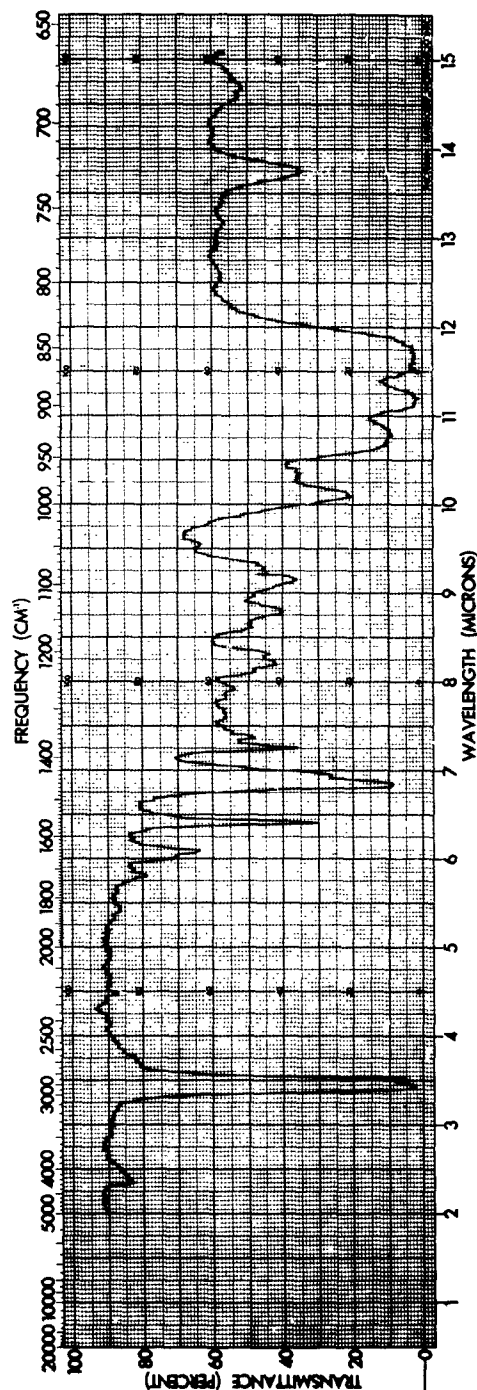


Figure 6. Infrared Spectrum of Dehydrofluorination Product
From 1,1-Bis(difluoramino)heptane

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(Table II) effectively eliminates any dimeric structure such as XIV e, since no mass peaks greater than 162 were observed. The boiling point (35-38°/2.5 mm; 61-63°/20 mm) was in accord with this conclusion. The ϵ -elimination necessary for the formation of XIV d, although favored sterically, would not have any great driving force due to electronic influences, and this structure can probably be discounted.

TABLE II
PARTIAL MASS SPECTRUM OF
DEHYDROFLUORINATION PRODUCT (XIV)

<u>m/e</u>	<u>Relative Intensity</u>	<u>Assignment</u>
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	$C_6H_{12}N^+$
110	2.6	$C_7H_{12}N^+$
129	6.2	$C_7H_{12}NF^+$
162	2.2	$C_7H_{12}N_2F_2^+$

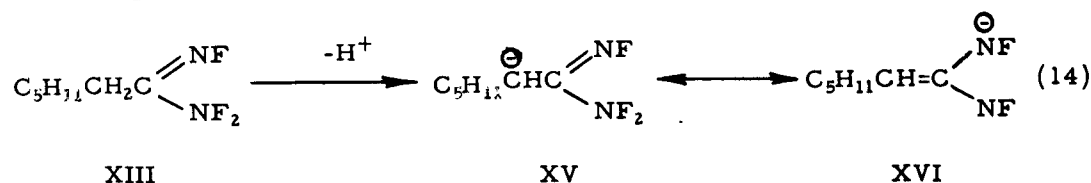
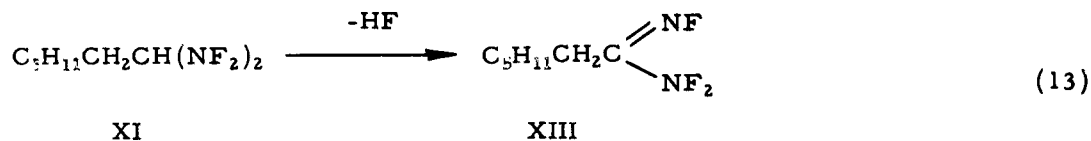
The detection of unsaturated fragments in the mass spectrum tends to favor structures XIV a and XIV c. The proton NMR spectrum, on the other hand, failed to show any olefinic C-H. The F^{19} NMR spectrum included resonance peaks at -45.9, -42.5, -16.1 and 9.8 ppm from $CFCl_3$, attributable to N-F, and a weak triplet at +138.6 ppm, possibly due to C-F. It is not possible to rationalize all of this evidence and select a single unambiguous structure at this time. Gas chromatographic analysis, in fact, indicates the possible presence of a second component; further investigation is required.

Reasonable mechanistic routes to the three plausible structures can be suggested. One may assume the initial formation of the amidine (XIII) via

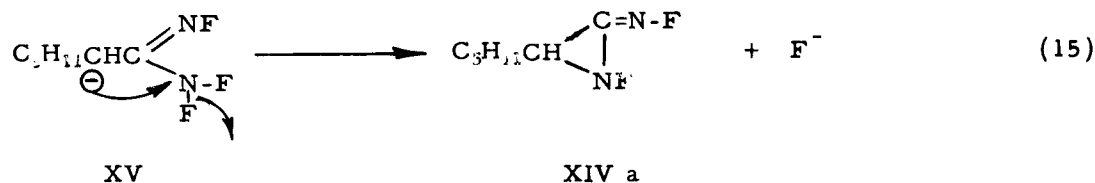
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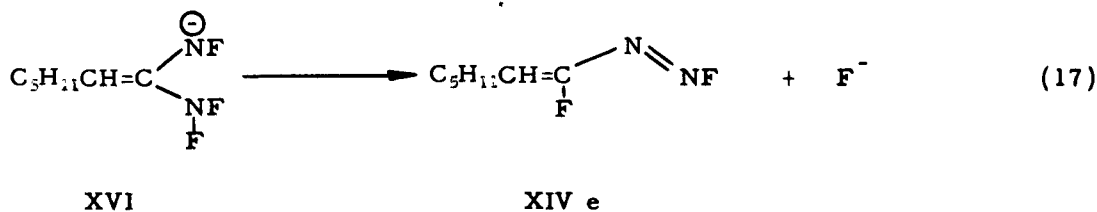
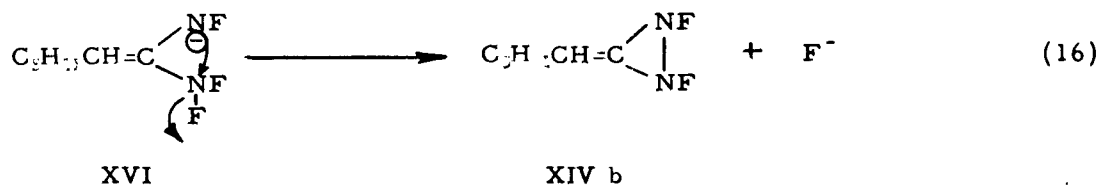
normal E2 elimination, and subsequent removal of the α -proton which would be expected to be activated by the electronegativity of the difluoramino and fluorimino groups. The carbanion (XV) can rearrange via an internal



nucleophilic attack ($\text{S}_{\text{N}}1$) on nitrogen; subsequent elimination of fluoride ion would result in the formation of XIV a.



The second canonical form of the ion (XVI) might react similarly to give the other cyclic product (XIV b). The ion XVI might also rearrange by means of a fluoride-shift to produce the acyclic structure XIV c. The latter process,

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if it occurs, would be a complex one, possibly involving a nitrene intermediate.

When the reaction described above was repeated, using a single equivalent of ion exchange resin and maintaining the reaction temperature at 16-20°C, 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; further work is needed in this area.

2. 1,2-Bis(difluoramino)cyclohexane

Several compounds have been dehydrohalogenated by reaction with ethyl-diisopropylamine (Ref.11) and the application of this reagent to a difluoramino compound was examined briefly during the report period. The amine did indeed prove to be useful in this connection since an 83% yield of 1,2-bis(fluorimino)-cyclohexane was obtained upon refluxing an ether solution of the amine and a cis-trans mixture of 1,2-bis(difluoramino)cyclohexane.

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III. EXPERIMENTAL

A. ATTEMPTED REACTION OF 1,2-BIS(FLUORIMINO)CYCLOHEXANE WITH PERFLUOROGUANIDINE

1. The fluorimine (1.35 gm, 9.1 mmoles), 1 gm urea, and 10 ml Freon-113 were placed, with a small magnetic stirring bar, in a glass pressure reactor (Fisher-Porter) which was cooled to -78° and evacuated. Perfluoroguanidine (25 mmoles) was then condensed into the reactor at -115° . The vessel was placed in a water-ice bath and allowed to warm to room temperature during a period of 20 hours. Residual pressure (at 0°) was 375 mm.

Unreacted PFG was flushed from the system, the residue treated with water, and the layers separated. The aqueous fraction was washed with CH_2Cl_2 and the combined organic solution dried over Na_2SO_4 and evaporated. The residual liquid (1.30 gm, 95%) was identified as starting material by its infrared spectrum.

2. A similar mixture containing 1.30 gm of the fluorimine and no urea was treated in the same fashion. Recovery of starting material amounted to 1.00 gm (77%).

B. ATTEMPTED REACTION OF 1,2-BIS(FLUORIMINO)CYCLOHEXANE WITH ISOCYANIC ACID

A Vycor tube (52.5 x 1.13 cm) was charged with 2.6 gm (0.02 mole) of cyanuric acid. The tube was placed in a Sargent Micro Combustion Apparatus and the outlet connected, by means of a ball joint, to a trap maintained at -78°C . A stream of dry N_2 was passed through the tube and the ovens were turned on. Both ovens were maintained at $500\text{--}600^{\circ}\text{C}$ for 30 minutes. The isocyanic acid which collected in the -78°C trap was purified by trap-to-trap distillation in a vacuum system. The pure isocyanic acid was then condensed into a two liter bulb containing 1.46 gm (0.01 mole) of 1,2-bis(fluorimino)cyclohexane. The mixture was held at -196°C for 20 minutes and then at -78°C for one hour. When the cooling bath was removed a clear homogeneous liquid phase was present in the trap but as the mixture warmed to room temperature a white solid formed. After standing overnight at room temperature, the bulb was not found to contain

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any gas. Most of the white solid was insoluble in CCl_4 and CH_2Cl_2 . Infrared analysis of the liquid residue from the organic solution showed it to be the starting fluorimino compound and the white solid was identified as cyanuric acid.

C. REACTION OF 1,2-BIS(FLUORIMINO)CYCLOHEXANE WITH SODIUM HYDROXIDE

1. A mixture of 1.46 gm (0.010 mole) of 1,2-bis(fluorimino)cyclohexane and 50.00 ml of 0.4995 N sodium hydroxide solution was stirred at room temperature for 48 hours. The color changed from pale yellow to red during the first 30 minutes and the mixture became homogeneous. The mixture was titrated potentiometrically with 0.4321 N HCl and was found to have inflections at pH of 7.25 (5.185 meq) and 5.30 (8.210 meq). Thus 19.80 meq of sodium hydroxide was consumed in the reaction, 3.025 meq being used to form the salt of a carboxylic acid. The acidified solution (pH = 2.0) was extracted with ether and CH_2Cl_2 . The combined organic extract was dried over sodium sulfate and evaporated to dryness to yield only a small amount of Kel-F grease. The aqueous solution was diluted to 500 ml and found to contain 420 mg (113%) of fluoride ion.

2. A mixture of 0.2 gm of 1,2-bis(fluorimino)cyclohexane and 12.00 ml of 0.500 N sodium hydroxide solution was stirred at 40°C for 24 hours. The color changed from pale yellow to orange and the mixture became homogeneous. The solution was titrated with 0.4921 N hydrochloric acid solution to the phenolphthalein end point and was found to require 6.0 ml. The acidified solution was extracted with ether and methylene chloride as before but only Kel-F grease was obtained. The solution was diluted to 250 ml and was found to contain 46.3 mg (90%) of fluoride ion.

D. PHOTOLYSIS OF 1,4-BIS(FLUORIMINO)CYCLOHEXENE-2

A 450 watt high-pressure mercury arc lamp (Hanovia No. 679A-36) with a water-cooled quartz immersion well having a 60/50 standard-taper joint has been obtained. A glass reactor was fabricated to fit as closely as possible (approximately 1 mm) to the sidewalls of the well. The reactor with well in place held 60 ml of liquid, about 1/3 of which was exposed to the direct rays of the lamp.

A solution of 0.72 gm (5 mmoles) of the bis(fluorimine) in 65 ml of reagent grade cyclohexane was prepared, and 5 ml was retained as a spectrophotometric reference. Upon irradiation of the remaining 60 ml at 20°, a distinct discoloration was apparent after 5-10 minutes. The solution became yellow and a brown

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solid was deposited on the walls of the quartz well. Five brief exposures were given with intermittent mixing. Evaporation of the filtered cyclohexane solution gave a pasty solid from which colorless crystals of starting material were obtained by trituration with pentane. Identification of the insoluble brown solid and the yellow solute have not yet been completed.

E. 1,1-BIS(DIFLUORAMINO)HEPTANE

1. Difluoramine was generated in the usual manner (Ref 12) by the acid hydrolysis of 30 gm of N,N-difluorourea in aqueous solution. The difluoramine-carbon dioxide mixture was passed through a drying tube and into a flask containing 5 ml of 105% fuming sulfuric acid and equipped with a Dry-Ice condenser. After all of the difluoramine had been generated, a solution of 6.0 gm (0.053 mole) of *n*-heptanal in 14 ml of Freon-113 was added dropwise to the mixture with stirring at 0°C. The mixture was stirred at 0°C for four hours. After the system was flushed with nitrogen to remove unreacted difluoramine, water was added and the organic layer separated. The aqueous layer was washed with methylene chloride, the organic solution dried over anhydrous magnesium sulfate and the solvents removed by evaporation. The residue was distilled to yield 4.02 gm (0.02 mole, 38%) of 1,1-bis(difluoramino)heptane, bp 58-58.5° (12 mm); n_D^{25} 1.3830 [Lit. (ref 8) n_D^{20} 1.3824]. The distillation was continued

Anal. Calcd. for $C_7H_{14}N_2F_4$: C, 41.58; H, 6.98; N, 13.85.

Found: C, 41.69; H, 7.05; N, 13.91.

and 1.65 gm of colorless liquid, bp 86-7°C (0.1 mm); n_D^{20} 1.4133, was obtained. The infrared spectrum showed absorptions indicative of an ether-containing an N-F group. The compound was assigned the structure bis(1-difluoraminoheptyl) ether.

Anal. Calcd. for $C_{14}H_{28}N_2F_4O$: C, 53.15; H, 8.92; N, 8.85.

Found: C, 53.17; H, 8.85; N, 8.90.

F^{19} NMR spectra were taken on a Varian Associates DP-60 spectrometer at 56.4 megacycles/sec. The samples were examined in 33-50% $CFCl_3$ solution containing 1-2% tetramethylsilane. The spectrum of the ether exhibited an extraordinary AB quartet with the following spectral constants: $J_{FF} = 596$ cps; $J_{FB}H = 17.3$ cps; $J_{FA}H = 19.7$ cps; $\Delta\nu = 73$ cps or 1.29 ppm. The smaller splittings are due to spin-spin interaction of the fluorine atoms with the hydrogen gem to the NF_2 group.

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2. Difluoramine was generated in the same manner as described in (1). However, only 3.0 gm (0.026 mole) of heptanal was used. The product was worked up as above and 2.50 gm (47%) of 1,1-bis(difluoramino)heptane and 0.15 gm (1%) of bis(1-difluoraminoheptyl)ether were obtained.

F. REACTION OF 1,1-BIS(DIFLUORAMINO)HEPTANE WITH AMBERLITE IR-45

1. A solution of 6.22 gm (0.031 mole) of 1,1-bis(difluoramino)heptane in 100 ml of ether was added to 12.0 gm (0.060 mole) 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 minutes. The mixture gradually cooled to room temperature and stirring was continued for 24 hours. The resin was filtered off and the ether solution evaporated to dryness. The residue was distilled to yield 1.5 gm of colorless liquid, bp 35-38° (2.5 mm). The -78°C trap was found to contain

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

an additional quantity of the product. This liquid was combined with the above product and distilled to yield 2.3 gm (46%) of colorless liquid, bp 61-3°C (20 mm). The compound was subjected to infrared, NMR, and mass spectral analysis

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 gm (5 mmoles) in 250 ml ethyl ether was added 1.00 gm (nominally 5 meq.) of Amberlite IR-45 and the mixture was stirred for 64 hours at 16-20° (water bath). The reaction mixture was worked up as described in (1) to give 0.75 gm 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} .

G. REACTION OF 1,2-BIS(DIFLUORAMINO)CYCLOHEXANE WITH ETHYLDIISOPROPYLAMINE

A mixture of 1.0 gm (5.4 mmoles) of 1,2-bis(difluoramino)cyclohexane, 1.4 gm (10.8 mmoles) of ethyldiisopropylamine (Ref 10) and 25 ml of ethyl ether was refluxed for 20 hours. A viscous brown oil had separated out at the end of this time. The mixture was treated with water and the aqueous solution extracted with ether. The combined ether extracts were dried over magnesium sulfate and evaporated to dryness to yield 0.65 gm (83%) of yellow liquid. The infrared

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spectrum of this product was almost identical to that of pure 1,2-bis(fluorimino)-cyclohexene.

H. 1,4-BIS(FLUORIMINO)CYCLOHEXENE-2 AND 1,2-BIS(FLUORIMINO)CYCLOHEXENE-3

The procedure described in Reference 9 was used to effect the reaction of 25.0 gm (0.312 mole) of 1,3-cyclohexadiene with 33.3 gm (0.320 mole) of tetrafluorohydrazine in 10 runs. The crude organic difluoramino mixture (50 gm) was dissolved in 50 ml of ether and added dropwise with cooling to a mixture of 110 gm (0.55 mole) of Amberlite IR-45 ion-exchange resin in 500 ml of ether. The temperature was maintained at 10-15°C during the addition and was allowed to warm gradually to room temperature. After stirring for 24 hours the resin was filtered off and the ether evaporated. The residue was triturated with pentane to yield 7.25 gm (16.1% overall yield) of 1,4-bis(fluorimino)cyclohexene-2, mp 49.5-51°C. The pentane filtrates were combined and evaporated to dryness to yield 14.4 gm of brown liquid. Distillation of this liquid yielded 4.0 gm of unreacted difluoramino compound and 6.1 gm (13.6%) of 1,2-bis(fluorimino)cyclohexene-2; yellow liquid; bp 103-5° (11 mm); mp 15-7°C. The infrared spectrum was almost identical to that of the 1,4-isomer. The proton NMR spectrum has been described above.

Anal. Calcd. for $C_6H_6N_2F_2$: C, 50.00; H, 4.20; N, 19.44.

Found: C, 49.97; H, 4.26; N, 19.38.

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IV. FUTURE WORK

During the next quarter research effort will be devoted to the following areas:

- Identification of the product obtained by treating 1,1-bis(difluoramino)-heptane with an excess of basic ion-exchange resin.
- Synthesis of 1-difluoramino-1-fluoriminoheptane.
- Exploration of the addition reactions of the double bond in a trifluoroamidine.
- Photolysis and photochemically initiated reactions of 1,4-bis(fluorimino)-cyclohexene and related compounds.
- Preparation and purification of larger quantities of 1,1-bis(difluoramino)-heptane for study by the Naval Ordnance Laboratories and the Bureau of Mines.

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Section II

Task 52

SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

II. TASK 52

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Section II

SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

A. P. Kotloby

D. D. Perry

Report RMD 5043-Q2-64

RMD Project 5043, Task 52
Report Period: 1 April 1964
to 30 June 1964

Contract No. NONr 4364(00)
ARPA Order No. 417
Project Code 4910

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FOREWORD

This report describes the work carried out during the period from 1 April 1964 to 30 June 1964 on the synthesis of organodifluoramines for use in the study of structure-sensitivity relationships (RMD Project 5043, Task 52).

The following personnel contributed to this effort: D. D. Perry (Section Supervisor), A. P. Kotloby (Project Scientist), W. H. Wieting (Synthesis), R. N. Storey, and D. Z. Chowanec (Instrumental Analysis).

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I. INTRODUCTION

This portion of the advanced oxidizer research program deals with the synthesis phase of a study aimed at an understanding of the structural and chemical factors affecting sensitivity in organic difluoramines. One of the principal problems involved in the use of these compounds in propellant formulations is their sensitivity to stresses such as heat and mechanical shock. The evaluation of the sensitivity data gathered from a sufficiently large number of organodifluoramines representing a selection of structural types and functional groups is useful in guiding research toward the synthesis of compounds having a minimum degree of sensitivity in relation to their energy.

In accordance with this goal Thiokol Chemical Corporation, Reaction Motors Division has undertaken the task of preparing a variety of organic difluoramines for sensitivity evaluation by the Naval Ordnance Laboratory, White Oak, Silver Spring Maryland. These compounds have been selected on a systematic basis to provide information concerning the effect on sensitivity of such factors as the NF_2 -to-carbon ratio, the type of NF_2 substitution, and the presence of various organofunctional groups. The sensitivity of these compounds is being measured by the thermal explosion delay test (Ref 1). Some of the data obtained on N-F materials have been described by Rosen et al. (Ref 2) and presented at the Second Sensitivity Seminar (Ref 3). These results show some interesting and potentially valuable correlations between vicinally and geminally substituted organo-bis difluoramines). This work has been extended to include the study of highly energetic tris(difluoramino)methoxy derivatives which are produced via addition reactions of perfluoroguanidine. Our activities in the past three months have been confined to attempts to synthesize derivatives and purify them to > 99% by gas-liquid chromatography.

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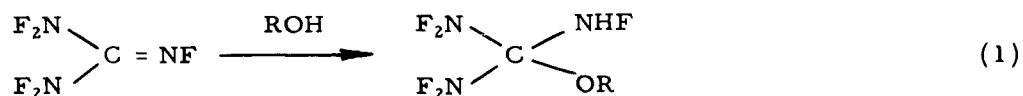
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II. DISCUSSION

A. SYNTHESIS OF TRIS(DIFLUORAMINO)METHOXYALKANES

The basic considerations in the selection of compounds to be used on this program have already been discussed in the previous report (Ref 4). During the past three months work was conducted mainly on the synthesis and purification of tris(difluoramino)methoxyalkanes. In addition, several chromatographically pure vicinal and geminal bis(difluoramino)-alkanes were prepared at the request of the Naval Ordnance Laboratory.

The nucleophilic addition reactions of perfluoroguanidine became known (Ref 5, 6, 7) soon after the compound was discovered (Ref 8).



Primary and secondary alcohols have been found to add readily and in high yields to the electron-deficient double bond in perfluoroguanidine.

In Table I are listed experimental conditions and the results obtained in the synthesis of the intermediate fluoramino adducts.

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TABLE I
EXPERIMENTAL CONDITIONS IN THE SYNTHESIS OF BIS(DIFLUORAMINO)FLUORAMINOMETHOXYALKANES

Alcohol	Moles	PFG (moles)	Freon-113 (ml)	Urea (gm)	Time (hr)	Temp (°C)	Yield (crude) (%)	Remarks
Butanol	0.03	0.05	10	1.0	16	0-23	---	Not isolated; fluorinated directly
Butanol	0.03	0.05	20	0.3	16	0-25	~90	Very shock sensitive; IR shows strong NH absorptions at 3300cm ⁻¹
Pentanol	0.05	2x0.015	10	---	32	20	0	Starting material recovered
Pentanol	0.045	0.05	10	1.0	16	24	---	Not isolated; fluorinated directly
Pentanol	0.03	0.05	20	0.3	16	0-32	83	Shock sensitive; NH absorption at 3300cm ⁻¹
Pentanol	0.03	0.05	20	0.3	16	0-36	92	Shock sensitive; NH absorption at 3300cm ⁻¹
Pentanol	0.03	0.05	20	0.3	16	0-36	92	Shock sensitive; NH absorption at 3300cm ⁻¹
3-Pentanol	0.03	0.05	10	0.3	16	0-25	90	Shock sensitive; NH absorption at 3300cm ⁻¹
Hexanol	0.03	0.05	20	0.3	16	0-23	---	Not isolated; fluorinated directly
Hexanol	0.03	0.05	20	1.0	16	0-27	89	Not isolated; fluorinated directly
Hexanol	0.03	0.05	20	0.3	---	---	---	Glass reactor broke
Hexanol	0.03	0.05	10	0.3	16	0-28	82	Shock sensitive; strong NH absorption at 3300cm ⁻¹
Hexanol	0.03	0.05	20	0.3	16	0-31	82	Shock sensitive; strong NH absorption at 3300cm ⁻¹
2-Hexanol	0.03	0.05	10	1.0	16	0-21	---	Not isolated; fluorinated directly
2-Hexanol	0.03	0.05	10	0.3	---	---	---	Explosion during condensation of PFG
3-Hexanol	0.03	0.05	10	0.3	16	0-19	---	Shock sensitive; strong NH absorption at 3300cm ⁻¹
Heptanol	0.03	0.05	10	1.0	16	0-26	---	Borderline sensitivity; strong NH absorption at 3300cm ⁻¹
Heptanol	0.03	0.05	20	0.3	32	0-29	99	Borderline sensitivity; strong NH absorption at 3300cm ⁻¹
Heptanol	0.03	0.05	20	0.3	16	0-28	---	Borderline sensitivity; strong NH absorption at 3300cm ⁻¹
Octanol	0.03	0.05	10	1.0	16	0-28	100	No fire under hammer; NH absorption at 3300cm ⁻¹
Octanol	0.03	0.06	20	1.0	16	0-23	90	No fire under hammer; NH absorption at 3300cm ⁻¹
Octanol	0.03	0.05	20	1.0	16	0-22	86	No fire under hammer; NH absorption at 3300cm ⁻¹
Nonanol	0.04	0.06	---	1.0	---	25	---	Acetonitrile (10 ml) used instead of Freon-113; explosion soon after reaction started
Nonanol	0.04	0.06	10	1.0	16	0-29	---	No fire under hammer; NH absorption at 3300cm ⁻¹
Nonanol	0.03	0.05	10	1.0	16	0-30	95	No fire under hammer; NH absorption at 3300cm ⁻¹

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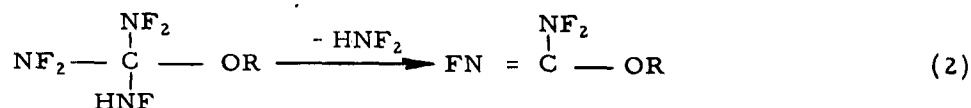
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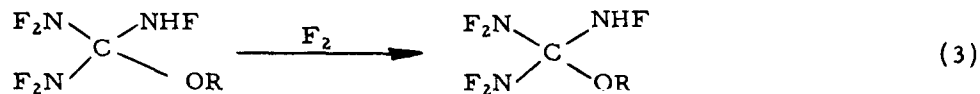
The uptake of perfluoroguanidine in these reactions was nearly quantitative. The infrared spectral analysis of the residual gas at the end of the reaction period showed it to be unreacted perfluoroguanidine contaminated with traces of Freon-113 which was used as a solvent. The amount of perfluoroguanidine remaining corresponded approximately to its excess over the quantity theoretically required by the stoichiometry of the reaction.

The addition of urea is known to facilitate this reaction (e.g., Ref 6). Although no optimum concentrations have been determined, the addition of 0.3 gm urea per 0.03 mole of alcohol proved to be sufficient. In one case where no urea was added, the starting materials were recovered at the end of 32-hours.

The fluoramino adducts from alcohols up to C₈ were sensitive to impact and could be detonated in a crude hammer test; those made from C₈ - C₉ alcohols did not fire. The adducts could be distilled without decomposition under reduced pressure, but they had only a limited stability when stored at 0 - 5° in glass containers. The infrared spectrum of freshly prepared materials showed, in addition to N-F absorptions (10.3, 11.1, 11.6μ), strong absorptions at 3.04μ corresponding to the N-H stretching. A partly decomposed sample showed the presence of the C = N bond at 5.96 - 6.10μ, indicating the elimination of the difluoramine from the molecule as shown in equation 2:



The bis(difluoramino)fluoraminomethoxy derivatives were fluorinated by bubbling fluorine, diluted to 2% by volume with nitrogen, into the solution at 0°. Table II presents the data obtained in the fluorination reactions.



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TABLE II
EXPERIMENTAL CONDITIONS IN THE SYNTHESIS OF TRIS(DIFLUORAMINO)METHOXYALKANES

$\begin{array}{c} \text{F}_2\text{N} \quad \text{NHF} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{F}_2\text{N} \quad \text{OR} \end{array}$					$\begin{array}{c} \text{F}_2\text{N} \quad \text{NF}_2 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{F}_2\text{N} \quad \text{OR} \end{array} \quad (\text{crude})$				
where R =	BP (°C/mm Hg)	Freon-113 (ml)	Acetonitrile (ml)	NaF (gm)	Yield (%)	BP (°C/mm Hg)	Remarks		
-(CH ₂) ₁ CH ₃	---	10	---	---	---	51-52/10.3	Very shock sensitive, IR shows absorptions due to NH, NF and possibly CF		
-(CH ₂) ₂ CH ₃	52-53/4.2	---	20	---	68	44-48/6.0	Analysis pending; F ₂ adduct (mole ratio is 2)		
-(CH ₂) ₄ CH ₃	---	10	---	---	---	---	Shock sensitive, g.c. shows two major components identified by IR as a mixture of C-NH and C-NF ₂ derivatives		
-(CH ₂) ₆ CH ₃	46/1.0	---	20	2	69	40/6.5	Shock sensitive, g.c. shows two major components identified by IR as C=NF (1640-1680cm ⁻¹) NH (3300cm ⁻¹)		
-(CH ₂) ₈ CH ₃	38-40/1.4	---	20	2	40	---	Shock sensitive; g.c. shows two major components identified by IR as C=NF (1640-1680cm ⁻¹) NH (3300cm ⁻¹)		
-(CH ₂) ₁₀ CH ₃	59-63/5.6	---	20	---	95	52-53/4.2	Shock sensitive; g.c. shows two major components identified by IR as C=NF (1640-1680cm ⁻¹) NH (3300cm ⁻¹)		
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}(\text{CH}_2)_2\text{CH}_3 \end{array}$	---	10	---	---	---	---	Analysis pending		
$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{CH} \\ \\ \text{CH}_2\text{CH}_3 \end{array}$	---	20	---	---	---	---	Analysis pending		
-(CH ₂) ₃ CH ₃	---	20	---	---	89	41-43/0.3	Analysis pending		
-(CH ₂) ₅ CH ₃	48-50/1.6	---	20	2	30	44-47/4.1	Analysis pending		
-(CH ₂) ₇ CH ₃	46-50/1.6	---	20	2	72	44-47/4.1	Analysis pending		
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}(\text{CH}_2)_2\text{CH}_3 \end{array}$	---	10	---	---	99	34/0.4	Analysis pending		
$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{CH}(\text{CH}_2)_2\text{CH}_3 \end{array}$	---	10	---	---	98	42-46/6.7	Analysis pending		
-(CH ₂) ₄ CH ₃	---	10	---	---	92	48-52/0.3	Borderline sensitivity, strong (IR) absorption in the N-H region and trace of C=N		
-(CH ₂) ₆ CH ₃	58-60/0.4	---	20	2	70	42/0.5	Borderline sensitivity, strong (IR) absorption in the C-N region, no NH		
-(CH ₂) ₈ CH ₃	50-52/0.2	---	20	2	68	42/0.5	Borderline sensitivity, strong (IR) absorption in the C-N region, no NH		
-(CH ₂) ₁₀ CH ₃	---	10	---	---	42	58-66/0.5	No fire under hammer, IR shows small absorption due to N-H, C=N, and N-F		
-(CH ₂) ₁₂ CH ₃	62-66/0.5	---	20	2	36	58/0.25	No fire under hammer, IR shows small absorption due to N-H, C=N, and N-F		
-(CH ₂) ₁₄ CH ₃	55-58/0.7	---	20	2	85	61-62/0.4	No fire under hammer.		
-(CH ₂) ₁₆ CH ₃	77-79/0.45	---	20	2	---	68-70/0.25	No fire under hammer, IR absorptions corresponding to C=N and C-F vibrations		
-(CH ₂) ₁₈ CH ₃	---	10	---	---	100	70-78/0.7	No fire under hammer, IR absorptions corresponding to N-H and C-F vibrations		

Note: F₂ adduct (mole ratio) is 1 in all cases except as noted in Remarks

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There was no significant difference in results obtained whether Freon-113 or acetonitrile was used as solvent, although the presence of NaF (as an HF scavenger) in the reaction mixture in many instances resulted in the loss of HNF_2 from the molecule. If NaF was added at room temperature to the solution of the fluoramino adduct, an exothermic reaction began immediately accompanied by HNF_2 evolution. The infrared spectrum showed the disappearance of the N-H stretching (3.04μ) in the spectrum of the starting material and the appearance of a strong absorption of $5.96 - 6.10\mu$ ($\text{C}=\text{N}$). The elimination of NaF from the reaction did not completely prevent the formation of the fluorimino derivative.

In addition to the starting material and the fluorimino compound, the other main byproducts in this synthesis were the tris(difluoramino)methoxyalkanes in which the alkyl chain of the molecule was partially fluorinated. No separation of these impurities could be effected by simple vacuum distillation. Because the objective of this program is to obtain products of >99% purity, a preparative gas chromatograph was purchased solely for use on this project. Since then efforts have been concentrated on the search for the optimum conditions for purifying the tris-compounds. The conditions (see Table III) are being worked out for a single compound, tris(difluoramino)methoxypentane.

TABLE III
VAPOR PHASE CHROMATOGRAPHIC CONDITIONS FOR PURIFICATION
OF TRIS(DIFLUORAMINO)METHOXPENTANE

Liquid Phase (%)	Solid Phase (mesh)	Column material (length x diameter)	Column Temp. (°C)	Remarks
SF-96 Methyl Silicone Fluid 20	Chromosorb P, regular 30-60	Al 20 ft x 3/8 in.	130	Decomposition: no separation
SF-96 Methyl Silicone Fluid 20	Chromosorb P, regular 30-60	Cu 20 ft x 3/8 in.	130	Too long retention time, no resolution. possible decomposition
Kel-F Oil No. 10 20	Chromosorb P, acid washed	Cu 6 ft x 1/4 in.	75	Poor resolution
SF-96 Methyl Silicone Fluid 20	Chromosorb P, acid washed	Cu 6 ft x 1/4 in.	75	Two major components; long retention time
SF-96 Methyl Silicone Fluid 20	Chromosorb P, acid washed	Cu 3 ft x 6 ft	75	Two major components; total retention time of ca. 70 min. Infrared spectra of both fractions indicate need for further purification

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As may be seen from the summary in Table III, the best separation was obtained so far with a 3 ft. x 1/4 in. Cu column filled with acid-washed Chromosorb P coated with SF-96 Silicone Oil. Copper tubing, prior to being charged with chromatographic material, was pressurized with fluorine and left overnight. The passivated column produced less decomposition of the tris-compound. At present a quantity of the two fractions is being accumulated for a second pass through the chromatographic column. The pure fractions will then be identified by the NMR or infrared spectral analysis.

B. SYNTHESIS OF BIS(DIFLUORAMINO)ALKANES

In addition to the main work on the synthesis and purification of tris-compounds, work was carried out on the synthesis of some additional bis-difluoramines which had been requested by the Naval Ordnance Laboratory. These compounds are listed in Table IV.

TABLE IV

BIS(DIFLUORAMINO)ALKANES

<u>Compound</u>	<u>BP</u> <u>°C/mm Hg</u>	<u>Remarks</u>
1,2-Bis(difluoramino)cyclohexane	41.0/50	23 gm separated on SF-96 Chromosorb P column to give 15 gm of chromatographically pure <u>cis</u> - and <u>trans</u> -mixture.
1,1-Bis(difluoramino)propane	31.0/160	6.3 gm chromatographically purified to give 0.5 gm of >99% pure cpd.
Ethyl 2,3-Bis(difluoramino)-butyrate	50.0/6	Purification by g.c. resulted in loss of NF ₂ groups.
1,1-Bis(difluoramino)hexane	53.0/25	Insufficient quantity-synthesis will be repeated.

The experimental procedure used in the preparation of these compounds has been described earlier in this program (Ref 9). Both compounds, after purification on a regular fire brick column (30/60 mesh) with Methyl Silicone Oil SF-96 (20%) as the liquid phase (column temperature 95°) were submitted to the Naval Ordnance Laboratory for sensitivity measurements.

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III. EXPERIMENTAL

A. MATERIALS

The perfluoroguanidine used in our work was obtained from the American Cyanamid Company. The compound was stored in a low-carbon steel cylinder at ambient temperature under 200-300 mm Hg pressure. After about three months of storage the gas mixture in the cylinder, according to its mass spectrum, had the following composition: perfluoroguanidine 81.6%, tris(difluoramino) fluoromethane 4.3%, SiF_4 0.6%, NO 2.3%, CO_2 2.2%, unknown 9.0%. Before each experiment the mixture after purification by trap-to-trap distillation at -120° , consisted of 94-98% perfluoroguanidine and traces of tris(difluoramino)fluoromethane. No decomposition of purified perfluoroguanidine was observed when the gas was stored at ambient temperature in Pyrex glass bulbs for 2-3 days.

Eastman reagent grade alcohols were used without further purification.

B. SYNTHESIS OF TRIS(DIFLUORAMINO)METHOXYALKANES

Onto a twice-degassed solution of an alcohol (0.03 mole) in 20 ml Freon-113 containing 0.3 gm of urea cooled to -120° (Freon-113/liquid N_2 slush bath) was condensed 0.05 mole of perfluoroguanidine (94-98% pure). The reactor was cooled and allowed to gradually come to 0° while being stirred with a Teflon-coated magnetic bar; after about an hour the reactants were brought to room temperature and kept so overnight. The uptake of perfluoroguanidine was nearly quantitative. The small excess of perfluoroguanidine was then removed, the solution flushed with dry nitrogen and the pressure in the reactor was brought to atmospheric. The solution was filtered, Freon-113 was stripped off, and the product diluted with 20 ml acetonitrile. Through the solution kept overnight at 0° was passed dilute fluorine (2% by vol. in N_2 0.04 mole of F_2). The solution of crude tris(difluoramino)methoxyalkane was flushed with nitrogen, stripped of the solvent under 10-20 mm Hg pressure, and distilled through a 10-inch glass column under reduced pressure.

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IV. FUTURE WORK

During the next quarter research effort will be devoted to the following areas:

- To continue the synthesis of tris(difluoramino)methoxyalkanes
- Vapor phase chromatographic purification of the tris-adducts
- The preparation of vicinal or geminal bis(difluoramino)alkanes as may be requested by the Naval Ordnance Laboratory

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Section III

Task 53

CHEMISTRY OF THE OXYGEN SUBFLUORIDES

Section III

CHEMISTRY OF THE OXYGEN SUBFLUORIDES

S. I. Morrow
A. R. Young

Report RMD 5043-Q2-64

RMD Project 5043, Task 53
Report Period: 1 April 1964
to 30 June 1964

Contract No. NONr 4364(00)
ARPA Order No. 417
Project Code 4910

FOREWORD

This section of the report summarizes the results of studies of the chemistry of dioxygen difluoride and of dioxygenyl salts during the period from 1 April 1964 to 30 June 1964. This program was monitored by Mr. R. Hanson of the Office of Naval Research.

Personnel contributing to these studies were: A. R. Young (Project Supervisor), S. I. Morrow (Principal Investigator), K. Tiger, J. Crothamel, R. Storey and R. Crooker.

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I. INTRODUCTION

The chemistry of dioxygen difluoride has been extensively explored for routes to new inorganic oxidizers. The most significant accomplishment of this research program was the discovery that reactions of dioxygen difluoride with arsenic pentafluoride and with antimony pentafluoride produce thermally stable salts of the dioxygenyl cation (O_2^+). It was thought that this discovery had opened a route to a new class of high-energy, solid oxidizers. However, attempts to prepare dioxygenyl salts of anions such as ClF_4^- , ClO_4^- , NO_3^- , and $C(NO_2)_3^-$, either by direct reactions of O_2F_2 or by metathetical conversion of O_2AsF_6 , have been unsuccessful. Since this approach to new high energy oxidizers appears to be unpromising, we have abandoned our studies of dioxygenyl salts and are seeking new reactions of the oxygen subfluorides that might lead us to high energy oxidizers. We have recently initiated a study of the chemistry of trioxygen difluoride in the hopes that this paramagnetic compound will exhibit a chemistry quite different from that of dioxygen difluoride.

Large transparent crystals of XeF_2 were obtained from the white solid (equation 1) by heating it to 50°C in a vacuum; the crystals condensed onto the cooler, upper surfaces of the Kel-F reactor. These crystals were identified as XeF_2 by means of single crystal x-ray analysis performed by Drs. W. Hamilton and J. Ibers of Brookhaven National Laboratories.

Although we were unable to isolate a significant amount of the liquid product (equation 1) for characterization, we did determine that it contains oxygen as well as xenon and fluorine. The reaction tube, which contains predominantly XeF_2 at room temperature, slowly evolves Xe , O_2 , and F_2 on standing. Since XeF_2 and XeF_4 are thermally stable, we thought it possible to deduce the composition of the unstable component from an analysis of the gas phase. The results of several such analyses were not reproducible and empirical formulas ranging from $\text{Xe}_{1.3}\text{OF}$ to $\text{Xe}_{2.7}\text{O}_2\text{F}$ were obtained. This variation could have been caused by the presence of two or more unstable compounds which were not always present in the same ratio.

2. Attempted Reaction of Krypton with O_2F_2

Since the ionization potential of krypton is less than 20% higher than that of xenon, we anticipated that O_2F_2 might be capable of oxidizing it to fluorides or oxyfluorides, as was the case with xenon. However, when the reaction of krypton and O_2F_2 was attempted under conditions similar to those used for xenon, the krypton was completely recovered. Since VonGrosse et al. have reported the synthesis of KrF_2 by passing Kr and F_2 through a discharge tube at -80°C (Ref 2), it is felt that O_2F_2 (a discharge product) should be capable of fluorinating krypton. It is possible that we failed to obtain sufficient contact of the reagents.

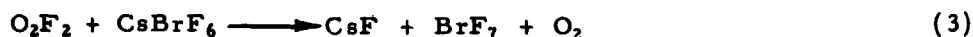
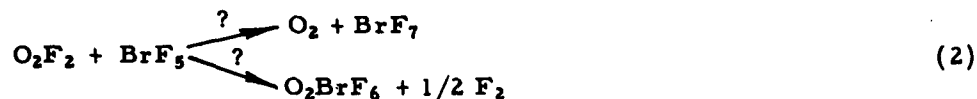
3. Attempted Reaction of Argon with O_2F_2

Although it was questionable whether O_2F_2 would react with argon (ionization potential almost 50% greater than xenon), this reaction was of sufficient interest, because of the low atomic weight of argon, to make it worthwhile evaluating. Argon and O_2F_2 were kept in contact with each other at -118°C for two hours. No evidence of reaction was detected.

B. REACTIONS of O_2F_2 WITH HALOGEN COMPOUNDS

In our efforts to uncover reactions of O_2F_2 leading to new oxidizers we investigated the reactions of O_2F_2 with BrF_3 , CsBrF_6 , and with Cl_2 in the

presence of CsF. The objectives of these reactions were to prepare new interhalogens, dioxygenyl salts, or oxyfluorides as shown in equations 2 through 4.



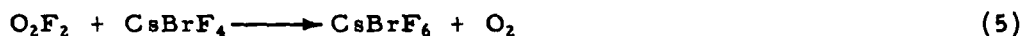
1. Attempted Reaction of O_2F_2 with BrF_5

Bromine pentafluoride was treated with dioxygen difluoride at -78°C . It was hoped that the low temperature at which O_2F_2 acts as a fluorinating agent would permit isolation of BrF_7 , which up to now has never been observed in high temperature $\text{Br}_2\text{-F}_2$ systems. The mixture was allowed to stand overnight at -78°C . After F_2 , O_2 , and unreacted O_2F_2 were removed from the system, the liquid residue was analyzed by nuclear magnetic resonance spectroscopy. The only constituents were BrF_5 and traces of HF . After the BrF_5 was pumped out of the reactor there was a trace of white solid left which evolved BrF_3 and oxides of nitrogen on heating. The solid was probably the known compound, NO_2BrF_4 . Traces of NO_2 and/or NO are often present in samples of O_2F_2 .

2. Attempted Reaction of CsBrF_6 with O_2F_2

An alternate approach to BrF_7 might be to fluorinate a BrF_6^- salt. Again we thought that the low temperatures at which O_2F_2 releases active fluorine should make this an ideal reagent for the preparation of BrF_7 . The preparation of CsBrF_6 was attempted by heating CsF and BrF_5 to 140°C in a Monel cyclinder for several hours. Since the loss of BrF_5 indicated conversion to the desired product, a sample of the solid recovered from the cyclinder was treated with O_2F_2 at -78°C . However, x-ray analysis of the solid used in the O_2F_2 reaction showed that it was not, in fact, CsBrF_6 . The material obtained after reaction of the $\text{BrF}_5\text{-CsF}$ product with O_2F_2 was identified by x-ray analysis as CsBrF_6 .

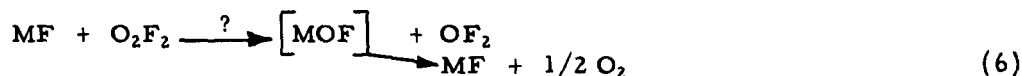
It is believed that the initial product of the high temperature CsF-BrF₅ reaction was CsBrF₄ which was converted to CsBrF₆ as shown in equation 5.



The CsBrF₆ was subjected to repeated contact with freshly prepared O₂F₂ at -78°C without any evidence of further reaction.

3. Reaction of Cl₂ with O₂F₂ in the Presence of CsF

Since various reactor materials as well as the conditions of their surfaces are known to significantly alter the rate of decomposition of O₂F₂, it was thought possible that certain solid compounds might also alter the mechanism of decomposition of O₂F₂ in such a way as to provide -OF groups. For example, a metal fluoride might interact with O₂F₂ as shown in equation 6. A reaction of



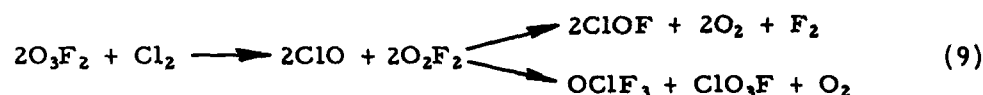
Cl₂ with O₂F₂ was carried out in the presence of CsF in the hope that a CsOF species would form and interact with Cl₂ to produce ClOF and CsCl₂. The only volatile products observed in the quartz system were SiF₄, ClO₂ and O₂. X-ray analysis of the residual solid has not been completed.

C. CHEMISTRY OF TRIOXYGEN DIFLUORIDE, O₃F₂

Studies of the reactions of O₃F₂ have not been undertaken on this program because of the difficulty anticipated in handling O₃F₂, which is even more unstable than O₂F₂. However, there are two excellent reasons for anticipating significant differences in the product obtainable from O₃F₂ and O₂F₂ reactions. In the first place, O₃F₂ is paramagnetic and, therefore, may undergo combination reactions with other odd electron molecules that do not occur with O₂F₂, a diamagnetic molecule. Examples of possible combination reactions of O₃F₂ are shown in equations 7 and 8.



Second, the mode of decomposition of O_3F_2 ($O_3F_2 \longrightarrow O\cdot + O_2F_2$) suggests that it may tend to act as an oxyfluorinating agent rather than primarily as a fluorinating agent, as is the case with O_2F_2 ($O_2F_2 \longrightarrow O_2 + 2F\cdot$). For example, a reaction of O_3F_2 with Cl_2 may yield $ClOF$ or $OCIF_3$ as shown in equation 9:



In view of these interesting possibilities, we have carried out a study of the preparation and analysis of O_3F_2 samples during this report period as a preliminary step in the investigation of its chemical properties. We plan to devote our efforts during the next quarter almost exclusively to this end.

We prepared trioxygen difluoride in a U-shaped quartz discharge tube similar to that used in some of our O_2F_2 preparations. We anticipate, however, that many of the reactions that we wish to study will yield products that are incompatible with quartz. In these cases we will either attempt to fashion Kel-F discharge tubes or distill the O_3F_2 from the quartz generator to a Kel-F reactor.

Samples of a mixture of oxygen and fluorine of nominally 3:2 molar ratio were analyzed by absorption of the fluorine in mercury and measuring the residual oxygen. In this way a reproducible value of 2.84:2.00 was obtained for the $O_2:F_2$ molar ratio. Additional samples of this mixture were subjected to a high voltage discharge at $-196^\circ C$ until the pressure (initially 10-20 min) in the discharge tube was reduced to a minimal value. A blood red condensate was observed in the discharge tube. This condensate melted almost at the instant the liquid nitrogen bath was removed, and shortly thereafter pressure began to build up in the reactor. When decomposition was complete, the gases were sampled and absorbed in mercury. An average composition of 58.7% O_2 and 41.3% F_2 was obtained for the blood red condensate by analyses of the decomposition gases from several preparations. Theory for O_3F_2 is 60% O_2 .

III. EXPERIMENTAL

A. REACTIONS OF DIOXYGEN DIFLUORIDE WITH NOBLE GASES

1. Reaction of O_2F_2 with Xenon

Two representative experiments with xenon are described below. Of the five performed there was little variation in the observed results except that an unidentified liquid produce fraction appeared in some of the runs. A number of different methods of analysis were tried in an effort to isolate and identify the constituents. These procedures are schematically summarized in Figure 1.

In the first experiment 2.04 millimoles of xenon were allowed to react with excess O_2F_2 at $-117^\circ C$ for two hours. The yellow solid obtained turned white when it was stored overnight at $-78^\circ C$. The product was pumped at $-78^\circ C$, thereby removing 0.694 millimoles of gases composed of COF_2 , CF_4 , C_2F_6 , SiF_4 , CO_2 , SF_6 , and a trace of xenon. Then the product was pumped at $-21^\circ C$ for several additional hours. This treatment produced 0.252 millimoles of gas composed of SiF_4 and a small amount of moisture. The sample was then stored at $-78^\circ C$.

Prior to carrying out analytical procedures, the temperature of the sample was raised in stages from $-196^\circ C$ to $0^\circ C$ and the gases evolved at each temperature were monitored by means of a Time-of-Flight mass spectrometer. At $-78^\circ C$, O_2^+ and Xe^+ were detected. There were also small amounts of BF_3 , CO_2 , HF , SiF_4 , and C_2F_6 which may have resulted from reactions occurring within the sampling system of the mass spectrometer. When the temperature was raised to $-21^\circ C$, O_2^+ and the fragmentation pattern of XeF_4 were observed. At $0^\circ C$ the XeF_4 pattern disappeared and only O_2^+ and Xe^+ peaks were observed. After recooling the sample to $-21^\circ C$, XeF_2^+ and XeF^+ peaks reappeared along with Xe^+ and O_2^+ . Recooling to $-78^\circ C$ resulted in the disappearance of all Xe-F peaks and again O_2^+ and Xe^+ were present. The mass spectral observations might be explained by the presence of an O-Xe-F compound or compounds, the cracking pattern of which contain O_2^+ and Xe^+ as the most intense ion fragments. As the temperature is raised, and hence the concentration of the species in

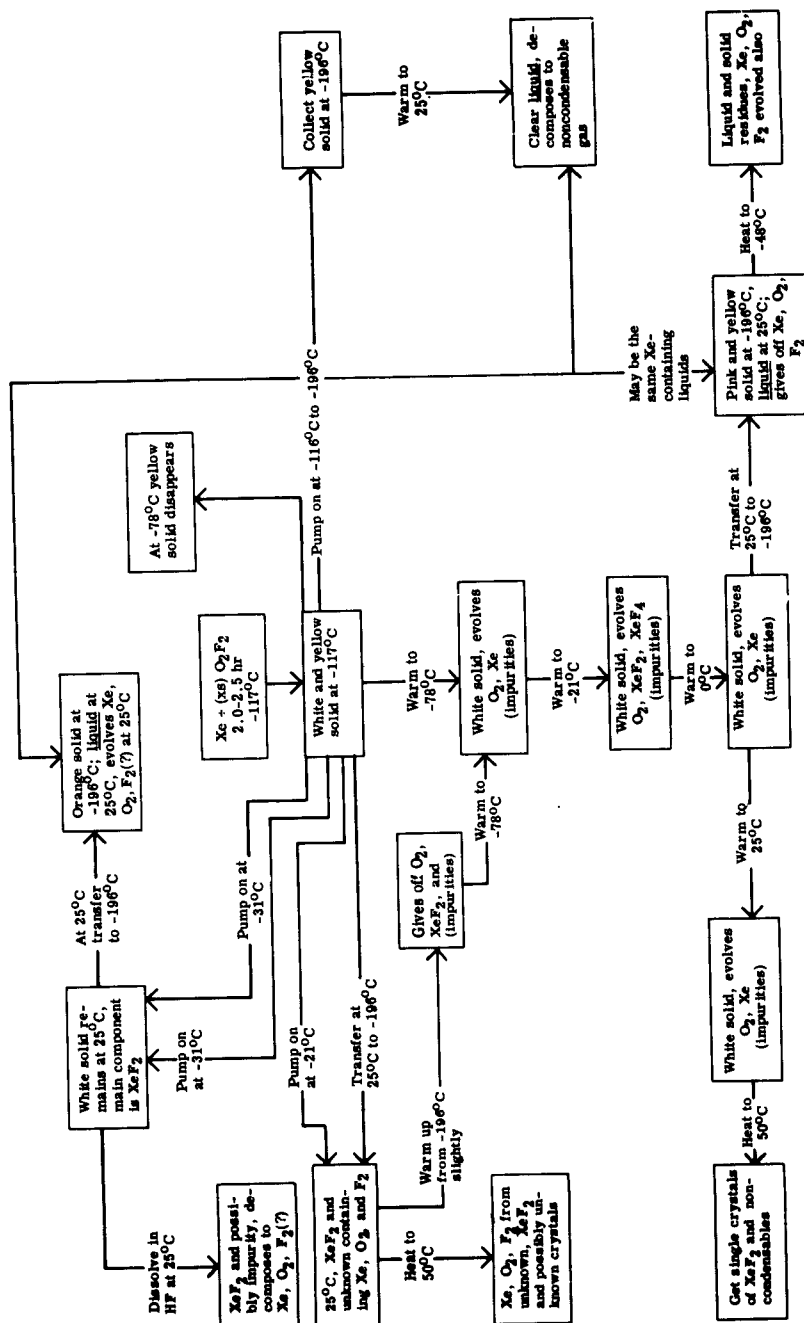


Figure 1. Reaction of O_2F_2 -Xe (Metal, Kel-F System)

the vapor phase, XeF_n^+ ion peaks appear in the pattern. At 0°C extensive decomposition occurs in the vapor phase leaving only O_2^+ and Xe^+ mass fragments.

The product remaining after the mass spectrometric analysis was completed was vacuum distilled from room temperature to a trap held at -196°C . The solid condensate exhibited white, yellow, and slightly pinkish bands at -196°C . When this material was warmed to room temperature both a white solid and a liquid were present. The gas present over the solid and liquid was sampled and analyzed by mercury absorption. The fluorine content was 20.8%. The gas fraction remaining after treatment with mercury was shown by mass spectrometric analysis to contain 90% Xe, 3% O_2 , 7% air and CO_2 . Calculation of the Xe:O:F ratio gave 1.7:0.1:1.0. The solid and liquid mixture in the reactor was heated to 48°C causing further decomposition and vaporization. The vapor phase at this temperature was analyzed by mercury absorption and was found to contain 24.9% F_2 . The residual gas after fluorine removal was composed of xenon and oxygen in a ratio of 4:1. Although there was some interfering SiF_4 present, the approximate Xe:O:F ratio of the vapor phase deduced from these data was 2:1:5. Decomposition of the sample appeared to be incomplete since small amounts of solid and liquid remained on cooling the reactor to room temperature.

In the second experiment 2.06 millimoles of xenon were allowed to react with excess xenon at -117°C for 2.5 hours. The product, a yellow/orange solid, was stored overnight at -78°C . Then it was pumped at 21°C for three hours. The material collected at -196°C was slightly orange in color. The fraction retained at -21°C was a white solid. When this was pumped on at room temperature part of it distilled over to a -196°C trap, and part was left as a white solid. The portion collected at -196°C was a white solid at room temperature. It was heated with a water bath at 50°C in a vacuum to induce decomposition so that the resultant gases could be analyzed. It was hoped that the composition of the solid material could be deduced from the composition of the gaseous break-down products. When the Kel-F trap was cooled, small transparent crystals formed on the wall at spots where water drops were left behind by the water bath. These were identified as XeF_2 by single crystal x-ray analysis.

The gases collected on heating the white sublimate were shown to contain 10.5% F_2 . The gases left after the removal of fluorine contained 63% xenon, 26% oxygen, and 11% air. The Xe:O:F ratio derived from these data was 2.7:2.0:1.0.

The white solid that remained when the product was pumped originally at room temperature was stored under nitrogen at -78°C for a week. Then it was transferred to another Kel-F tube, pumped at -78°C (to remove xenon) and heated to 49°C for about 15 minutes. Crystals of XeF_2 were formed as before. Analysis of the gases produced by decomposition of an unstable component in the solid showed a Xe:O:F ratio of 1.33:1.00:1.04. This is not too far from the ratio required for XeOF .

A mass spectrometric study of a sample of XeF_4 obtained from Argonne National Laboratories was made. The results were compared to those obtained under similar conditions with the white solid product from the reaction of O_2F_2 with xenon. It was particularly desirable to determine whether oxygen would be evolved when XeF_4 was introduced into the mass spectrometer, as was the case when the products from xenon and dioxygen difluoride were analyzed in this instrument.

When XeF_4 was held at -78°C and the vapor analyzed by the mass spectrometer, only background peaks were evident. At -23°C the reported fragmentation pattern of XeF_4 was observed (Ref 3), although the relative intensities of the ions were not identical to those reported. No oxygen was observed. The same results were obtained at room temperature.

A comparison of the cracking patterns at -23°C of XeF_4 and of the $\text{Xe-O}_2\text{F}_2$ product (excluding the O_2^+ peaks observed in the latter cracking pattern) is given in Table I.

TABLE I
MASS SPECTRA OF XeF_4 AND SOLID FROM $\text{Xe} + \text{O}_2\text{F}_2$ REACTION

<u>M/E</u>	<u>Ionic Species</u>	<u>XeF_4</u>	<u>$\text{Xe} + \text{O}_2\text{F}_2$ (solid)</u>
132	$\text{Xe}(132)^+$	100.0	100.0
151	$\text{Xe}(132)\text{F}^+$	47.5	50.8
170	$\text{Xe}(132)\text{F}_2^+$	43.0	27.7
189	$\text{Xe}(132)\text{F}_3^+$	64.0	1.2
208	$\text{Xe}(132)\text{F}_4^+$	9.0	0.17

These data show that the O_2F_2 -Xe product contains XeF_4 at $-23^\circ C$. The presence of XeF_4 is indicated by the ratio of m/e 189 to m/e 208 which is 7:1 in both spectra.

However, after the ion peaks due to XeF_4 were subtracted from those of the experimental solid, the intensity ratios of the residual peaks did not agree well with those reported for XeF_2 in the literature (Ref 3). It is concluded (from this and the observation of a high intensity oxygen peak in the cracking pattern of the Xe- O_2F_2 product at -78 and at $-23^\circ C$) that a xenon-oxygen species was present which undoubtedly also contained fluorine. It may have been XeO_2F_2 although no Xe-O ion fragments were observed.

2. Reaction of O_2F_2 with Argon

Dioxygen difluoride was prepared at $-196^\circ C$ in a quartz U-trap. The trap was warmed to $-118^\circ C$ and pressurized with an atmosphere of argon. The pressure in the system did not decrease as might be expected if a reaction were taking place between the two reagents. No evidence of a reaction of argon with O_2F_2 was detected.

3. Reaction of O_2F_2 with Krypton

This experiment was performed in the same manner as the one with argon. Oxygen difluoride was pressurized at $-118^\circ C$ with 332 mm of krypton. The 42 mm pressure rise over a three-hour period was attributed to the decomposition of O_2F_2 . The only materials recovered other than krypton were NO_2 and SiF_4 .

B. REACTIONS OF O_2F_2 WITH HALOGEN COMPOUNDS

1. Reaction of BrF_3 with O_2F_2

An attempt was made to prepare BrF_7 by allowing O_2F_2 to act upon BrF_3 at $-78^\circ C$ in a vacuum. The BrF_3 used in this reaction was purified by passing it over a bed of NaF pellets at $100^\circ C$ to remove HF and BrF_3 . The material so obtained was light amber in color. When such a sample was vacuum-distilled at room temperature in a Kel-F trap the residue became almost colorless. However, when the colorless material was passed through the vacuum system, it too became colored. The only way the BrF_3 could be maintained colorless in the liquid state was to avoid transferring it from trap to trap in the vacuum system. Whenever a sample of colorless BrF_3 was

exposed to a previously unpassivated section of the vacuum system, it became dark brown and evolved a brown gas (probably Br_2) at room temperature.

A 1.0 cc liquid sample of BrF_5 , which was pale straw colored (high purity), was transferred to a Kel-F trap. The sample became slightly darker in color but still appeared to be a reasonably pure sample of BrF_5 . Excess O_2F_2 was transferred to the reactor and the mixture was allowed to stand overnight in a vacuum.

The next day a brown liquid and a yellow solid were observed in the trap at -78°C . This mixture was pumped on at -78°C , and the gases removed in this way were found to be composed of COF_2 , SiF_4 , SF_6 , fluorocarbon materials, and an unidentified material that exhibited an infrared absorption at 730 cm^{-1} . After the mixture had been pumped on at -78°C , a white solid remained. When the cold bath was removed this solid slowly melted to a slushy, clear liquid. There was a small amount of white solid left after all of the volatile material had been pumped off at room temperature to a trap held at -196°C . As the material condensed at -196°C was warmed to room temperature, it turned into a light yellow liquid. Distillation of this material to a Kel-F tube for nuclear magnetic resonance spectroscopic analysis resulted in its becoming blood red in color. Analysis showed only the presence of BrF_5 and traces of HF . The latter was presumably derived from impurities in the vacuum system used for the experiment.

The small amount of white solid residue left in the reactor was still present several days later when it was submitted for analysis. Decomposition of the solid at 75°C into a mass spectrometer showed the presence of BrF_3 , or BrF_5 , NF^+ , NO_2 , N_2O , Cl_2 (trace), SiF_4 , and fluorocarbon materials from the Kel-F container.

2. Reaction of CsBrF_6 with O_2F_2

The preparation of CsBrF_6 was undertaken by heating 9.65 gm of CsF and 10.5 cc of BrF_5 in a stainless steel bomb overnight at 100°C . A 6.0 cc quantity of BrF_5 was recovered from the bomb. The bomb was recharged with the same BrF_5 and reheated overnight at 140°C . Again 6.00 cc of BrF_5 was recovered and it was concluded that the reaction had gone to completion. The consumption of 4.5 cc of BrF_5 was exactly equal to that expected for 100% conversion of CsF to CsBrF_6 . A sample of the solid $\text{CsF}-\text{BrF}_5$ product was treated with O_2F_2 .

Quite unexpectedly the x-ray pattern of the product was different than that of CsBrF_6 . (This was not learned until after we had reacted the product with O_2F_2 , as described in the next paragraph.)

A 2.92 gm sample of CsF-BrF_5 product was loaded into a Kel-F reactor. Over a period of several days successive batches of O_2F_2 were prepared and transferred to the reactor. At first the O_2F_2 was allowed to react with this material at -107°C . Then a -78°C bath was placed around the reactor. After treatment with an excess of O_2F_2 in this way, the solid became gray in color. When it was pumped at -78°C , a small amount of volatile material was collected at -196°C . This produced a noncondensable gas at room temperature. No identification of this unstable material could be accomplished.

When the solid product was pumped on at room temperature, the principal volatile material obtained was BrF_5 , with lesser amounts of CO_2 , COF_2 , SiF_4 , and fluorocarbon materials. Although we had some difficulty with leaks in the system during work-up of the product, there was some evidence that a component may have been present which gives off oxygen at room temperature. The x-ray pattern of the solid obtained matched that of the known pattern for CsBrF_6 . Although the x-ray pattern of CsBrF_4 is not available, we suspect that this was undoubtedly the composition of the original product we obtained from the thermal treatment of CsF and BrF_5 . This CsBrF_6 was treated further with O_2F_2 at -107°C and then at -78°C without further change in its composition and with no evidence of BrF_7 formation.

3. Reaction of O_2F_2 with Cl_2 and CsF

Two mmoles of Cl_2 were condensed on CsF at -196°C in the discharge trap. Approximately 2 mmoles of O_2F_2 were then generated and condensed on the Cl_2 and CsF . Some purple color formation was noted. After warming to room temperature the gaseous products were found to be CF_4 , SiF_4 , Cl_2 , ClO_2 and O_2 .

IV. FUTURE WORK

During the next quarter work will be conducted in the following areas:

- Studies of the reactions of O_3F_2 with odd electron molecules will be initiated.
- Further studies will be made of the decomposition of O_2F_2 over metal fluoride catalysts.
- The reaction of O_2F_2 with $CsCl_2$ will be examined as an approach to the anion, $ClO_2F_2^-$.
- The reaction of BrF_5 with O_2F_2 will be attempted under high pressure conditions.

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Section IV

Task 54

**STABILIZATION OF NITRONIUM PERCHLORATE
BY COMPLEXATION**

Section IV

STABILIZATION OF NITRONIUM PERCHLORATE
BY COMPLEXATION

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Report RMD 5043-Q2-64

RMD Project 5043, Task 54
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to 30 June 1964

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FOREWORD

This section of the advanced oxidizer report summarizes work carried out during the period from 1 April 1964 to 30 June 1964 on synthetic efforts directed toward the stabilization of nitronium perchlorate (RMD Project 5043, Task 54).

Contributors to the research were: A. R. Young (Project Supervisor), J. Dvorak (Principal Investigator), E. Egbert, J. Creatura, and R. Storey.

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I. INTRODUCTION

This research program is concerned with improving the physical and chemical properties of nitronium perchlorate via complexation of the nitronium cation. It is believed that such complexes, by virtue of the increased size of the cation, would have greater ionic character and hence, lower reactivity than nitronium perchlorate.

During this report period attempts were made to prepare complexes of nitronium perchlorate with pyridine, PCl_3 , and PF_3 .

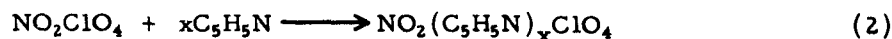
II. DISCUSSION

Pyridine forms numerous complexes with metallic and nonmetallic perchlorates (Refs 1, 2, 3). Moreover, complex salts containing non-metal cations such as $I(py)_2ClO_4$ and $Cl(py)NO_3$ are less hygroscopic and more thermally stable than their respective parent salts. It was believed, therefore, that a pyridine complex of the nitronium cation might be stable. Such a complex could be a useful intermediate in the synthesis of more energetic complexes of nitronium perchlorate, as shown in equation 1.



The following approaches were explored as routes to $NO_2(py)_xClO_4$:

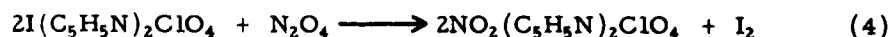
The direct interaction of NO_2ClO_4 with pyridine (eq. 2);



The reaction of nitryl chloride with silver bis-pyridine perchlorate (eq. 3);



The reaction of iodonium bis-pyridine perchlorate with nitrogen dioxide (eq. 4);



These experiments gave some indication that a pyridine complex of NO_2ClO_4 may be prepared, although isolation of a complex in high purity has not yet been achieved.

Attempts to form complexes of NO_2ClO_4 with PF_3 and PCl_3 were totally unsuccessful.

A. REACTION OF NO_2ClO_4 WITH PYRIDINE

Since the direct interaction of NO_2ClO_4 with pyridine at ambient temperatures was expected to result in considerable degradation of the reactants, preliminary experiments were conducted at low temperatures and in the presence of diluents such as acetonitrile and Freon-113. The results of these experiments have been reported (Ref 4). It was noted that the solid product obtained when equimolar amounts of NO_2ClO_4 and pyridine were allowed to react in Freon-113 had an x-ray powder pattern consistent with that of NO_2ClO_4 . The infrared spectrum of the solid product, however, did show absorptions attributable to pyridine; elemental analysis suggested that the product was not homogeneous. In order to determine whether a reaction of pyridine with NO_2ClO_4 could be driven to completion, a three-fold excess of pyridine was added to a suspension of nitronium perchlorate in Freon-113. The solid recovered upon removal of the Freon-113 and excess pyridine again produced an x-ray pattern (Figure 1) almost identical to that of pure NO_2ClO_4 , although chemical analysis of the solid is consistent with a monopyridine complex of about 80% purity (Table I).

TABLE I

ANALYSIS OF NITRONIUM PERCHLORATE-PYRIDINE PRODUCT

<u>Element</u>	<u>Found (%)</u>	<u>Calcd. for $\text{NO}_2(\text{C}_5\text{H}_5\text{N})\text{ClO}_4$ (%)</u>
C	20.07	26.78
H	2.02	2.23
N	10.03	12.47

The solid gradually darkens in color on storage at ambient temperatures. This color change may be indicative of a slow nitration of the pyridine ring.

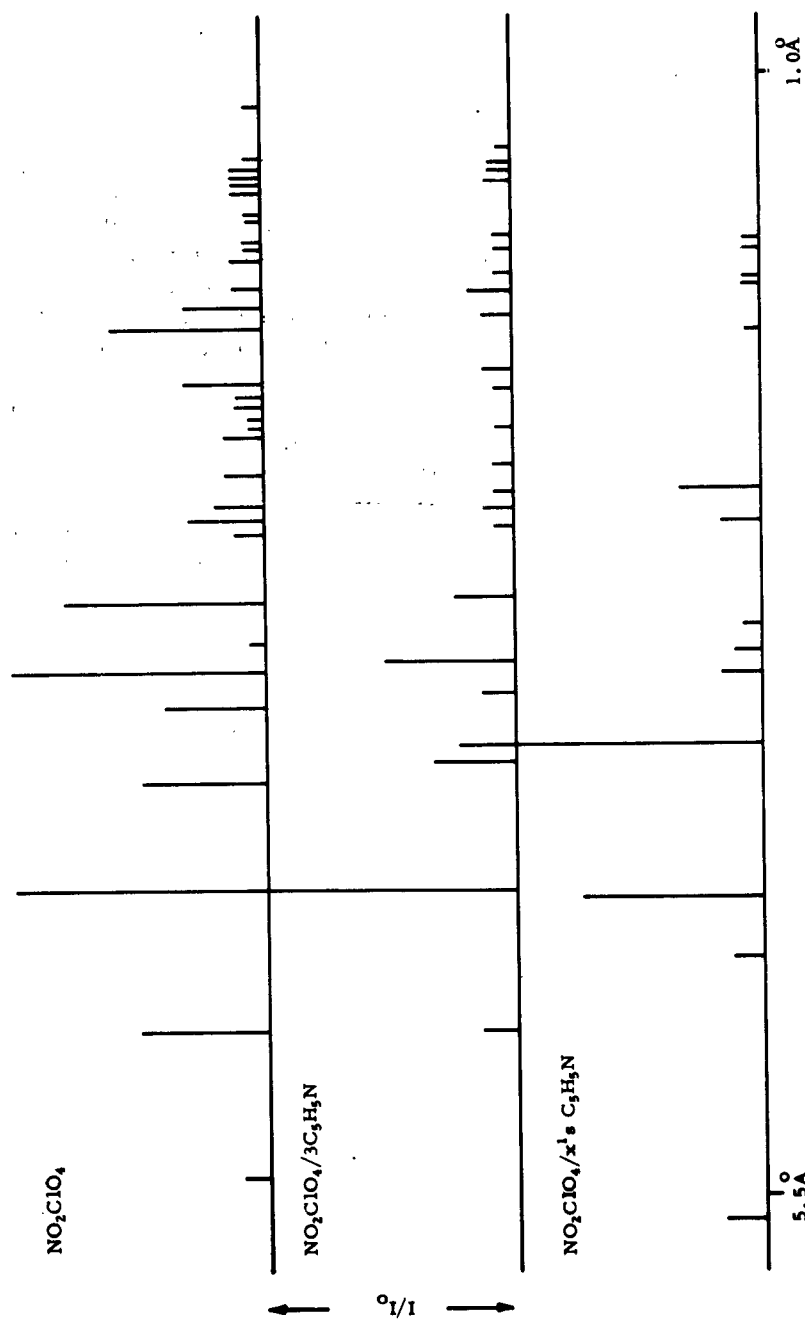
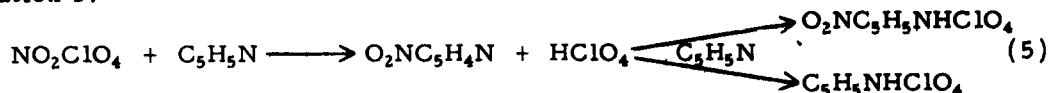


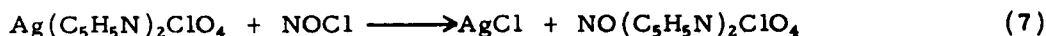
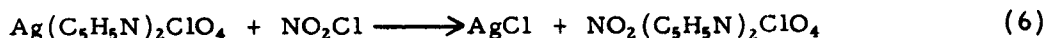
Figure 1. X-ray Diffraction Patterns of $\text{NO}_2\text{ClO}_4\text{-C}_3\text{H}_5\text{N}$ Reaction Products

When NO_2ClO_4 was allowed to react with a large excess of pyridine in the absence of a solvent, different results were obtained. The infrared spectrum of the solid product shows absorptions attributable to a pyridinium ($\text{C}_5\text{H}_5\text{NH}^+$) salt such as $\text{C}_5\text{H}_5\text{NHClO}_4$; the x-ray powder pattern of the product is unlike that of NO_2ClO_4 (Figure 1). A possible reaction of nitronium perchlorate with pyridine which would lead to the formation of pyridinium salts is shown in equation 5.



B. REACTION OF $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ WITH NO_2Cl

A possible alternative method for preparing a pyridine complex of nitronium perchlorate is by means of a reaction of NO_2Cl with $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ (equation 6). The feasibility of this approach was pursued initially using commercially available NOCl (equation 7), rather than NO_2Cl , which is difficult to prepare in high purity.



When NOCl was added to a nitromethane solution of AgClO_4 and pyridine, AgCl precipitated as predicted by equation 7, but nitric oxide was simultaneously liberated. Removal of the solvent in vacuo yielded a solid product having an x-ray diffraction pattern (Figure 2) similar to that obtained when NO_2ClO_4 is allowed to react with excess pyridine. This indicated that the product consisted of pyridinium salts. Upon hydrolysis the solid gave a negative test for NO_2^- and a positive test for ClO_4^- . The infrared spectrum showed absorptions attributable to NO_3^- , ClO_4^- , and $\text{C}_6\text{H}_5\text{NH}^+$. Chemical analysis (Table II) indicated that the product was a mixture of $\text{C}_5\text{H}_5\text{NHNO}_3$ and $\text{C}_5\text{H}_5\text{NHClO}_4$.

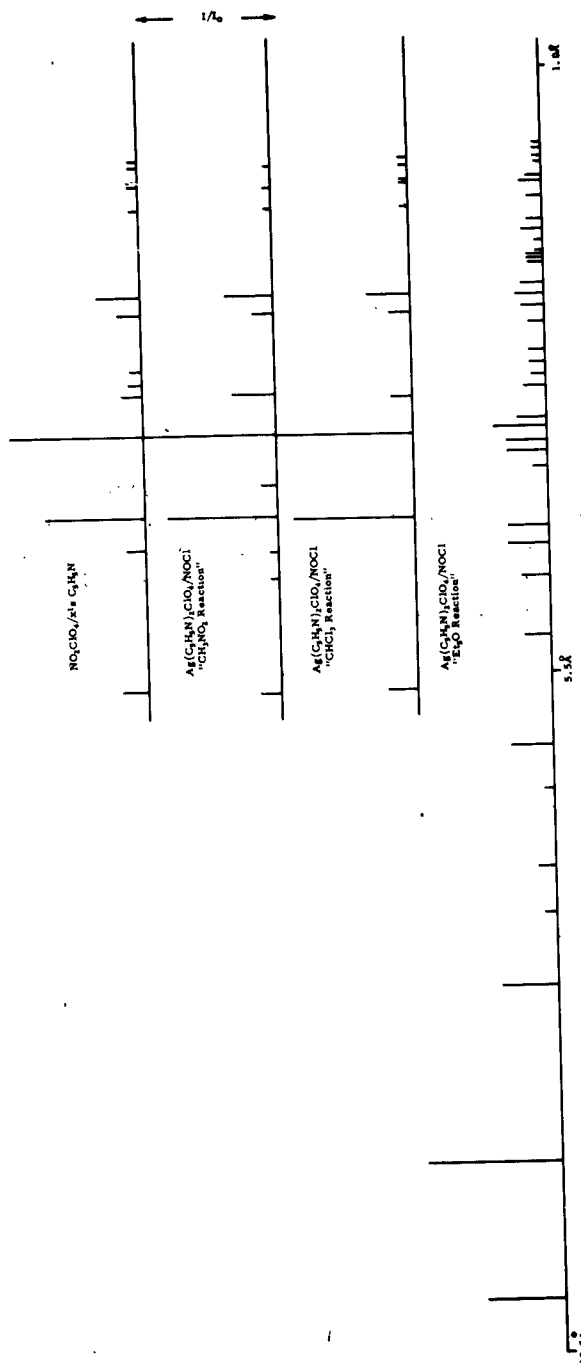


Figure 2. X-ray Diffraction Patterns of Ag(C₆H₅N)₂ClO₄/NOCl Reaction Products

TABLE II
ANALYSIS OF $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ - NOCl REACTION PRODUCT
(IN NITROMETHANE)

Element or Group	Found (%)	Calcd. for 1:1 Mixture of $\text{C}_5\text{H}_5\text{NHNO}_3/\text{C}_5\text{H}_5\text{NHCIO}_4$ (%)
C	37.75, 36.21	37.32
H	3.79, 4.03	3.73
ClO_4^-	34.1	30.94
N	8.67	13.06

When NOCl was added to a chloroform solution of $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$, AgCl precipitated without evolution of nitric oxide. After the AgCl was separated by filtration, the filtrate was evaporated in vacuo. The residual solid contained NO^+ , although considerably less than the theoretical amount (Table III). The x-ray powder pattern of the solid product is also comparable to that of the product of the reaction of excess pyridine with NO_2ClO_4 (Figure 2), which has been tentatively identified as predominantly pyridinium perchlorate. The infrared spectrum shows absorptions attributable to NO_3^- , ClO_4^- and the pyridinium ion. The product evidently contains only a small amount of the desired complex, $\text{NO}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$.

TABLE III
ANALYSIS OF $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ - NOCl REACTION PRODUCT
(IN CHLOROFORM)

Element or Group	Found (%)	Calcd. for $\text{NO}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ (%)
C	36.33, 36.18	41.73
H	3.59, 4.05	3.43
ClO_4^-	53.2	34.60
N	7.6	14.60
NO	1.63	10.43

In a similar reaction NOCl was added to a chloroform solution of $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ and the precipitated AgCl was separated by filtration. The filtrate was added to an equal volume of ether which yielded an insoluble white solid. The solid has infrared absorptions attributable to NO_3^- , ClO_4^- and pyridine. Its x-ray powder pattern (Figure 2) is not similar to those of previous products. Chemical analysis which is not yet complete fails to show more than a trace of ClO_4^- . These results are not presently understood.

C. REACTION OF $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ WITH NO_2

A preliminary investigation into the preparation and reactivity of $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ has been reported (Ref 4). It has since been determined that $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ is readily obtained by the reaction of I_2 with $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ in chloroform (equation 8). It is a white solid that discolors on standing several days at room temperature. Chemical analysis of the product is given in Table IV.



TABLE IV

ANALYSIS OF $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ - I_2 REACTION PRODUCT

Element or Group	Found (%)	Calcd. for $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ (%)
C	32.87	31.25
H	3.19	2.66
ClO_4^-	27.4	26.28
I	25.3	33.04

The infrared spectrum and x-ray diffraction pattern are given in Figures 3 and 4, respectively.

An investigation was conducted of the usefulness of $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ as an intermediate in the preparation of the complex perchlorate, $\text{NO}_2(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ (equation 9). When NO_2 was added to a chloroform solution of $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$, a solid precipitated and the solution became intensely violet, indicating that

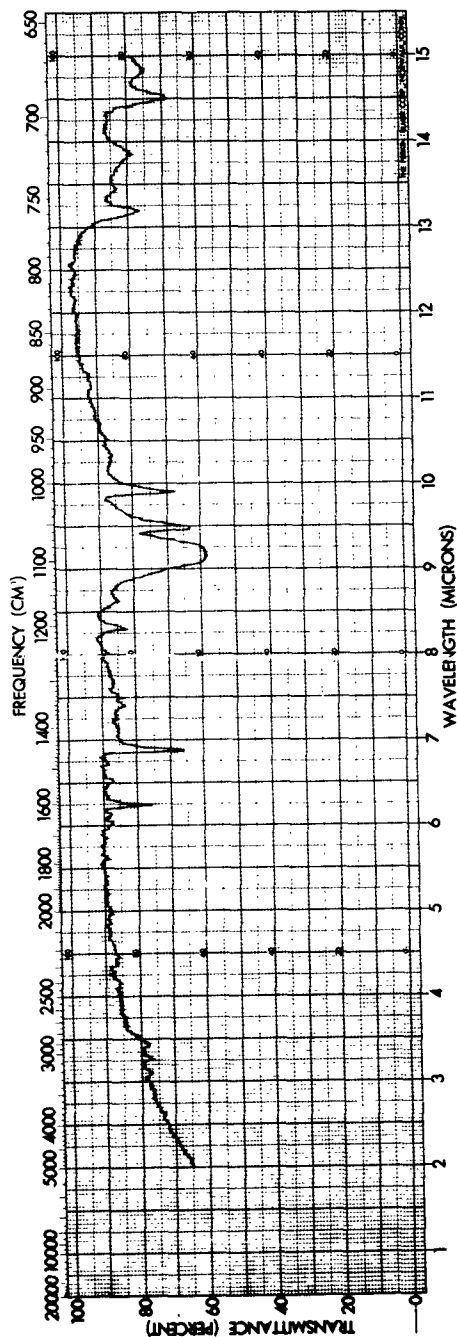


Figure 3. Infrared Spectrum of $I(C_5H_5N)_2ClO_4$

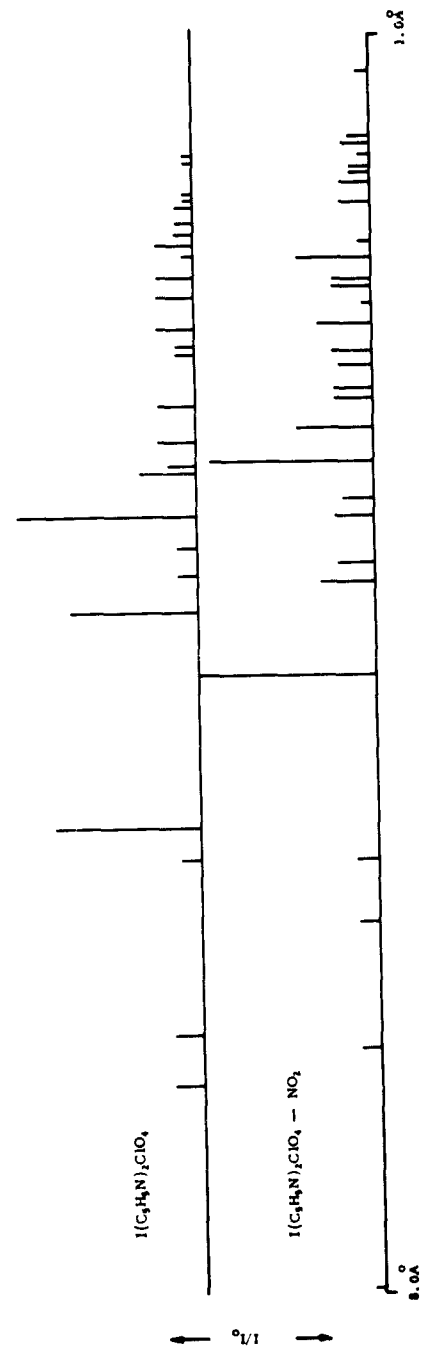
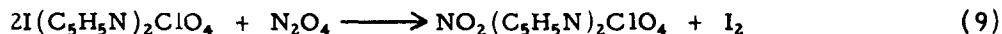


Figure 4. X-ray Diffraction Patterns of $I(C_5H_5N)_2ClO_4$ Reaction Product

iodine had been liberated. The x-ray powder pattern of the reaction product was quite different from that of $I(C_5H_5N)ClO_4$ (Figure 4). Chemical analysis of the product is pending.



D. REACTION OF $I(C_5H_5N)_2ClO_4$ WITH AMMONIA

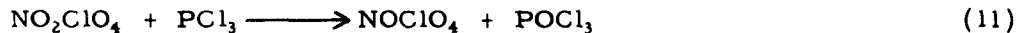
The reaction of $I(C_5H_5N)_2ClO_4$ with ammonia was investigated in an attempt to determine whether pyridine could be displaced from the complex salt (equation 10).



When ammonia was added to a chloroform solution of $I(C_5H_5N)_2ClO_4$, a black precipitate formed which turned pale yellow after the reaction mixture was stirred at room temperature for several hours. The solution became orange/brown and was found to contain free iodine. Since pyridine solutions of iodine are brown, the orange/brown color is indicative of liberated pyridine, as well as iodine. However, the x-ray and infrared patterns produced by the pale yellow precipitate indicated that it was predominantly ammonium perchlorate.

E. REACTION OF NO_2ClO_4 WITH PF_3 AND WITH PCl_3

In order to determine whether a phosphorous donor might complex with NO_2ClO_4 , reactions of PF_3 and of PCl_3 with NO_2ClO_4 were examined. No reaction occurred between NO_2ClO_4 and PF_3 , but PCl_3 was found to react with NO_2ClO_4 to yield $NOCIO_4$ and $POCl_3$ (equation 11). The solid product was characterized by its x-ray diffraction pattern; the volatile reaction product was identified as $POCl_3$ by its mass spectrum.



III. EXPERIMENTAL*

A. REACTION OF NO_2ClO_4 WITH PYRIDINE

1. In Freon-113

To a mixture of 0.4994 g (3.43 mmole) of NO_2ClO_4 and 25 ml of Freon-113 at -196°C was added 0.83 cc (10.29 mmoles) of pyridine. The reaction mixture was stirred and allowed to warm slowly to -20°C . After stirring several hours the solvent was removed in vacuo. The residual solid was sampled for x-ray and infrared analysis and then stirred at -78°C . The x-ray powder pattern (Figure 1) was consistent with that of NO_2ClO_4 . Chemical analysis is given in Table I.

2. In Excess Pyridine

To 0.3957 g (2.72 mmoles) of NO_2ClO_4 at -196°C was slowly added approximately 25 ml of pyridine. The reaction mixture was then allowed to slowly warm to -20°C . After stirring for several hours at -20°C the solvent was removed in vacuo. The x-ray powder pattern of the product is given in Figure 1.

B. REACTION OF $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ WITH NOCl

1. In Nitromethane

To 12.8 mmoles of pyridine in 20 ml of CH_3NO_2 was slowly added 1.3447 g (6.4 mmoles) of AgClO_4 . The resultant solution was cooled to -196°C and 7 mmoles of NOCl was introduced. The reaction mixture was allowed to warm to room temperature. The head vapor was sampled for mass spectroscopic analysis and found to contain NO . The precipitated AgCl was separated by filtration. The filtrate was evaporated. Chemical analysis of the residual solid is given in Table II.

2. In Chloroform

To 4.5715 g (0.022 moles) of AgClO_4 at -196°C was added 3.63 cc (0.45 moles) of pyridine. This mixture was allowed to warm to room temperature and stirred for several hours; 25 cc of chloroform was then added while

* All solid reagents were handled in a dry box.

stirring. When all the $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ dissolved, the reaction mixture was cooled to -196°C and 0.022 moles of NOCl introduced. The reaction mixture was allowed to warm to room temperature and the AgCl separated by filtration. The chloroform filtrate was evaporated. Chemical analysis of the residual solid is given in Table III and its x-ray powder pattern is given in Figure 2.

3. In Chloroform With Ether Precipitation

The reaction was conducted as described in subparagraph 2 except that the chloroform filtrate was added to an equal volume of diethyl ether and allowed to stand several hours. The precipitated solid was separated by filtration and dried in vacuo. Chemical analysis is pending. The x-ray powder pattern is given in Figure 2.

C. PREPARATION OF $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$

To 1.6786 g (8.1 mmoles) of AgClO_4 at -196°C was added 1.31 cc (16.2 mmoles) of pyridine. After warming the system to room temperature and stirring it for several hours, 25 cc of chloroform was added. When the resultant solution became clear, 2.0558 g (8.1 mmole) of I_2 was slowly added. Vigorous stirring was maintained. When the reaction was complete the mixture was filtered and the filtrate added to an equal volume of ether. The precipitated $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ was separated and dried in vacuo; chemical analysis appears in Table IV. The infrared spectrum and x-ray diffraction pattern of the reaction product are given in Figures 3 and 4, respectively.

D. REACTION OF $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ WITH NO_2

A chloroform solution of $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ was prepared from $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ and I_2 as described in paragraph B and cooled to -196°C . A calculated amount of NO_2 was then added. The mole ratio of NO_2 to $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ was 1:1 based on the amount of AgClO_4 used. After warming to room temperature, the resultant precipitate was separated by filtration and dried. Chemical analysis is pending. The x-ray diffraction pattern is given in Figure 4.

E. REACTION OF $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ WITH NH_3

To a chloroform solution of 5.4 mmoles of $\text{I}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ (based on the amount of AgClO_4 used) was added 10.8 mmoles of anhydrous NH_3 at -196°C . The reaction mixture was allowed to warm to room temperature and stirred for several hours. The solid which precipitated was found to be predominantly NH_4ClO_4 .

F. REACTION OF PF_3 WITH NO_2ClO_4

To 0.4780 g (3.3 mmoles) of NO_2ClO_4 at -196°C was added 10 mmoles of PF_3 . The reaction mixture was stirred at -150°C for several hours. It was then allowed to warm to room temperature. The gas was recondensed on the solid several times. Both PF_3 and NO_2ClO_4 were recovered.

G. REACTION OF PCl_3 WITH NO_2ClO_4

To 0.3827 g (2.63 mmoles) of NO_2ClO_4 at -196°C was added 3.00 mmoles PCl_3 . After warming to room temperature the volatile materials were collected and found to be POCl_3 . The solid residue was found to be NOClO_4 .

IV. FUTURE WORK

During the next quarter research effort will be devoted to the following areas:

- Attempts will be made to prepare and evaluate addition compounds of perchloric acid with NO_2ClO_4 , $\text{HONH}_3\text{ClO}_4$, and NOF .
- Attempts will be made to prepare and evaluate substituted ammonium perchlorates such as; $\text{NH}_3\text{ClO}_4^+\text{ClO}_4^-$ and $\text{H}_3\text{NONO}_2^+\text{ClO}_4^-$.

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2. G. Brauer, Handbook of Preparative Inorganic Chemistry, Vol. 1, Academic Press (1963).
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4. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q1-64, Advanced Oxidizer Research, March 1964.

Section V

Task 55

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

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Section V

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

C. J. Grelecki

W. Cruice

Report RMD 5043-Q2-64

RMD Project 5043, Task 55
Report Period: 1 April 1964 to
30 June 1964

Contract No. NONr 4364(00)
ARPA Order No. 417
Project Code 4910

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FOREWORD

This section of the advanced oxidizer report summarizes work carried out during the period from 1 April 1964 to 30 June 1964 on the thermal stability of advanced solid oxidizers (RMD Project 5043, Task 55).

Contributors to the research were: C. Grelecki (Project Supervisor) and W. Cruice (Principal Investigator).

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I. INTRODUCTION

The objective of this program is to study the kinetics of the thermal reactions of high energy oxidizers in order to understand the mechanism by which they decompose. Work previously reported included highlights of a preliminary literature search and results of experimental work on the vapor pressure of anhydrous HClO_4 .

Additional work on the vapor pressure and thermal decomposition of anhydrous HClO_4 has been performed. Thermal decomposition studies on high purity HP have been initiated and the results are compared with other work in the field. Other solid amino-perchlorate oxidizers are being prepared and purified for experimentation.

This report includes a summary of experimental work done in the second quarter and a brief summary of projected experiments for the following quarter.

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II. SUMMARY

During this report period vapor pressure and thermal decomposition studies on anhydrous HClO_4 were continued and thermal decomposition studies on hydrazine perchlorate have been initiated.

The vapor pressure of anhydrous HClO_4 was found to be 71 mm Hg at 41°C which is in excellent agreement with work previously reported. The presence of chlorine oxides in a second sample of anhydrous HClO_4 reduced the vapor pressure at 55°C considerably from the value expected in view of previous work. The qualitative aspects of the decomposition reaction are as indicated by previous published papers. Computation of the activation energy of decomposition gives values of 23.1 kcal/mole and 22.4 kcal/mole (two different methods) in excellent agreement with the value of 22.2 kcal/mole reported in recent Soviet papers. Results of a vapor decomposition run on HClO_4 indicated that the vapor decomposes very slowly at 139°C .

Hydrazine perchlorate has been synthesized in high purity for experimental work. A DTA thermogram is included in the report. Hydroxylamine perchlorate has also been synthesized, but the purity is not yet high enough for good experimental work.

High purity hydrazine perchlorate has been found to undergo measurable thermal decomposition at 140°C . The pressure vs time curve follows the theoretical plot for nucleation according to a power law and normal growth thereafter. The expressions describing the curve are $P = 2.29 \times 10^{-4} t^2$ up to 1100 min and $P = 0.491 t - 270$ to over 2000 min. A second run performed at 150°C showed a marked increase in stability following the plot of $P = 0.085 t + 30$ after 250 min to atmospheric pressure at about 8500 min. The marked difference in thermal decomposition characteristics through the fusion point is assumed to be a result of the disappearance of high-energy strain areas and reactant product concentration gradients present in the crystalline form.

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III. EXPERIMENTAL

A. PROCEDURES

1. Vapor Pressure and Thermal Stability of Anhydrous Perchloric Acid

Thermal decomposition of anhydrous perchloric acid was studied in an all glass reactor with a pressure sensitive glass diaphragm. The apparatus is described in detail in the first quarterly report. The anhydrous acid was introduced into this Sickie gage reactor, degassed and then the loading arm was sealed under vacuum. Pressure readings were taken at frequent intervals until the rate of pressure rise was too great for accurate measurement and the sensitive glass diaphragm was in danger of rupture. Extrapolation of the pressure-time plot to $t = 0$ yields the vapor pressure of the anhydrous acid at the temperature of the experiment.

2. Thermal Decomposition of Hydrazinium Perchlorate

A slightly modified version of the sickie gage has been adopted for use in solid phase decomposition experiments (Figure 1). The use of the spherical bottom removes the possible effects of packing, excessive contact with the glass, reduced thermal conductivity, etc. A further modification, i.e., addition of a break seal arm for gas sampling, has been adopted for future use in both liquid decomposition cells and solid decomposition cells.

High purity HP was placed into a sickie gage and degassed for 30 minutes prior to seal-off in the usual manner. The gage was then immersed in a bath of Cellolube-220 at a specified temperature and pressure was monitored as a function of exposure time.

B. MATERIALS

1. Anhydrous Perchloric Acid

The method of preparation and purification of anhydrous perchloric acid was described in detail in the first quarterly report.

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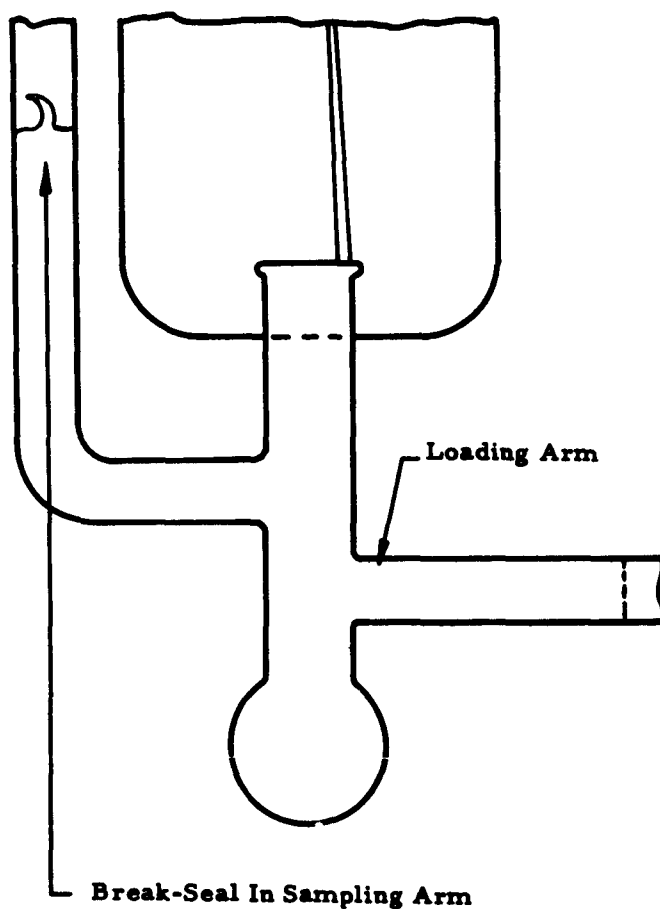


Figure 1. Modified Version of the Sickel Gage Decomposition Apparatus

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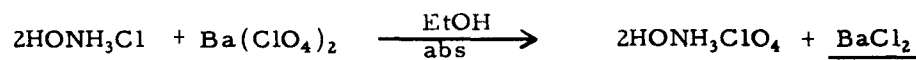
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2. Hydrazinium Perchlorate

Hydrazinium perchlorate (HP) has been produced according to the method of Barlot and Marsaule (1) in limited quantities suitable for our research purposes. The method as stated, however, appears to allow a considerable amount of water of hydration to remain in the salt. Material dried for two hours under a vacuum of < 1 mm Hg at 70°C assayed 99.94% and 99.83% by potentiometric titration (two separate batches). The DTA curves of this material are extremely sharp and well-defined, showing the melt endotherm beginning at 139°C and the deflagration exotherm beginning at 220°C . The extremely small quantity of water present is visible as a slight endothermic peak at 95°C (see Figure 2).

3. Hydroxylammonium Perchlorate

Hydroxylammonium perchlorate (HAP) has been synthesized by using the method of Robson (2) which is completely non-aqueous; the initial reaction is:



The absolute alcohol is removed by flash evaporation. The crude HAP is redissolved in diethyl ether and reprecipitated by the slow addition of anhydrous benzene. The material is then dried at moderate temperature for an extended period. The drying procedure has been thoroughly investigated at Thiokol Chemical Corp., Elkton Division, (3), but batches produced to date at Thiokol -RMD have not been sufficiently pure for experimental purposes. This disparity is probably a result of using considerably different drying apparatus. Further study of the purification process is currently under way.

4. Guanidinium Perchlorate

A quantity of guanidinium perchlorate (GP) on hand is being prepared for experimentation. A study is being made to determine methods of purification and criteria of purity.

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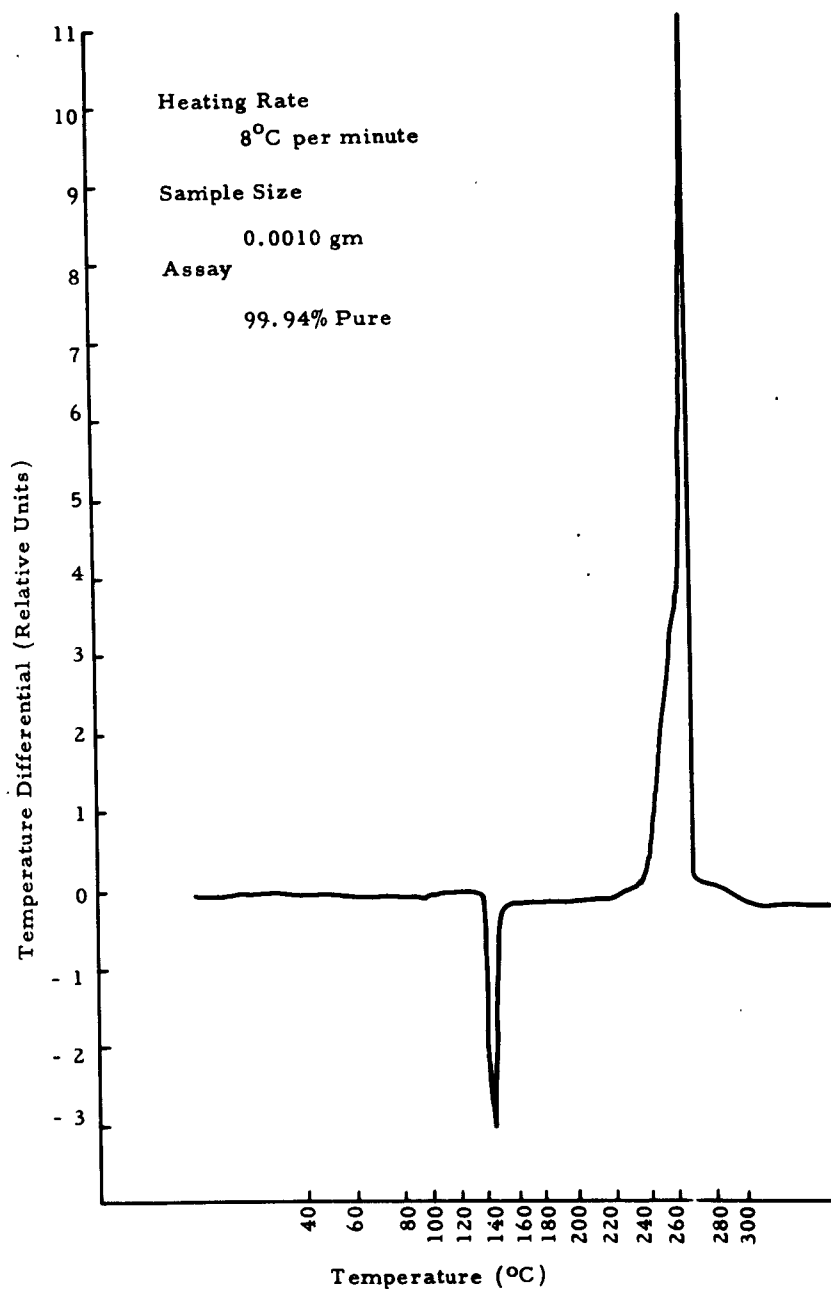


Figure 2. DTA Curve of High Purity Hydrazinium Perchlorate

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IV. RESULTS AND DISCUSSION

A. DECOMPOSITION OF PERCHLORIC ACID

The pressure vs time curve for the decomposition of liquid anhydrous perchloric acid at 41°C is shown in Figure 3. The pressure increased gradually until $t = 129$ min; from this point on the slope of the curve increased rapidly until it was nearly vertical. The acceleration was accompanied by a progressive color change beginning shortly after introduction of the reactor into the bath. The pure acid was clear and colorless; it became pale yellow (scarcely detectable), then amber, orange, red, and deep reddish brown. Extrapolation of the pressure-time plot to $t = 0$ gave a vapor pressure of 71 mm Hg at 41°C, which is in excellent agreement with our first quarter report (RMD 5034 Q2-64). The slope of the straight line portion of the curve is 0.533 mm Hg/min ($t = 0$ to $t = 129$).

A subsequent run at 55°C performed in the same manner was very similar in the shape of the pressure-time curve (Figure 3) and in color characteristics. When the curve was extrapolated to $t = 0$, however, the vapor pressure reading was 120 mm Hg, a value which is lower than previously reported. The acid assayed at 104.6% by titration, indicating the presence of some oxide of chlorine. Since the initial material was colorless, the oxide was probably Cl_2O_7 produced by excessive dehydration of the 70-72% acid used in the production step.

In order to calculate temperature coefficients from this data, the assumption was made that the concentration of all reactants was the same after an equivalent amount of reaction had occurred. Then the time to a fixed amount of decomposition is inversely proportional to the specific rate constant. Rates were compared at two degrees of reaction. First, a point corresponding to a relatively rapid dP/dt was selected to minimize the error caused by the difference in initial assays. This corresponds to 59 minutes at 55°C and 285 minutes at 41°C. Combining the Arrhenius equation at $T_1 = 41^\circ\text{C}$ and $T_2 = 55^\circ\text{C}$, gives:

$$\ln \frac{t_1}{t_2} = \frac{E}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

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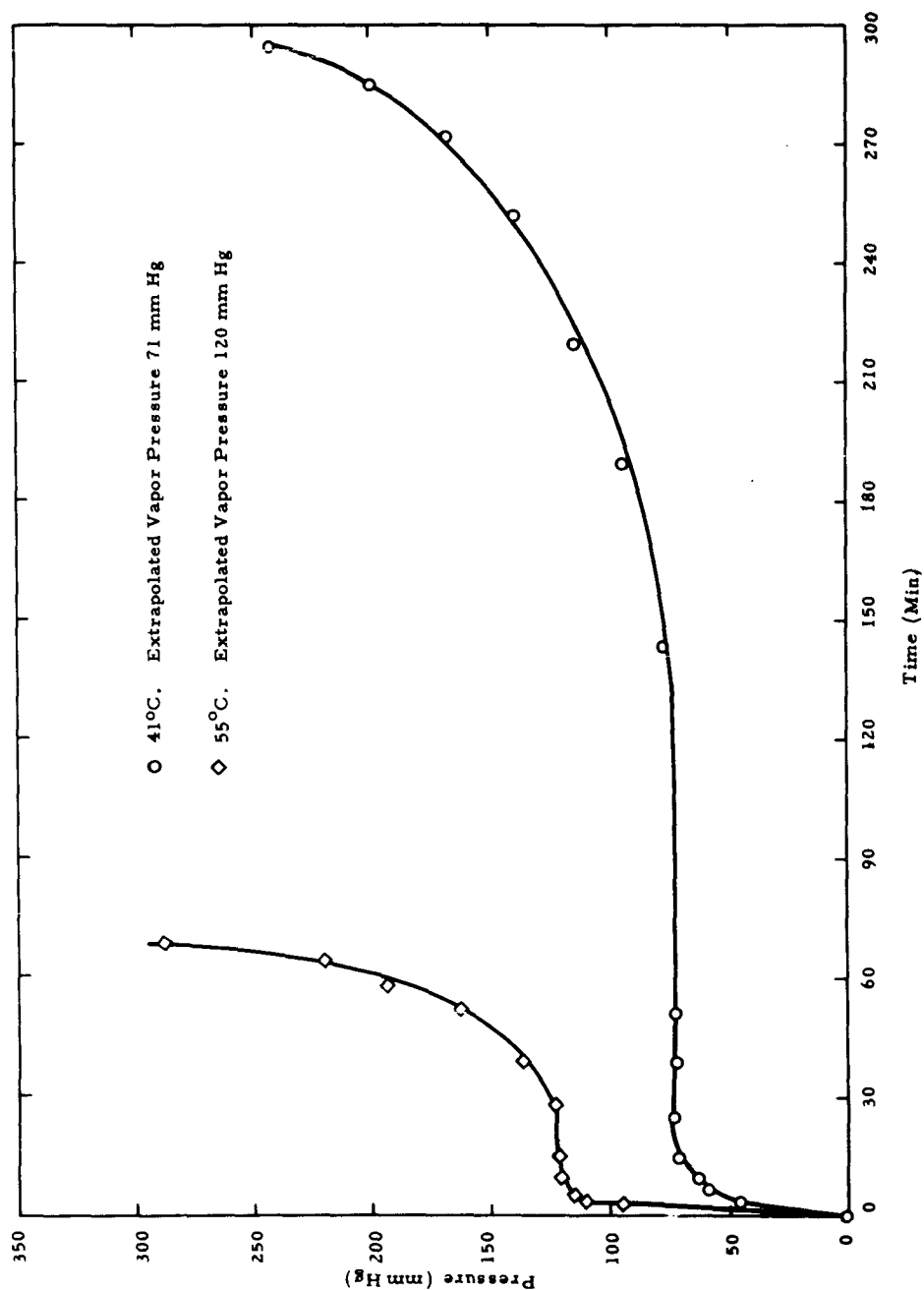


Figure 3. Pressure Versus Time Curves for Anhydrous HClO_4

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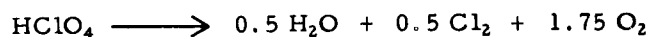
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The activation energy thus calculated is 23.1 kcal/mole, substantially in agreement ($\sim 5\%$ deviation) with the value of 22.2 kcal/mole reported by Soviet investigators (4). The second method was to obtain the time at which the linear portion of the curve terminates (induction period) which is also inversely proportional to the rate constant. The induction period at 41°C is 129 min, at 55°C is 28 min. Using the same expression, an activation energy of 22.4 kcal/mole was obtained. This is in excellent agreement with the Soviet report previously mentioned.

A single experiment was performed on the thermal decomposition of anhydrous HClO_4 in the vapor state at 139°C . The initial pressure of the vapor at 139°C was 67 mm Hg. After almost 65 hours at 139°C the pressure had risen to 85 mm Hg. Assuming a linear pressure-time relationship, this corresponds to 4.65×10^{-3} mm/min.

If the reaction is assumed to be first order, and following the stoichiometry:



as proposed by Levy (5), the first order constant can be calculated from:

$$\text{Log} \left(\frac{1.75 P_0}{2.75 P_0 - P} \right) = \frac{kt}{2.3}$$

The value of k thus obtained (1.16×10^{-4}) is approximately within the range predicted by extrapolation of Levy's plot of first order rate constants versus temperature, but the scatter in points obtained at the lower temperatures of his experiments make such an extrapolation almost insignificant.

B. DECOMPOSITION OF HYDRAZINIUM PERCHLORATE

The initial experiment with hydrazinium perchlorate was an exploratory one designed to determine the temperature at which it decomposes at a measurable rate. The sample was first heated for five hours at 90°C and there was no detectable pressure rise. No detectable pressure was observed after subsequent heating at 100°C for five hours, 110° for eight hours, 120° for three hours and 130° for three hours. At 140°C no pressure was evident after 60 min, but after 135 min a pressure of 56 mm Hg was observed. Thereafter the pressure rose linearly with time to over 500 mm Hg at 500 min, when the run was discontinued. The fact that the material had been subjected to extended preheating makes the data inaccurate from the point of view of a kinetic study; the primary objective (i.e. - to discover the "threshold" of thermal decomposition detectable in our system) was accomplished.

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A new sample of the same high purity HP was run at 140°C. The total duration of the run was over 50 hours with no sign of sudden acceleration of the type characteristic in hydrazine dperchlorate (HP-2). The pressure-time curve (Figure 4) is classical in solid-phase decompositions, corresponding to nucleation according to a power law and normal growth of nuclei thereafter to over 2000 min. The curve is very closely approximated by: $P = 2.29 \times 10^{-4} t^2$ up to 1000 min, thereafter following $P = 0.491t - 270$ to over atmospheric pressure. The residue (solid) was still white and crystalline, showing no evidence of having melted during the run.

Another sample of high purity HP was run at 150°C for over 7500 min (125 hours) before atmospheric pressure was attained. The earliest reading obeyed the power law ($P = Ct^n$) with $n = 2$ and a value of C approximately double that found at 140°C. A decline in rate was then observed and the plot from that point (~250 min) follows a linear relationship with a slope of 0.085 mm Hg/min, a much lower rate than that observed for the upper (linear) portion of the run at 140°C (Figure 5). For a more accurate comparison, N/N_0 was calculated for each run: where N = moles of gaseous products and N_0 = initial moles of HP. The combined plot is shown in Figure 6. The material was quite definitely molten during the run; upon removal from the bath it congealed in a fraction of a second to a single solid mass.

These experiments, while not yet sufficiently extended to allow computation of activation energies, are in accord with work done recently at Aerojet-General (6) where activation energies for three temperature regions were calculated on the basis of thermogravimetric experiments. For the region from 124°C to 142°C, $E_A = 22$ kcal/mole; for the region from 142°C to 160°C $E_A = 96$ kcal/mole; for the region from 160°C to 180°C, $E_A = 24$ kcal/mole. These experimentors found the melting point to be 142°C. A rather recent Soviet paper (7) lists percent weight loss per six minute period at varying temperatures in the 180°C-240°C region. Assuming the percent weight loss to be directly proportional to the rate constant, activation energy may be calculated using the expression

$$\text{Log } \frac{\% \text{ loss at } T_2}{\% \text{ loss at } T_1} = \frac{E_A}{2.3 R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Values of E_A obtained by this means are inconsistent, but the average value is approximately 24.5 kcal/mole, in very good agreement with Aerojet-General's value above 160°C.

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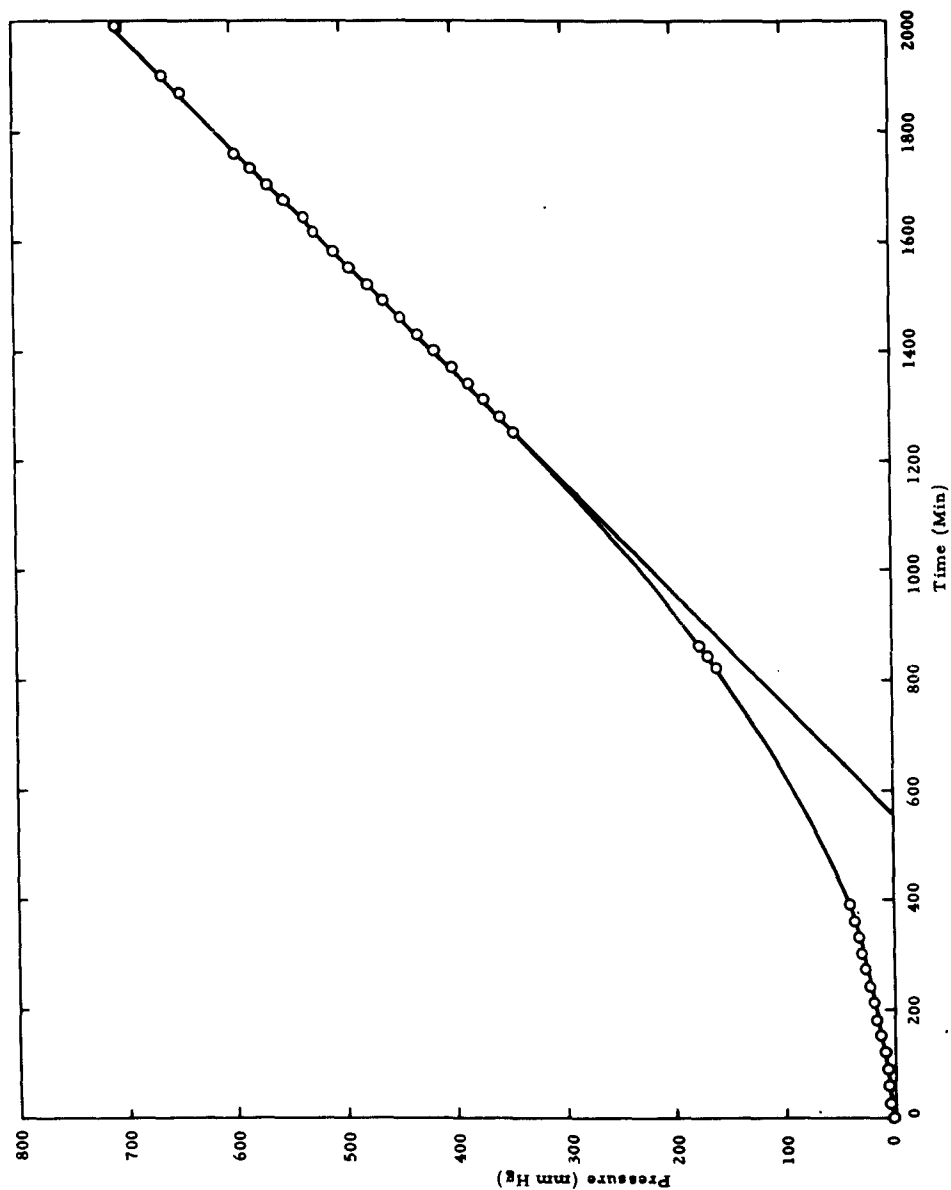


Figure 4. Pressure Versus Time Curve for Hydrazinium Perchlorate at 140°C

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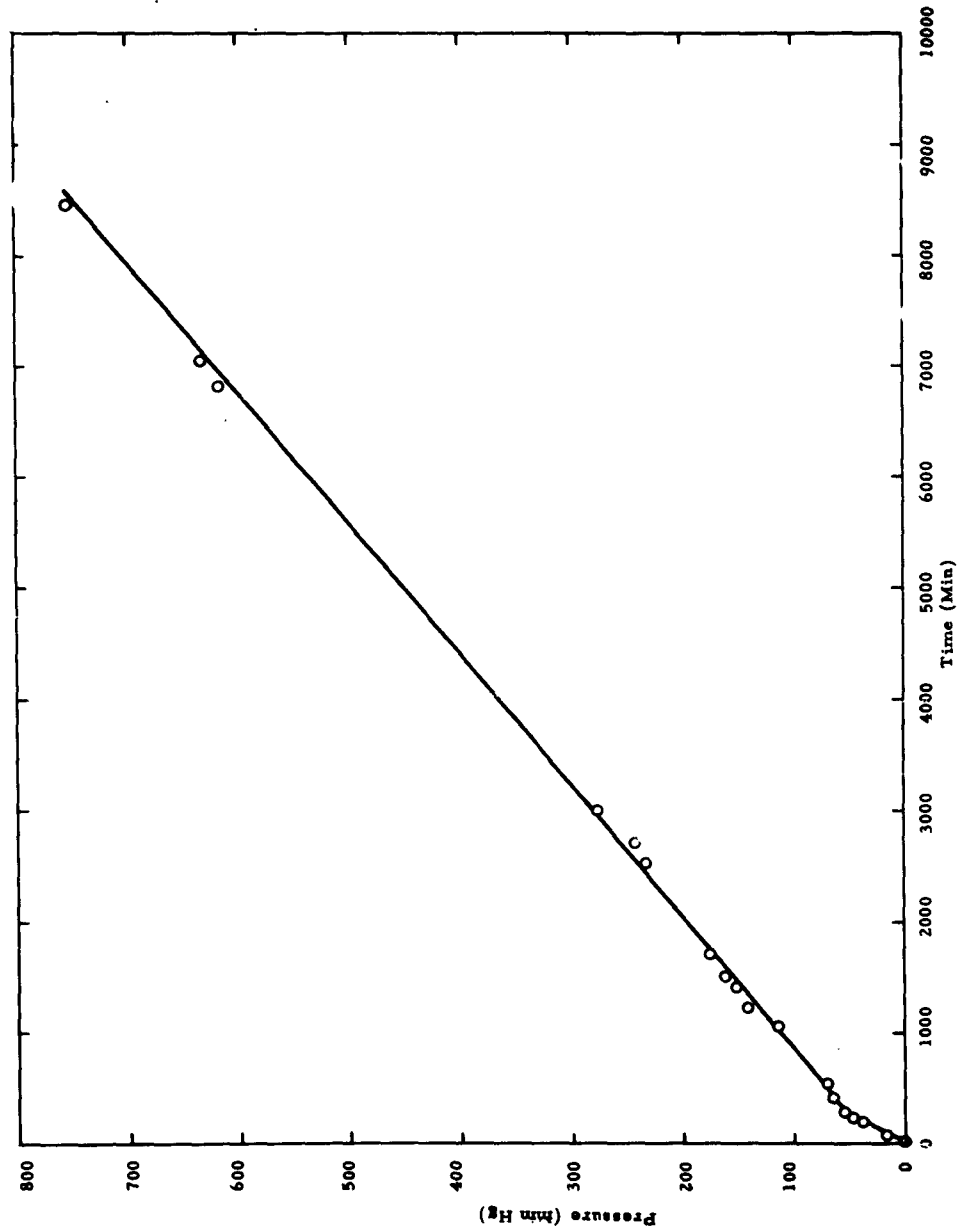


Figure 5. Pressure Versus Time Curve for Hydrazinium Perchlorate at 150°C

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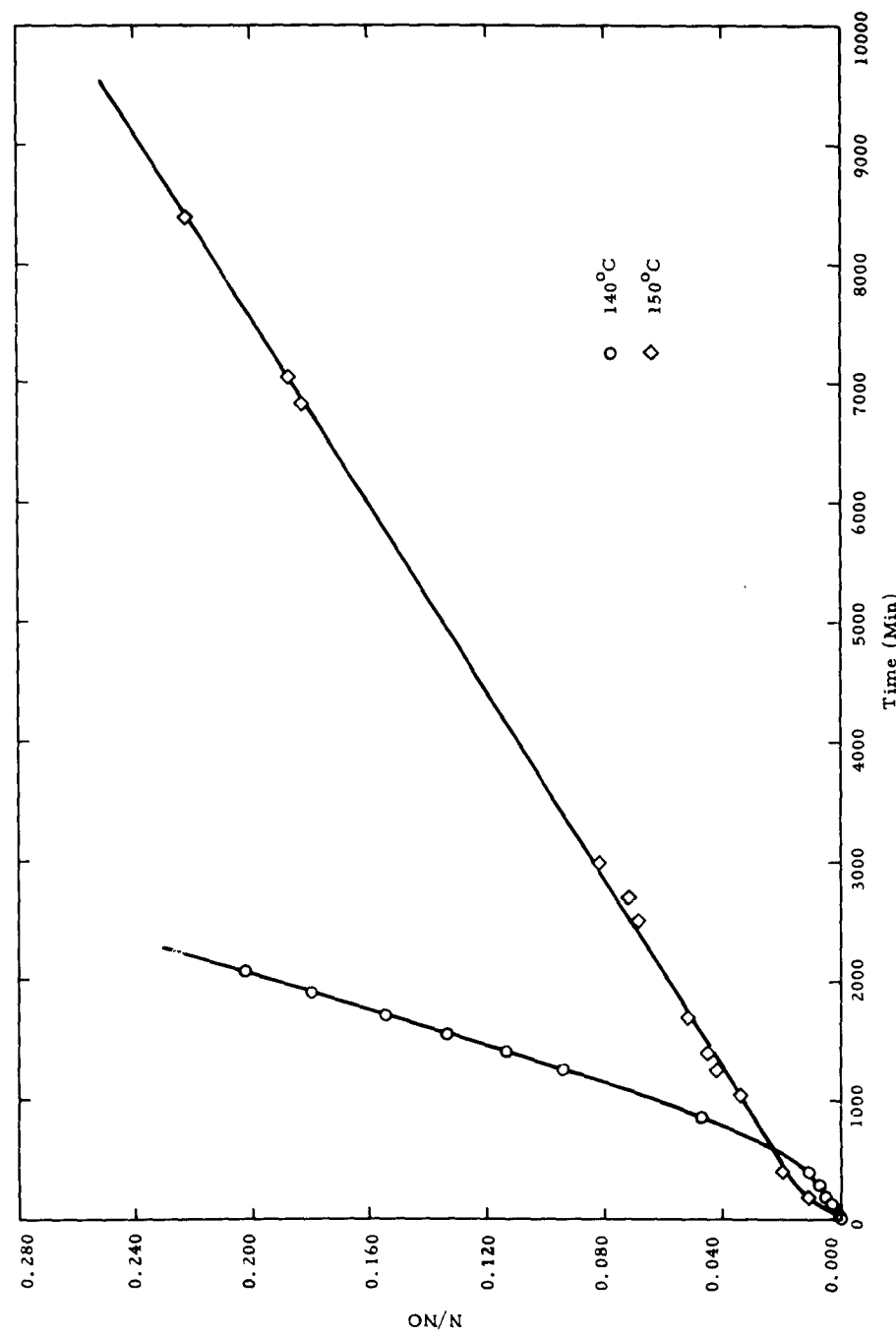


Figure 6. Fraction of Hydrazinium Perchlorate Decomposed as a Function of Time

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This peculiar increase in stability from 140°C to 150°C may be a result of the fusion of the solid at 141-142°C. Disappearance of decomposition nuclei which exist in the solid state would tend to slow the reaction somewhat by removing high-energy crystal dislocations. However, even in the light of the sudden increase in E_A at 142°C reported by Aerojet-General, the reaction would be expected to proceed more rapidly at the higher temperature. Therefore, these experiments should be regarded as preliminary and additional experiments will be performed in order to clarify the nature of the reaction in this temperature region.

It is of interest to note that the activation energies of HP and HP-2 are quite similar in the solid state reaction (22 kcal/mole and 23 kcal/mole, respectively), and that these compare remarkably well with the value of E_A for the decomposition of liquid anhydrous HClO_4 (22-23 kcal/mole). This lends additional weight to the proposition that HClO_4 is the effective decomposing agent in all cases and indeed suggests the strong possibility that the rate-determining step is the same in these cases at least.

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V. FUTURE WORK

During the next period extensive efforts will be made to establish the activation energies, stoichiometry, and mechanisms of the thermal decomposition of HP. It is hoped that elucidation of the characteristics of the HP reaction will provide information leading to a full understanding of the decomposition of HP-2 and other amino-perchlorate oxidizers.

Additional work is scheduled on anhydrous HClO_4 . The determination of vapor pressures at temperatures above the range already covered, and confirmation of pressures already reported, as well as stoichiometry studies, are considered critically important to the goals of the program.

Purification of HAP and determination of its vapor pressure and thermal decomposition characteristics are also scheduled for the coming quarter.

Specific experiments planned for the future include:

- Extension of thermal decomposition studies of HP to both higher and lower temperatures.
- Determination of the vapor pressures of HAP.
- Determination of the thermal decomposition characteristics of HAP
- Extension of vapor pressure measurements on anhydrous HClO_4 to higher temperatures
- Determination of thermal decomposition characteristics of anhydrous HClO_4 .

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Section VI

Task 56

CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE

Section VI

CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE

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D. Moy

Report RMD 5043-Q2-64

RMD Project 5043, Task 56
Report Period: 1 April 1964 to
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Contract No. NONr 4364(00)
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FORWORD

This section of the Advanced Oxidizer Research report summarizes work carried out on a new task (Task 56) which was added to Project 5043 on April 1, 1964. This task is directed toward the synthesis of inorganic N-F oxidizers from difluorodiazine and from nitrosyl fluoride.

Contributors to the studies conducted during the period from 1 April 1964 to 30 June 1964 were: A. R. Young (Project Supervisor), D. Moy (Principal Investigator), J. Crothamel, D. Kates, and E. Egbert.

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I. INTRODUCTION

This research program is concerned with the chemistry of difluorodiazine and nitrosyl fluoride, the ultimate objective being the synthesis of N-F containing solid oxidizers from these reagents.

cis-Difluorodiazine has been observed to form a solid compound with arsenic pentafluoride. The studies made on this compound to date indicate that it is ionic and contains the fluorodiazonium cation (N_2F^+). We have, therefore, initiated studies directed toward the utilization of N_2FAsF_6 as a precursor to new solid N-F oxidizers.

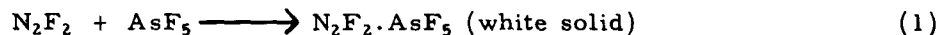
II. DISCUSSION

This report describes in detail the synthesis of a 1:1 solid adduct of cis-difluorodiazine with arsenic pentafluoride, and its characterization as fluorodiazonium hexafluoroarsenate, N_2FAsF_6 . It also describes attempts to trap $\cdot N_2F$ radicals generated from N_2FAsF_6 by reduction of the N_2F^+ cation.

A. REACTION OF cis-DIFLUORODIAZINE WITH ARSENIC PENTAFLUORIDE

During the first year of this program considerable effort was expended in attempts to carry out the addition of radicals to the $N=N$ bond of difluorodiazine (Ref 1). As an extension of this study we decided to examine the possibility that Lewis acids, such as AsF_5 , might promote addition to the $N=N$ bond of difluorodiazine. In our initial attempt to utilize arsenic pentafluoride as an addition catalyst it was observed that this reagent reacted rapidly with cis- N_2F_2 to form a white solid which is stable to above $100^\circ C$.

By studying the formation of this solid adduct when the proportions of the starting reagents were varied, it was established that the product is a 1:1 adduct (equation 1). The data leading to this conclusion are summarized



in Table I. The study also showed that only the cis-isomer of N_2F_2 forms an adduct with AsF_5 , and that impurities in the arsenic pentafluoride, such as SiF_4 and BF_3 , do not react with cis- N_2F_2 under the conditions which are effective in the formation of cis- $N_2F_2 \cdot AsF_5$.

B. CHARACTERIZATION OF cis- N_2F_2 - AsF_5 PRODUCT

The formation of a solid 1:1 adduct from N_2F_2 and AsF_5 was of interest because of the possibilities that (a) it might be conic, or (b) it might undergo addition reactions more readily than gaseous N_2F_2 . A thorough characterization of the product was therefore carried out.

The white solid adduct of AsF_5 and cis- N_2F_2 is stable in glass in an inert atmosphere at room temperature. It decomposes without melting at

approximately 200°C. It has essentially no vapor pressure at room temperature. The adduct is readily soluble in anhydrous HF at room temperatures, but insoluble in nonpolar solvents such as CHF₃, CF₃Cl, C₃F₆ and C₄F₈. It decomposes rapidly at room temperature in AsF₃, forming AsF₅ and N₂.

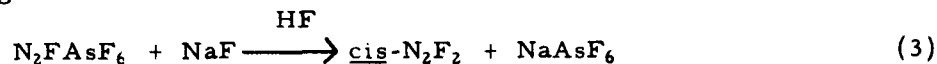
1. Stoichiometry

In addition to the evidence presented in Table I, the stoichiometry of the white solid can be inferred from quantitative studies of its reactions with water and with sodium fluoride in anhydrous hydrogen fluoride. Reactions of the adduct with water consistently gave nitrous oxide in quantities which were in excellent agreement with the calculated yields predicted by the reaction shown in equation 2. The fact that difluorodiazine does not react



readily with water suggested that the adduct was probably not a molecular complex.

The reaction of the adduct with sodium fluoride in HF also serves to confirm the 1:1 stoichiometry. The total nitrogen was recovered in excess of 98% of theoretical according to equation 3 as cis-difluorodiazine with a small nitrous oxide impurity. A small amount of water in the sodium fluoride reagent



can account for the formation of some nitrous oxide.

Finally, elemental analysis of a sample of the adduct gave the following results

Found	As, 31.6; F, 56.8; N, 11.8
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Theory for N ₂ FAsF ₆	As, 31.8; F, 56.4; N, 11.8
---	----------------------------

2. Mass Spectrum

A mass spectrum of N₂FAsF₆ was obtained at 150°C (Table II). It shows only peaks which are identifiable with the compound N₂FAsF₆, or a mixture consisting predominantly of the cis-isomer of N₂F₂ and AsF₅, formed by

TABLE I
PREPARATION OF $N_2F_2 \cdot AsF_5$



N_2F_2 (mmole)	AsF_5 (mmole)	Volatile Products
1	1	< 0.2 mmole $\left\{ \begin{array}{l} \text{trans-}N_2F_2 \\ SiF_4 \\ BF_3 \end{array} \right.$
2	1	~ 1 mmole $\left\{ \begin{array}{l} \text{cis-}N_2F_2, \text{trans-}N_2F_2 \\ SiF_4, BF_3 \end{array} \right.$
1	2	~ 1 mmole $\left\{ \begin{array}{l} AsF_5 \\ SiF_4, BF_3, \text{trans-}N_2F_2 \end{array} \right.$



TABLE II
MASS SPECTRUM $N_2F \cdot AsF_6$ AT $150^\circ C$

M/e	Ion	Relative Intensity
19	F^+	8.9
28	N_2^+	93.0
33	NF^+	5.2
47	N_2F^+	93.0
66	$N_2F_2^+$	3.1
75	As^+	6.0
94	AsF^+	6.2
113	AsF_2^+	8.6
132	AsF_3^+	14.2
151	AsF_4^+	100.0

thermal decomposition of the adduct. The intensity of the $N_2F_2^+$ (m/e, 66) peak suggests that some trans- N_2F_2 is formed when the adduct decomposes thermally.

3. Fluorodiazonium Ion, N_2F^+

The data obtained up to this point offered no conclusive evidence concerning the ionic or covalent nature of the cis- N_2F_2 - AsF_5 adduct. The fact that the reaction of N_2FAsF_6 with NaF in HF liberated only the cis-isomer of N_2F_2 suggested that the solid was a molecular complex. On the other hand, the rapid conversion of the adduct to N_2O by water seemed to be evidence for proposing an ionic structure since cis- N_2F_2 does not react readily with water. The results subsequently obtained from studies of the infrared spectrum, F^{19} NMR spectrum, and x-ray powder diffraction pattern of the solid strongly supported the ionic structure $N_2F^+AsF_6^-$.

4. Infrared Spectrum of N_2FAsF_6

The infrared spectrum of a thin film of N_2FAsF_6 (Figure 1) definitely shows the presence of the hexafluoroarsenate anion by the intense band at 700 cm^{-1} . The characteristic absorption bands due to AsF_5 (Ref 2) and cis- N_2F_2 (Ref 3) are absent. The band at 1050 cm^{-1} is in the region normally assigned to N-F stretching vibrations, and is believed to be characteristic of the fluorodiazonium ion NF_2^+ .

5. F^{19} NMR Spectrum

Additional evidence that N_2FAsF_6 is a fluorodiazonium salt was obtained from the F^{19} NMR spectrum of an HF solution at room temperature (Figure 2). The spectrum shows a fluorine on nitrogen triplet at a chemical shift of -179 ppm from trifluoroacetic acid (TFA) which was used as an external reference. The N-F coupling constant is 328 cps. A comparison of these values with the corresponding chemical shifts and coupling constants of cis- and trans-difluorodiazine (Ref 4) shows the chemical shift of the fluorodiazonium ion to be 29 ppm upfield of cis-difluorodiazine and 12.4 ppm downfield of the trans-isomer (Table III). The magnitude of the N-F coupling rules out the presence of cis- or trans-difluorodiazine. Moreover, the large increase in the N-F coupling constant in the adduct relative to that of cis- N_2F_2 suggests an increase in the "s" character of the nitrogen bonding orbital as would be the case in going from N_2F_2 (sp^2) to $:N\equiv NF^+$ (sp).

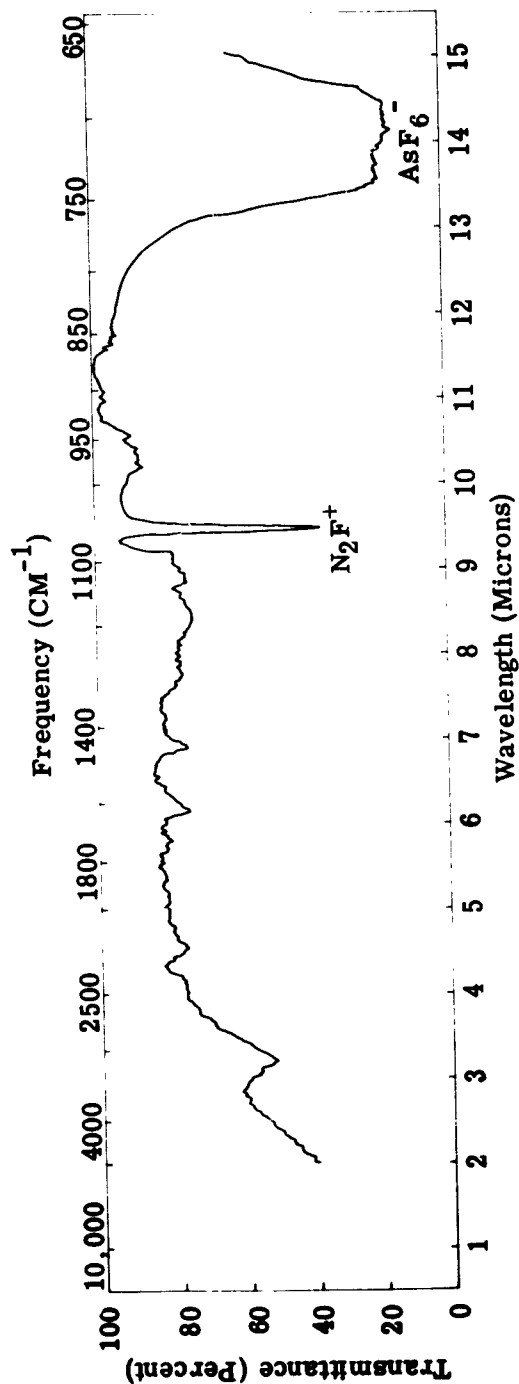


Figure 1. Infrared Spectrum of $N_2F^+AsF_6^-$ Film on AgCl

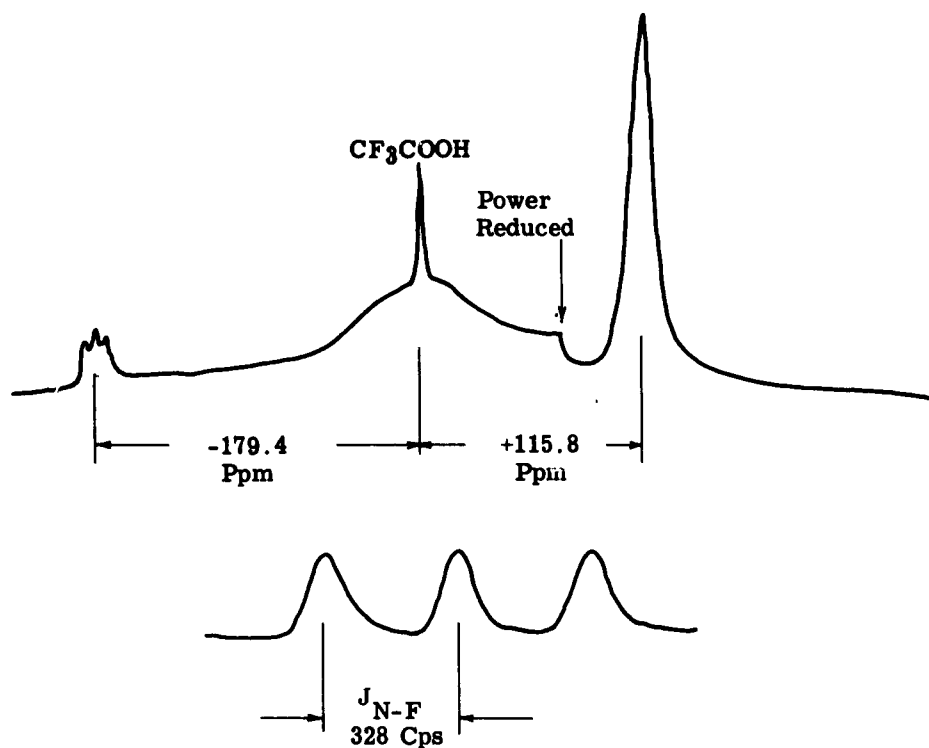


Figure 2. F¹⁹NMR Spectrum of N₂FAsF₆ in Anhydrous HF

TABLE III

F¹⁹ CHEMICAL SHIFTS OF N-F COMPOUNDS

Compound	δ (Ppm from CF ₃ COOH)	J_{N-F} (Cycles)
<u>cis</u> -N ₂ F ₂	-208	145
<u>trans</u> -N ₂ F ₂	-167	136
N ₂ FAsF ₆	-179.4	328

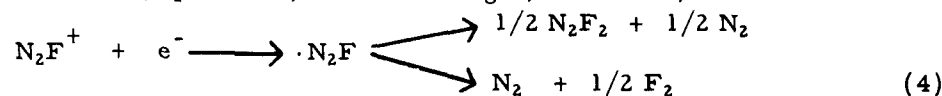
There is no F^{19} resonance peak assignable to the AsF_6^- ion in this spectrum. The HF peak is displaced by approximately 10 ppm upfield relative to pure HF and these are conditions indicative of rapid fluoride exchange between HF and the AsF_6^- ion (Ref 4).

6. X-Ray Diffraction Pattern *

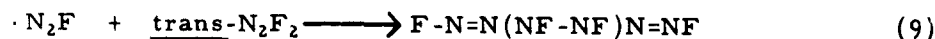
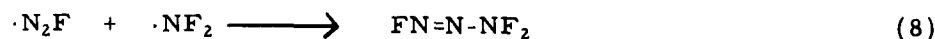
The powder diffraction lines of N_2FAsF_6 were indexed on a rhombohedral unit cell (Table IV) having the following cell constants: $a = 11.49 \text{ \AA}$ and $\alpha = 103^\circ$. All of the hexafluoroarsenate salts of the larger univalent metal cations crystallize in the rhombohedral system (Ref 5). The volume of a rhombohedral unit cell having the dimensions given above is $1369 \text{ \AA}^3$. If one assumes that there are 10 molecules per unit cell, a molecular volume is obtained for N_2FAsF_6 ($136.9 \text{ \AA}^3$) which is slightly larger than that of $CsAsF_6$ (Table V). On this basis, a crystal density of 2.8 gm/cc is predicted for N_2FAsF_6 . The observed density of 2.6 gm/cc is in quite good agreement with this value.

C. REACTIONS OF N_2FAsF_6

The initial product of the reduction of the N_2F^+ cation should be an $\cdot N_2F$ radical (equation 4). It was thought, therefore, that the reduction



of N_2FAsF_6 might lead to new compounds containing the fluorazine group ($-N=NF$), as shown in the reactions proposed below (equations 5 through 9).



However, to date we have been unable to produce any fluorazine derivatives other than cis- N_2F_2 by this approach.

*A single crystal study of N_2FAsF_6 is presently being conducted at Shell Development Laboratories, Emeryville, California

TABLE IV
DIFFRACTION PATTERN OF N_2FAsF_6

Rhombohedral Unit Cell: $a = 11.49 \text{ \AA}$, $\alpha = 103^\circ$, $\rho_{\text{obs}} = 2.6 \text{ gm/cc}$, $\rho_{\text{calc}} = 2.85 \text{ gm/cc}$, $Z = 10$

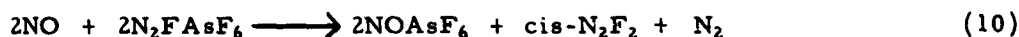
h, k, l	$d \text{ (calc \AA)}$	$d \text{ (obs \AA)}$	$I/I_0 \text{ (rel)}$
1, 1, $\bar{2}$	5.18	5.18	40
1, 1, 1	4.92	4.92	60
1, 2, $\bar{1}$	4.58	4.56	50
2, 2, $\bar{1}$; 1, 2, 1	3.57	3.57	100
1, 2, $\bar{3}$	3.41	3.41	20
2, 2, 1	2.93	2.90	20
3, 3, 0; 1, 1, 4; 4, 2, $\bar{3}$	2.24	2.23	30
2, 2, 4; 4, 2, 2	1.79	1.79	30

TABLE V
LATTICE CONSTANTS OF HEXAFLUOROARSENATES

Compound	$r_+ \text{ (\AA)}$	Lattice Type	Constants	Molecular Vol. ($\text{\AA}^3$)
KAsF ₆	1.33	Rhombohedral	$a = 4.92 \text{ \AA}$, $\alpha = 97.2^\circ$	120.9
RbAsF ₆	1.48	Rhombohedral	$a = 5.00 \text{ \AA}$, $\alpha = 96.1^\circ$	124.6
CsAsF ₆	1.69	Rhombohedral	$a = 5.20 \text{ \AA}$, $\alpha = 96.0^\circ$	131.2
N_2FAsF_6	1.84	Rhombohedral	$a = 11.49 \text{ \AA}$, $\alpha = 103^\circ$	136.9

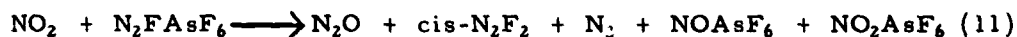
1. Reaction of NO With N_2FAsF_6

NO was oxidized on standing with N_2FAsF_6 at room temperature with the formation of $NOAsF_6$. The gaseous fraction consisted only of unreacted NO, cis- N_2F_2 and N_2 .



2. Reaction of NO_2 With N_2FAsF_6

NO_2 was easily and rapidly oxidized by N_2FAsF_6 at room temperature as evidenced by the rapid disappearance of its brown color. Analysis of the gases showed only N_2 , cis- N_2F_2 and N_2O . The solid residue was identified as a mixture of $NOAsF_6$ and NO_2AsF_6 by x-ray analysis.



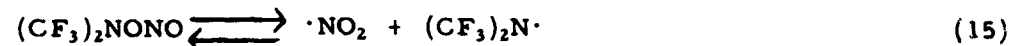
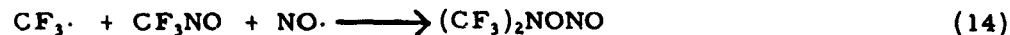
3. Reaction of CF_3NO With N_2FAsF_6

Attempts were made to prepare CF_3N_2F by the following reaction:



CF_3NO and N_2FAsF_6 reacted rapidly below room temperature to give a complex mixture of compounds. Fluorocarbons, $(CF_3)_2NONO$, CF_3NO_2 and $(CF_3)_2N-NO$ were identified. There was also a small amount of unidentified material present but no evidence was obtained by mass spectral or infrared analysis for N-F bonding. The solid residue was identified as $NOAsF_6$. The desired compound, CF_3N_2F was not detected.

The appearance of the mixture of fluorocarbons $(CF_3)_2NONO$, CF_3NO_2 and $(CF_3)_2NNO$ can be accounted for by the reaction of $CF_3\cdot$ (equation 13) and $NO\cdot$ radicals (present in CF_3NO) with CF_3NO and subsequent reaction products according to the reactions shown in equations 14-17.





4. Reaction of CF_3I With N_2FAsF_6

N_2FAsF_6 and CF_3I reacted very vigorously below -80°C to give a mixture of fluorocarbons and noncondensable gases. A red solid residue was left which slowly decomposed to give iodine.

5. Attempted reaction of HCF_3 and ClCF_3 With N_2FAsF_6

Neither HCF_3 nor ClCF_3 appeared to undergo any reaction with N_2FAsF_6 at temperatures from -196°C to room temperature.

6. Reactions of NOCl and HCl With N_2FAsF_6

Attempts were made to prepare ClN_2F by the reaction of N_2FAsF_6 with NOCl and HCl . Excess NOCl reacted rapidly with N_2FAsF_6 on warming the cold mixture to room temperature. cis- N_2F_2 , Cl_2 , N_2O and N_2 were identified as gaseous products of this reaction. The solid residue was NOAsF_6 .

A reaction of N_2FAsF_6 with HCl produced Cl_2 , cis- N_2F_2 , N_2 and AsF_5 .

7. Attempted Reactions of N_2F_4 and trans- N_2F_2 With $\text{N}_2\text{F}^\cdot$ Radical

The $\text{N}_2\text{F}^\cdot$ radical was liberated by the reaction of NO with N_2FAsF_6 . No apparent coupling of the $\text{N}_2\text{F}^\cdot$ radical with either NF_2 or trans- N_2F_2 was observed, however, when N_2FAsF_6 was reacted with mixtures of NO and N_2F_4 , and NO and trans- N_2F_2 .

8. Attempted Reaction of $\text{N}_2\text{F}^\cdot$ Radicals With Perfluoro-olefins

C_3F_6 and C_4F_8 were recovered intact from reaction mixtures of N_2FAsF_6 with C_3F_6 and NO , and C_4F_8 and NO . N_2FAsF_6 reacted violently with C_2F_4 below -80°C to give a mixture of fluorocarbons, AsF_5 and N_2 . Addition of Freon solvents had no moderating effect on the reaction.

III. EXPERIMENTAL

A. REACTION OF cis-DIFLUORODIAZINE WITH ARSENIC PENTAFLUORIDE

Arsenic pentafluoride (Peninsular Chem Research) contained small amounts of SiF_4 and BF_3 as impurities. cis-Difluorodiazine (Air Products) contained small amounts of trans- N_2F_2 as the principal impurity. The reagents were used without further purification.

Quantities of cis- N_2F_2 and AsF_5 were measured separately in a calibrated Monel bulb then condensed into a Kel-F reaction tube at -196°C . The tube was allowed to warm to room temperature. After 1-2 hours the residual pressure in the tube was measured and gas samples taken for infrared analysis.

Less than 10% of the original reactants were recovered on mixing a 1:1 ration of cis- N_2F_2 and AsF_5 . The residual gas was identified as SiF_4 , BF_3 and trans- N_2F_2 , all known impurities in the starting materials. When a two-fold excess of one reagent or the other was used, a complete recovery of the excess reagent was obtained at the end of the preparative run.

In a separate experiment, trans- N_2F_2 and AsF_5 did not react to form a stable product.

B. HYDROLYSIS OF N_2FAsF_6

Two samples of N_2FAsF_6 (0.73 mmole and 1.14 mmole) produced 0.67 mmole (93% of theoretical) and 1.12 mmole (98.5% of theoretical) respectively of N_2O on hydrolysis in a closed Kel-F tube. N_2O was distilled from the hydrolysis tube at -80°C and identified by its IR spectrum.

C. REACTION OF N_2FAsF_6 With NaF in HF

Anhydrous HF was obtained by reacting water-contaminated HF with N_2FAsF_6 until N_2O was no longer evolved. The anhydrous HF was recovered and used in subsequent experiments.

To a solution of 0.87 mmole of N_2FAsF_6 in approximately 5 ml of anhydrous HF was added excess NaF. After shaking for several minutes the gaseous evolution ceased. The reactor was cooled to $-80^\circ C$ and 0.85 mmole (98% of theoretical) of gas ($>95\%$ cis- N_2F_2 , balance N_2O) was obtained. These were identified by their IR spectra.

D. MASS SPECTRUM

A sample of N_2FAsF_6 in a small Monel tube was attached to a Bendix Time-of-Flight mass spectrometer. It was evacuated and heated to $150^\circ C$ in vacuo while open to the mass spectrometer.

E. INFRARED SPECTRUM

A 1:1 mole ratio of AsF_5 and cis- N_2F_2 were condensed on a silver chloride window at $-196^\circ C$. The window was warmed to room temperature and the residual gases removed. By this procedure a thin film of N_2FAsF_6 was formed on the window. The film was then scanned on a Perkin-Elmer 21 Spectrometer from 2 to 15μ .

F. $F^{19}NMR$ SPECTRUM

The $F^{19}NMR$ spectrum of N_2FAsF_6 in anhydrous HF (approximately 40% solution) was obtained on a Varian HR-60 Spectrometer at room temperature. Tri-fluoroacetic acid (TFA) was used as an external reference. Approximate chemical shift (uncorrected for bulk susceptibility effects) and N-F coupling constants were obtained from the location of TFA side bands with an accuracy of ± 10 cps. Sample tubes were made by fitting a $6'' \times 0.5''$ Teflon tube to a valve and ball joint by means of Swagelok connections. The TFA reference capillary was taped to the outside of the tube.

G. X-RAY POWDER DIFFRACTION PATTERN

X-ray powder patterns were obtained on samples of N_2FAsF_6 from separate preparative runs and a sample recovered from HF solution. All of the patterns were identical. The powder diffraction patterns were photographed with $CuK\alpha$ radiation from a nickel filter. The x-ray samples were sealed under nitrogen in Pyrex capillaries.

H. DENSITY OF N_2FAsF_6

The density of FC-75* ($d_{25} = 1.77$ gm/cc) was determined with a 2 ml pycnometer. The density of N_2FAsF_6 was determined to be 2.6 gm/cc by displacement of FC-75.

*Minnesota Mining and Manufacturing Co.

I. REACTIONS OF N_2FAsF_6

1. With Nitric Oxide

2.3 mmole N_2FAsF_6 and 1.1 mmole NO were mixed at $-196^\circ C$ and allowed to warm to room temperature. After standing for several hours, the gases were analyzed by mass spectral and IR methods. The principal components were cis- N_2F_2 and N_2 (in roughly equivalent amounts). The solid residue was analyzed by IR and x-ray analysis and found to be $NOAsF_6$. Varying the ratio of N_2FAsF_6 :NO did not change the reaction product.

2. With Nitrogen Dioxide

1.25 mmole each of N_2FAsF_6 and NO_2 were mixed at $-196^\circ C$. On warming, the brown color of NO_2 quickly disappeared. Analysis of the bases by IR showed predominantly N_2O , with much smaller amounts of N_2 and cis- N_2F_2 . The solid was determined to be a mixture of $NOAsF_6$ and NO_2AsF_6 .

3. With CF_3NO

1:1 and 1:2 mole ratio mixtures of N_2FAsF_6 and CF_3NO gave essentially identical results. The materials were mixed together at $-196^\circ C$ and allowed to warm slowly. Rapid evolution of gas occurred well below room temperature with a gradual disappearance of the blue color of CF_3NO . The mixture of gases was fractionated at $-80^\circ C$, $-120^\circ C$ and $-196^\circ C$ and analyzed by IR and mass spectral methods. $(CF_3)_2NONO$, CF_3NO_2 , CF_3N-NO and unreacted CF_3NO were identified. A small fraction collecting at $-80^\circ C$ had unidentified IR bonds at the 6.15 μ , 10.3 μ and 7-8 μ regions, but mass spectral analysis failed to detect any N-F mass fragments. The solid residue was identified as $NOAsF_6$.

4. With CF_3I

0.8 mmole CF_3I was condensed on 0.8 mmole N_2FAsF_6 at $-196^\circ C$. On warming to $-80^\circ C$ a rapid reaction occurred leaving an unstable red residue and a mixture of fluorocarbons and noncondensable gases. The red residue liberated iodine on standing.

5. With HCF_3 and $ClCF_3$

Equimolar amounts of HCF_3 and N_2FAsF_6 and $ClCF_3$ and N_2FAsF_6 appeared to undergo no reaction at temperatures from $-196^\circ C$ to room temperature.

6. With Nitrosyl Chloride

0.5 mmole N_2FAsF_6 and 3 mmole $NOCl$ were mixed at $-196^\circ C$ and underwent a rapid reaction at temperatures below room temperature. On fractionation, approximately 50% N_2 was obtained. The condensable fraction consisted mainly of Cl_2 with a smaller amount of cis- N_2F_2 .

7. With HCl

1.2 mmole of HCl and 1.2 mmole N_2FAsF_6 reacted below room temperature to give predominantly noncondensable gases. The condensable fraction contained mostly Cl_2 with only traces of cis- N_2F_2 .

8. With N_2F_4

A mixture of 0.8 mmole of N_2FAsF_6 and 0.8 mmole N_2F_4 gave no reaction on standing for 24 hours. To the mixture was added 0.8 mmole NO . After reacting at room temperature for several hours the gases were fractionated at $-196^\circ C$ and $-160^\circ C$. Approximately 95% of the original amount of N_2F_4 was recovered unchanged. Traces of N_2O and NF_3 were observed in the -196° trap. Noncondensables made up the balance of the gaseous fraction.

9. With trans- N_2F_2

No evidence of an addition of $N_2F^\cdot$ radicals was observed in mixing equimolar amounts of N_2FAsF_6 , trans- N_2F_2 and NO .

10. With C_2F_4

An equimolar mixture of C_2F_4 and N_2FAsF_6 reacted below $-80^\circ C$. Fractionation of the gases gave approximately 35% N_2 , 60% CF_4 , 5% of C_2F_6 , COF_2 and AsF_5 .

IV. FUTURE WORK

During the next quarter work will consist of attempts to synthesize energetic fluorodiazonium salts by further reactions of cis- N_2F_2 and by metathesis from $N_2F^+AsF_6^-$.

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