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Report RMD 5043-Q3-65

Contract No. NOnr 4364(00)

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ADVANCED OXIDIZER RESEARCH

Report Period: 1 July 1965 to 30 September 1965

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DECLASSIFIED AFTER 12 YEARS

Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

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ADVANCED OXIDIZER RESEARCH

Report RMD 5043-Q3-65

Report Period: 1 July 1965 to 30 September 1965

Report Date: 30 September 1965

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

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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 Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer.

This report consists of the three following sections:

Section	Task No.	Title
I	51	Organic Difluoramine Chemistry
II	53	Inorganic Oxidizer Synthesis
III	55	Thermal Stability of Advanced Solid Oxidizers

ABSTRACT

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

SECTION I - ORGANIC DIFLUORAMINE CHEMISTRY

Further experiments on the dehydrofluorination of secondary alkyldifluoramines are described. A new partially dehydrofluorinated product, 1-difluoramino-2-fluoriminocyclohexane, has been obtained by treating bis-(difluoramino)cyclohexane with basic ion exchange resin for a limited time.

Bis(difluoramino)fluoraminomethoxypentane was synthesized by the addition of pentanol to perfluoroguanidine. The adduct was stable to vacuum distillation but lost the elements of HNF_2 to yield N, N, N'-trifluoropentoxyformamidine upon exposure to a Halocarbon chromatographic column.

1, 1-Bis(difluoramino)phenylethane and 1, 1-bis(difluoramino)heptane were synthesized in sufficiently high purity for thermal sensitivity and heat of formation determinations, respectively.

SECTION II - INORGANIC OXIDIZER SYNTHESIS

Elemental analyses of the N_2F_4-AsF_5 adduct give a composition, $N_2F_4(AsF_5)_{1.33}$, indicating a mixture of adducts having 1:1 and 1:2 N_2F_4:AsF_5 ratios. Evidence presented previously that the adduct is ionic and contains the $N_2F_3^+$ cation still appears valid. The structure of the 1:2 adduct is possibly $N_2F_3^+As_2F_{11}^-$.

The reaction of N_2F_4 with $HAsF_6$ gives a solid N-F compound having X-ray and infrared spectra different from $N_2F_3AsF_6$. No reaction occurred when N_2F_4 was treated with $HClO_4$ in HF. Unsuccessful attempts were made to prepare $N_2F_3ClO_4$ by reacting $N_2F_3AsF_6$ with metal perchlorates in HF.

The reaction of O_2AsF_6 with $CsClF_4$ produces O_2 and Cl_2, as well as $CsAsF_6$, at about 0°C. The reaction of NO_2 with AsF_5 does not give a molecular adduct $NO_2 \cdot AsF_5$ as reported in the literature, but rather a mixture of $NOAsF_6$ and NO_2AsF_6.

SECTION III - THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

The presence of ammonium perchlorate as a decomposition product of hydroxylammonium perchlorate was found to be dependent on the removal of oxidizing species from the system and, hence, non-stoichiometric. The oxidation of ammonium perchlorate by anhydrous perchloric acid at elevated temperatures was demonstrated.

SECTION I

TASK 51

ORGANIC DIFLUORAMINE CHEMISTRY

Section I

ORGANIC DIFLUORAMINE CHEMISTRY

Harry F. Smith
Joseph J. Dvorak

Report RMD 5043-Q3-65

RMD Project 5043, Task 51
Report Period: 1 July 1965
to 30 September 1965

Contract No. NOnr 4364(00)
ARPA Order No. 417
Project Code 5910

FOREWORD

This section of the quarterly progress report on advanced oxidizers describes research performed from 1 July 1965 to 30 September 1965 on the synthesis and chemical reactions of organic fluoronitrogen compounds, and on the preparation of selected difluoramino compounds for structure-sensitivity correlation studies.

Technical personnel contributing to this effort were: H. F. Smith (Project Supervisor), J. J. Dvorak, W. H. Wieting, and P. Shapiro (Synthesis). Analytical support was provided by D. G. Chowanec, J. A. Creatura, D. F. Kates, and D. N. Pregler.

ABSTRACT

Further experiments on the dehydrofluorination of secondary alkyldifluoramines are described. A new partially dehydrofluorinated product, 1-difluoramino-2-fluoriminocyclohexane, has been obtained by treating bis(difluoramino)cyclohexane with basic ion exchange resin for a limited time.

Bis(difluoramino)fluoraminomethoxypentane was synthesized by the addition of pentanol to perfluoroguanidine. The adduct was stable to vacuum distillation but lost the elements of HNF_2 to yield N, N,N'-trifluoropentoxyformamidine upon exposure to a Halocarbon chromatographic column.

1,1-Bis(difluoramino)phenylethane and 1,1-bis(difluoramino)heptane were synthesized in sufficiently high purity for thermal sensitivity and heat of formation determinations, respectively.

CONTENTS

ILLUSTRATIONS

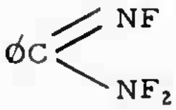
I. INTRODUCTION

The research described in this report has been directed toward the same two objectives that guided our earlier work. Our primary objective has been to elucidate some of the chemistry of organic fluoronitrogen compounds pertaining to the field of high-energy propellant oxidizers. A smaller effort is directed toward the synthesis of certain difluoramino compounds for studies seeking to correlate thermal sensitivity with structure.

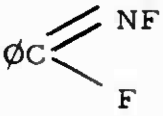
The immediate area of interest of the exploratory portion of our program is an investigation of the chemical reactions of compounds containing the ketofluorimino group, $>C=NF$. Some effort was devoted to the synthesis of one of the simplest of such model compounds, cyclohexylidenefluorimine (I), and to studying the intricacies of the dehydrofluorination of other difluoramines. Several new model compounds containing substituents of high electronegativity

1

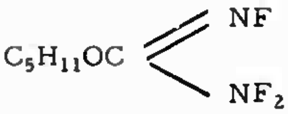
(II, III, IV) have been synthesized and an exploration of their addition



II



III



IV

reactions has begun. These models are electronically analogous to perfluoroguanidine, and it is anticipated that some of the same kinds of reaction will occur.

Two new compounds have been synthesized in high purity for physicochemical studies in other laboratories. These are 1,1-bis(difluoramino)-phenylethane (V) for sensitivity evaluation at the Naval Ordnance Laboratory and 1,1-bis(difluoramino)heptane (VI) for heat-of-formation determination at the Bureau of Mines. In addition, an old sample of 1, 2-bis(difluoramine)

$\phi\overset{NF_2}{\underset{NF_2}{C}}CH_3$

V

$C_6H_{13}CH(NF_2)_2$

VI

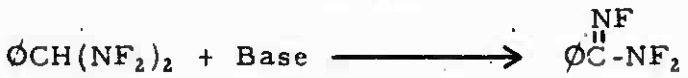
ethane was repurified for sensitivity studies.

II. DISCUSSION

A. DEHYDROFLUORINATION REACTIONS

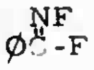
The dehydrofluorination of three compounds, cyclohexyldifluoramine, 1,2-bis(difluoramino)cyclohexane and α,α-bis(difluoramino)toluene, was conducted in order to obtain appropriate fluorimino model compounds which could be used in elucidating the chemistry of the ketofluorimino group, $>C{=}NF$.

Dehydrofluorination of α,α-bis(difluoramino)toluene (VII), as previously reported (Ref 1), again resulted in a two-component mixture which contained the desired N,N,N'-trifluorobenzamidine (Equation 1). On the basis of infrared spectral data, the second component has been tentatively assigned the structure III. Unfortunately, sufficient material for an unequivocal characterization of this second component has not been obtained.



$$\phi CH(NF_2)_2 + \text{Base} \longrightarrow \phi\overset{NF}{\overset{\|}{C}}\text{-}NF_2 \qquad (1)$$

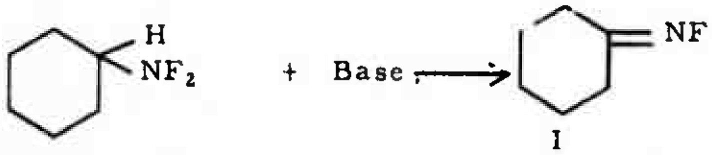
VII II



$$\phi\overset{NF}{\overset{\|}{C}}\text{-}F$$

III

Some difficulties have been encountered in the dehydrofluorination of cyclohexyldifluoramine (Equation 2). In several instances, the distillation of

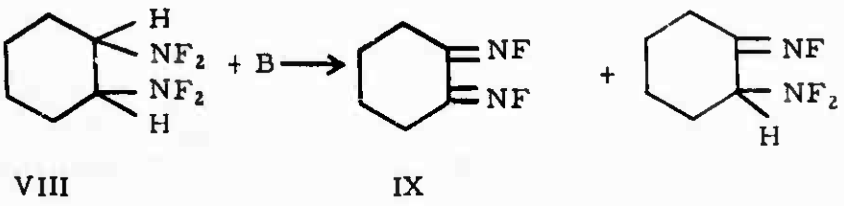


(2)

the crude product, obtained by treating the cyclohexyldifluoramine with basic ion exchange resin, was accompanied by decomposition. Surprisingly, decomposition appeared to occur in the condenser. Any liquid returning to the pot from the distillation column remained colorless. As yet, we can offer no explanation for this observation.

In one experiment, decomposition was observed as soon as the cyclohexyldifluoramine was added to an ether suspension of the resin. In this instance, however, the batch of resin used was different from that used for the previous successful dehydrofluorination of VII. Presumably, some contaminant in the resin, such as water, contributed to the decomposition.

A very interesting result was obtained in one experiment in which the time for reaction between 1,2-bis(difluoramino)cyclohexane (VIII) and Amberlite IR-45 resin was cut short. Normally, the difluoramino compound subjected to dehydrofluorination is allowed to react with the resin for approximately 20 hr. In this instance, however, after 6 hr. the resin appeared to be consumed and the reaction was quenched by filtering the mixture. Distillation of the crude reaction product gave three fractions. The first and predominant fraction consisted of unreacted 1,2-bis(difluoramino)cyclohexane (VIII). The third fraction consisted of 1,2-difluoriminocyclohexane (IX). The infrared spectrum of the second fraction, however, indicates the presence of both fluoramino ($-NF_2$) and fluorimino($=NF$) groups, possibly in the same molecule (Figure 1). Infrared curves of VIII and IX are shown for reference in Figures 2 and 3, respectively. These results suggest that dehydrofluorination of a difluoramino group



(3)

B = Amberlite IR-45 resin

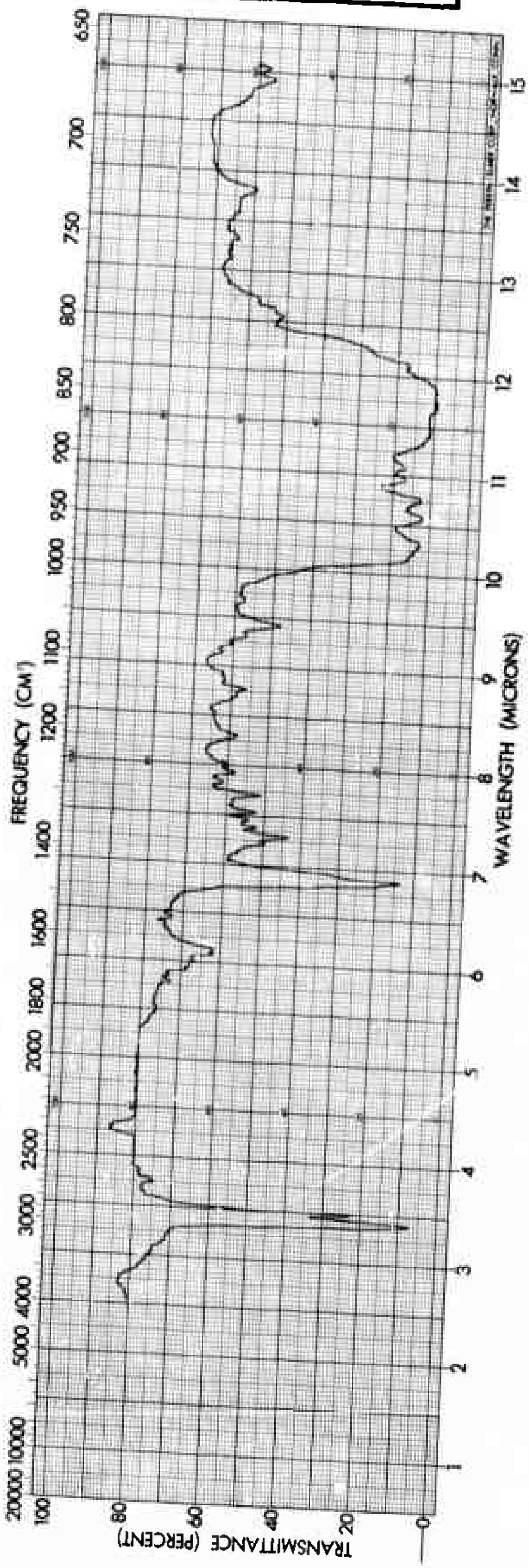


Figure 1. Infrared Spectrum of Partially Dehydrofluorinated 1,2-Bis(difluoramino)cyclohexane

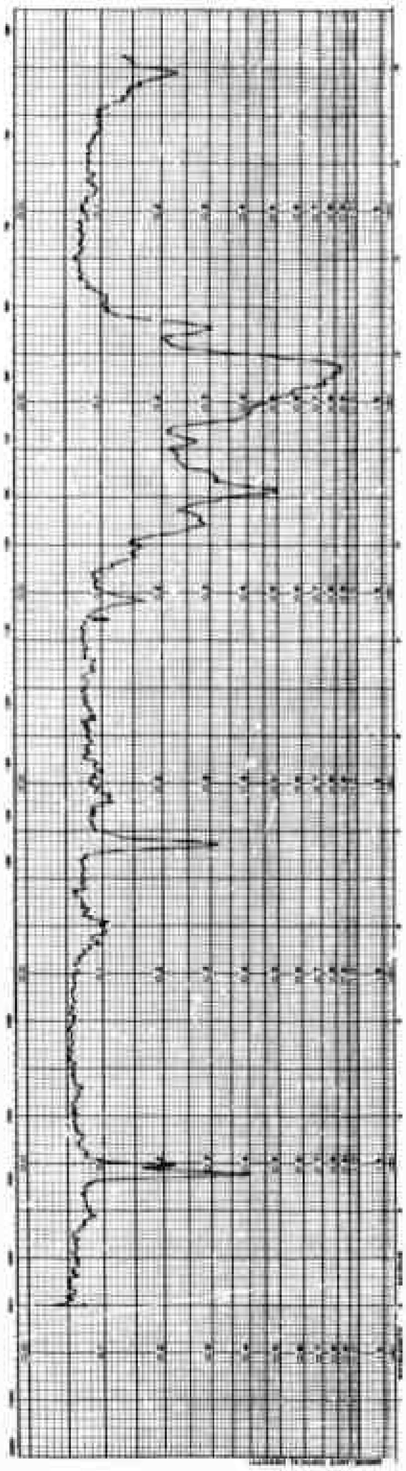


Figure 2. Infrared Spectrum of 1,2-Bis(difluoramino)cyclohexane

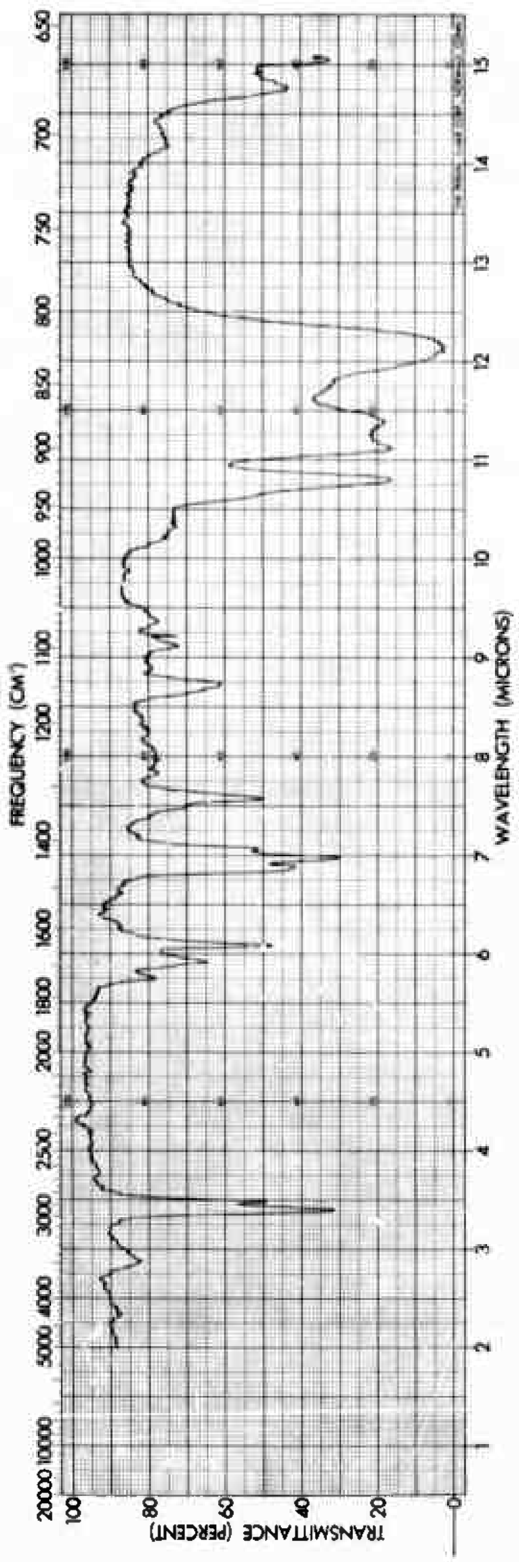
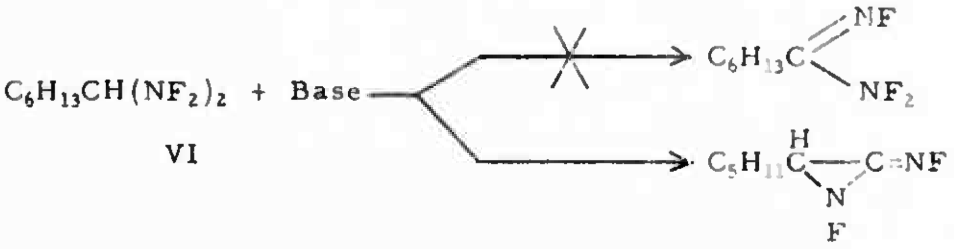


Figure 3. Infrared Spectrum of 1,2-Difluoriminocyclohexane

in a position vicinal to a fluorimino group proceeds somewhat more rapidly than the initial dehydrofluorination producing the first fluorimino group. It is problematical whether this observation has any bearing on the dehydrofluorination of gem-bis(difluoramines) to trifluoroamidines. The elimination of a second equivalent of hydrogen fluoride, in the reaction of 1,1-bis(difluoramino)heptane (VI) for example (Ref 2), gave a product of probable structure



(4)

X

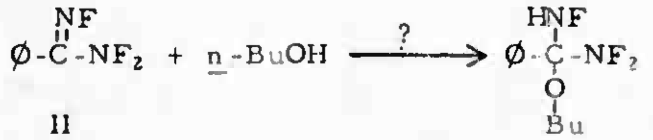
X, rather than the desired amidine. In future dehydrofluorination experiments, the effect of introducing the base into an excess of the difluoramine will be examined.

In one experiment, VIII was treated with ethyldiisopropylamine in place of the ion exchange resin. Subsequently, the reaction mixture was washed with water and the organic layer was separated and dried. After the solvent was evaporated at room temperature, the crude yellow oil spontaneously darkened and rapidly decomposed. The cause of this decomposition is unknown.

B. ADDITION REACTIONS OF ACTIVATED FLUORIMINES

In order to define the nature and scope of reactions involving the ketofluorimine group, $>C=NF$, an investigation of the chemical reactions of new model compounds containing electronegative substituents has been initiated. Of these model compounds, N,N,N'-trifluorobenzamidine (II) was selected for intensive study.

Since perfluoroguanidine is known to undergo addition reactions with alcohols, an investigation of the reaction of II with n-butanol (Equation 5)



$$\underset{\text{II}}{\phi\text{-}\overset{\overset{NF}{\|}}{C}\text{-}NF_2} + n\text{-}BuOH \xrightarrow{?} \phi\text{-}\underset{\underset{\underset{Bu}{|}}{O}}{\overset{\overset{HNF}{|}}{C}}\text{-}NF_2 \qquad (5)$$

was started in order to determine those factors which influence the course and extent of reaction and the physical and chemical stability of the products.

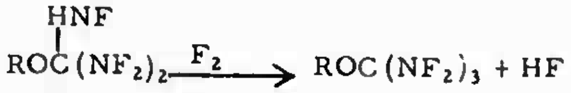
In a preliminary experiment, II was added to a mixture of n-butanol and urea in Freon-113. The reaction mixture was stirred for several hours at 0°C and then overnight at ambient temperature. Under these conditions no reaction was found to occur. In future experiments, the effects of heat, pressure and a variety of catalysts will be explored.

C. CHEMISTRY OF BIS(DIFLUORAMINO)FLUORAMINOMETHOXYALKANES

A route to one of the most energetic classes of difluoramino compounds involves the addition of alcohols to perfluoroguanidine (Equation 6)

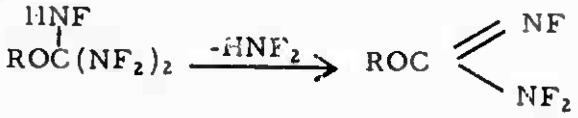
$$ROH + FN{=}C(NF_2)_2 \longrightarrow RO\overset{HNF}{\overset{|}{C}}(NF_2)_2 \qquad (6)$$

and the subsequent fluorination of the fluoramino intermediate (Equation 7). The



$$RO\overset{HNF}{\overset{|}{C}}(NF_2)_2 \xrightarrow{F_2} ROC(NF_2)_3 + HF \qquad (7)$$

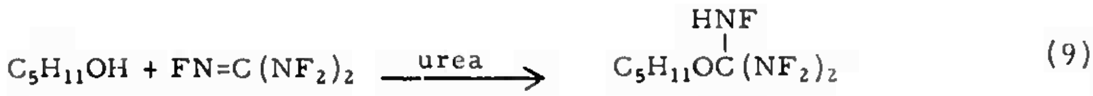
relative instability of the intermediate, which tends to eliminate the elements of HNF_2 to form an alkoxyformamidine (Equation 8), has been a major source of difficult



$$RO\overset{HNF}{\overset{|}{C}}(NF_2)_2 \xrightarrow{-HNF_2} ROC\begin{cases} =NF \\ -NF_2 \end{cases} \qquad (8)$$

and has impeded the successful utilization of this system (Ref 3). We have undertaken an investigation of the conditions which favor this decomposition reaction in order to provide information which will be valuable in avoiding it. At the same time, we will be producing a compound containing an electronegatively activated fluorimino group, which will be useful in reaction studies aimed at defining the scope and limitations of addition reactions.

An adduct (XI) was prepared from pentanol and perfluoroguanidine (Equation 9)

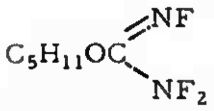


$$C_5H_{11}OH + FN{=}C(NF_2)_2 \xrightarrow{\text{urea}} C_5H_{11}O\overset{\overset{\textstyle HNF}{|}}{C}(NF_2)_2 \qquad (9)$$

XI

using previously established procedures (Ref 3). The crude product was shown by its infrared absorption curve (Figure 4) to be principally XI. An N-H peak was observed at about 3150 cm.$^{-1}$ along with N-F absorptions in the 850-1000 cm.$^{-1}$ region, but there was no indication of C=N at 1800 cm.$^{-1}$. When this material was chromatographed on a Halocarbon oil column, it appeared to contain three major components (Figure 5). Fractional distillation under vacuum gave no clearly defined boiling point plateaus. Three distillation fractions were separated, and each exhibited a three-peak v.p.c. trace similar to that of the crude mixture. When the fraction represented by peak B was collected and repassed through the v.p.c. column, it gave a major peak at essentially the same retention time, accompaned by a small peak corresponding to peak A (Figure 6). The infrared spectrum of this fraction (Figure 7) contained the expected absorptions for IV (C=N at 1800 cm.$^{-1}$, no N-H at 3150 cm.$^{-1}$) plus smaller peaks due to water and acetone which apparently condensed with the fraction during its collection. Upon rechromatographing material collected from peak C, we obtained a trace containing a prominent peak corresponding to B and a very small residual peak at C (Figure 8).

From these observations, we conclude that the adduct XI was the principal product



IV

formed in the reaction, and that this compound was stable to distillation under vacuum. Passing through the Halocarbon oil v.p.c. column caused the decomposition of XI (peak C) leading to IV (peak B). The identity of the compound which produced peak A in the chromatogram of the crude reaction product has not been determined.

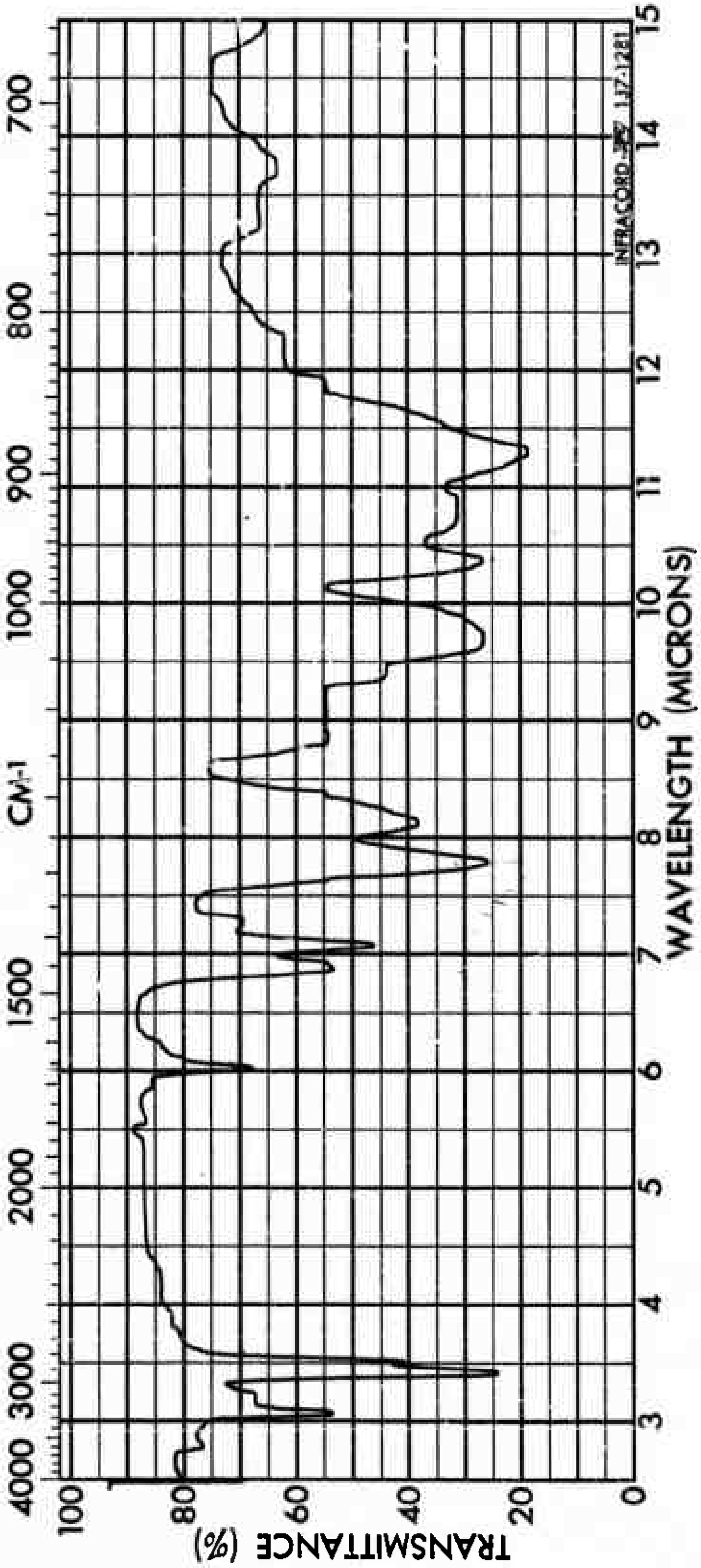


Figure 4. Infrared Spectrum of Crude Pentanol Adduct of Perfluoroguanidine

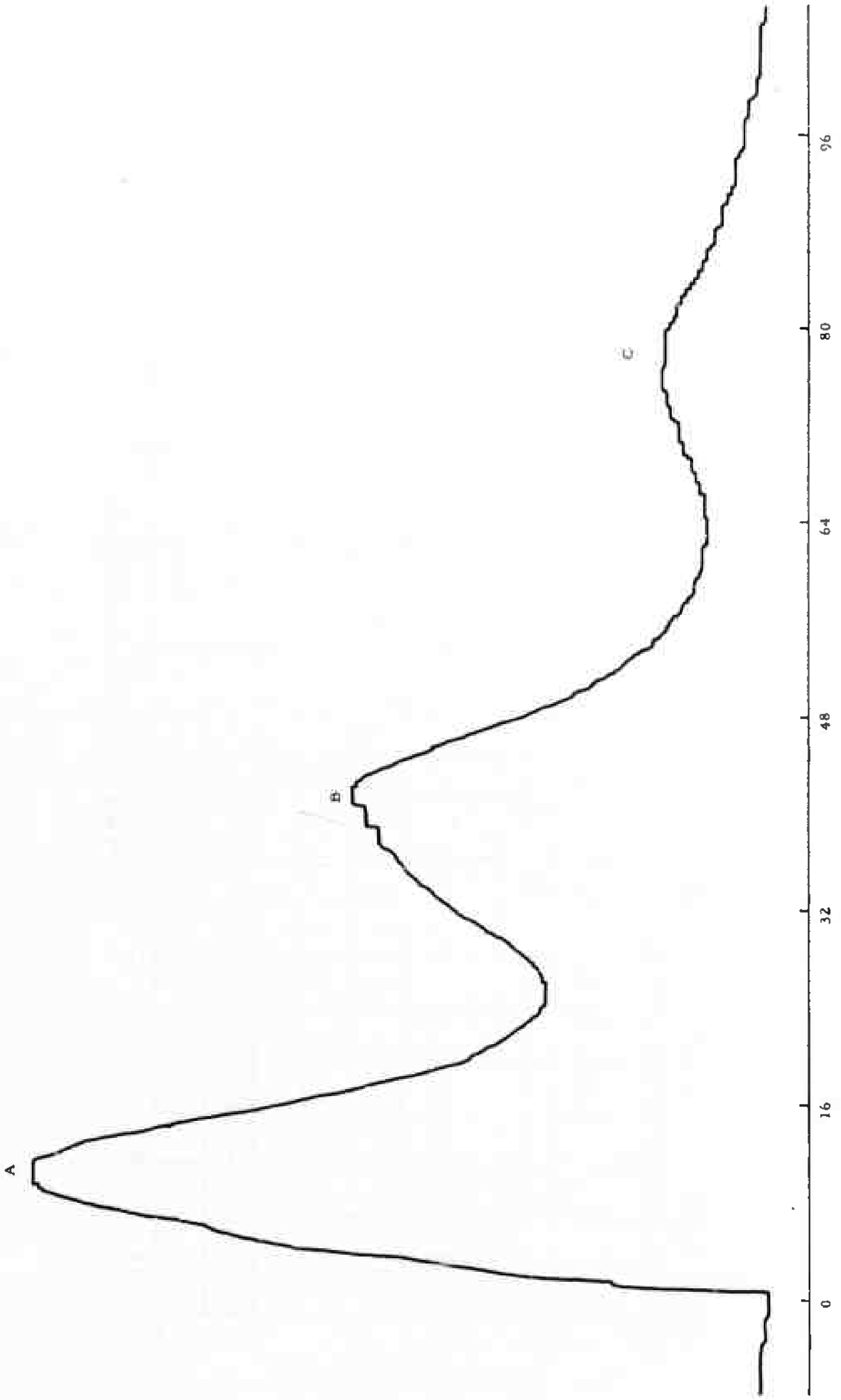


Figure 5. V.P.C. of Crude Pentanol Adduct of Perfluoroguanidine

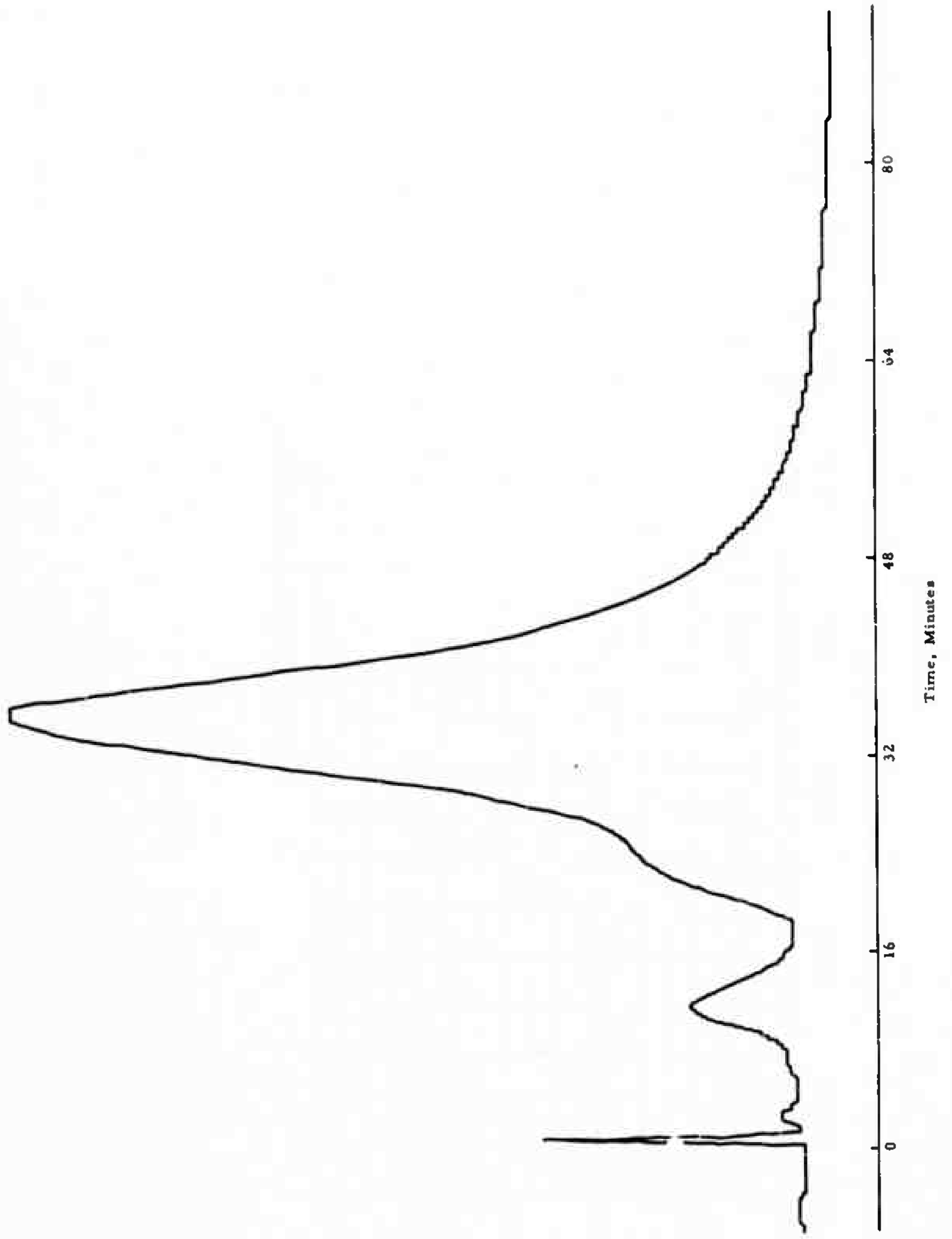


Figure 6. Repass V.P.C. of Fraction Under Peak B

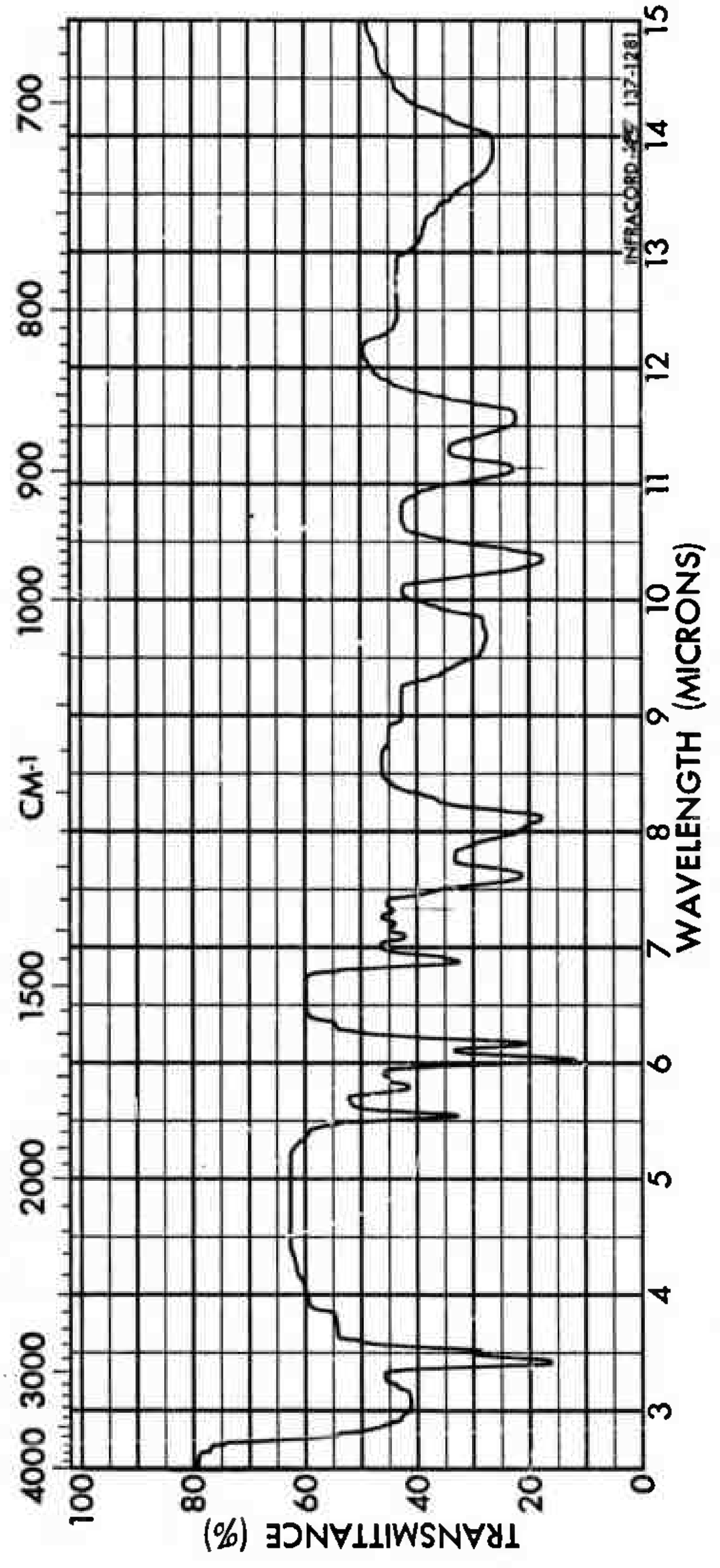


Figure 7. Infrared Spectrum of Fraction Under Peak B

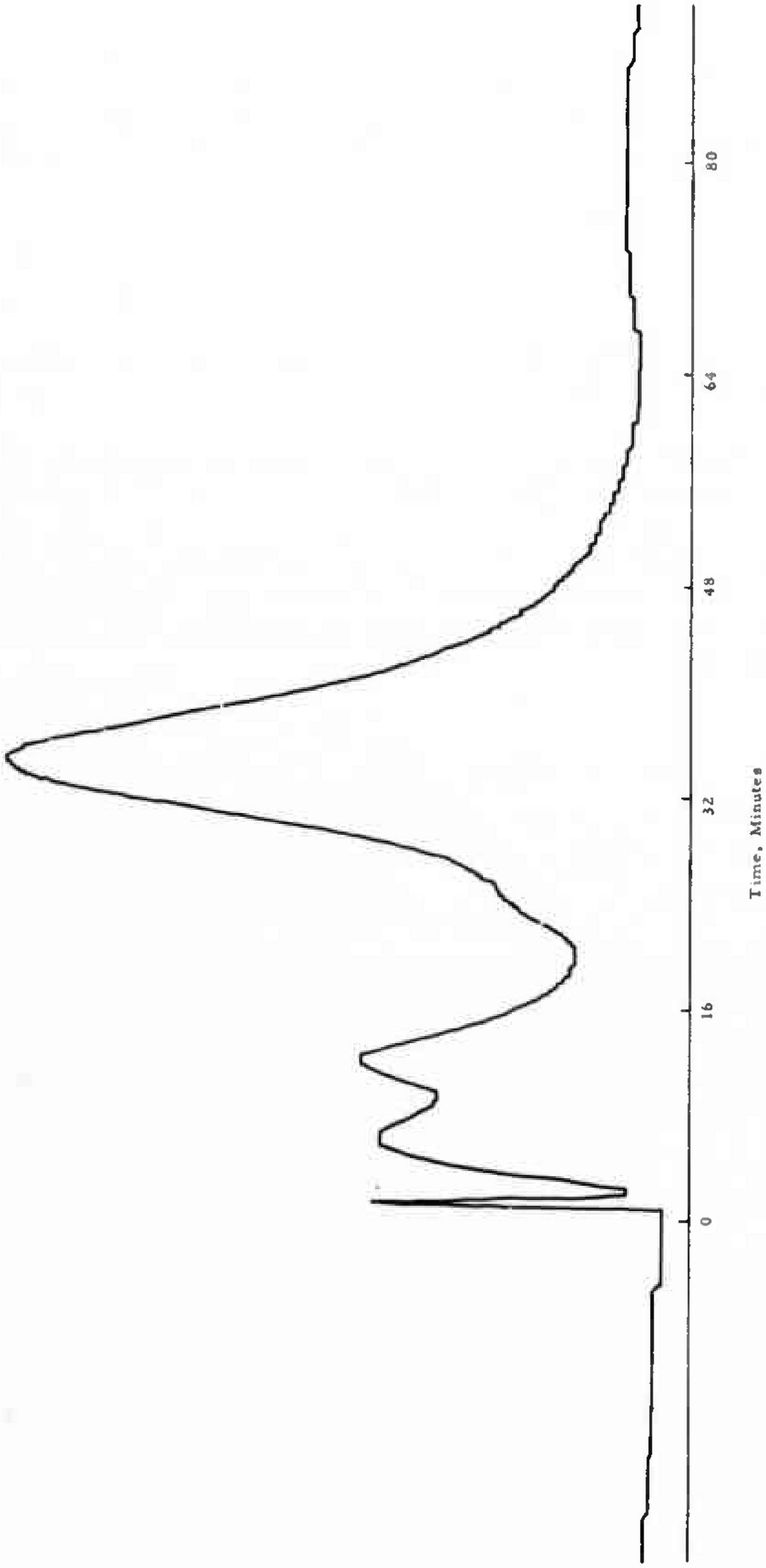


Figure 8. Repass V.P.C. of Fraction Under Peak C

A portion of the material collected under peak B was purified by an additional v.p.c. pass to provide a sample for characterization. The results of infrared (Figure 9) and elemental analyses were completely in accord with the assigned structure IV.

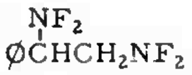
Anal. calcd. for $C_6H_{11}N_2F_3O$: C, 39.13; H, 6.02; N, 15.21
Found: C, 40.64; H, 6.32; N, 14.47

D. SYNTHESIS AND PURIFICATION OF 1,1-BIS(DIFLUORAMINO)-PHENYLETHANE

The sensitivity of various difluoramino compounds to thermal shock is being measured at the Naval Ordnance Laboratory, Silver Spring, Md., in an effort to correlate such sensitivity with a variety of structural features. As a part of this program, we have undertaken to supply samples of a series of isomeric aromatic difluoramino compounds. This series consists of 1,1- 1,2- ,and 2,2-bis(difluoramino)phenylethane (XII, XIII, and XIV, respectively).

$\varnothing\overset{NF_2}{\underset{NF_2}{C}}CH_3$

XII



$\varnothing\overset{NF_2}{C}HCH_2NF_2$

XIII

$\varnothing CH_2CH(NF_2)_2$

XIV

The preparation and purification of the vicinal disubstituted compound (XIII) has been described in an earlier report (Ref 4) and some aspects of the synthesis of XIV have also been discussed (Ref 1). The synthesis of XII was accomplished by the reaction of difluoramine with acetophenone (Equation 10) in the usual manner.

$$\varnothing COCH_3 + 2HNF_2 \xrightarrow{H^+} \varnothing C(NF_2)_2CH_3 + H_2O \qquad (10)$$

XII

Purification was complicated by the fact that XII could not be separated from acetophenone either by vacuum distillation or by v.p.c. on a variety of stationary phases. Purification to a satisfactory level (99%) was accomplished by extracting a Freon-113 solution of the crude product with concentrated sulfuric acid. Distillation of the washed material gave a product free

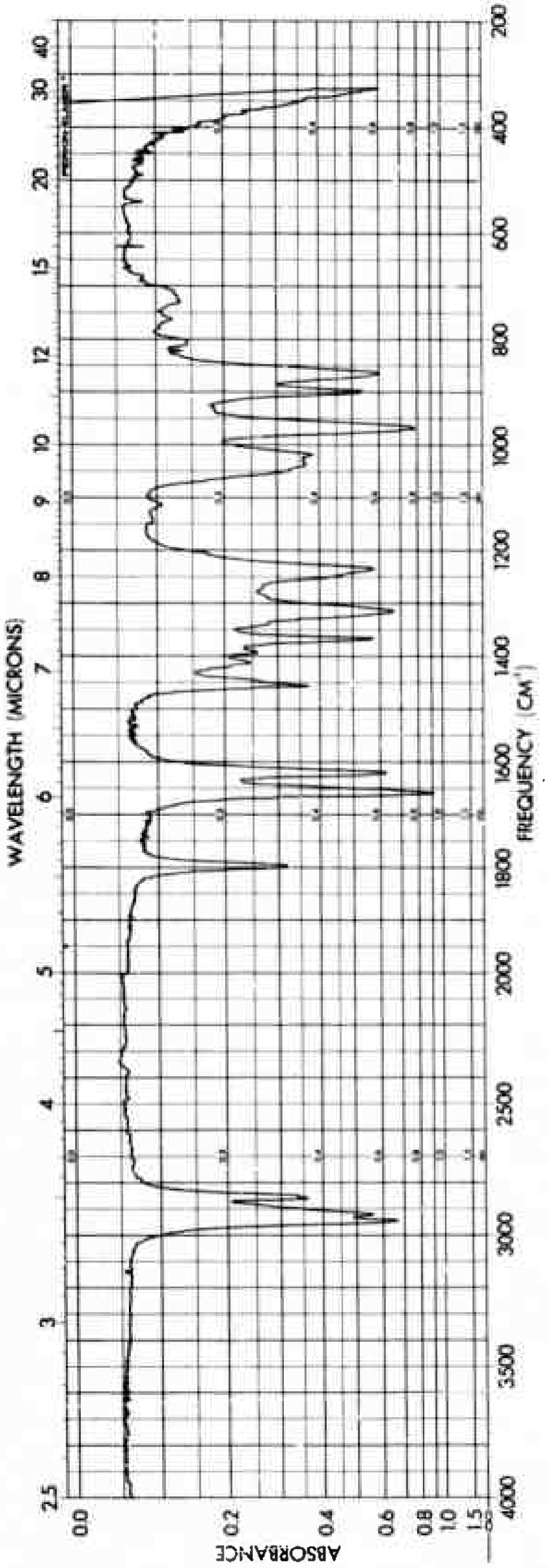


Figure 9. Infrared Spectrum of N, N, N'-Trifluoropentoxyformamidine

of carbonyl contaminants, as indicated by its infrared spectrum (Figure 10).

E. PURIFICATION OF 1,2-BIS(DIFLUORAMINO)ETHANE

The title compound became of interest again for thermal sensitivity studies at NOL. A sample of this material, which had been in storage at 0° for 22 months, was reexamined and found to contain an impressive array of contaminants. The v.p.c. trace is reproduced in Figure 11. Since v.p.c. equipment was not available at the time the compound was originally synthesized (Ref 4), no direct comparison with the fresh material is possible. Elemental analysis of the newly prepared material was sufficiently close to theory, however, to suggest strongly that at least a part of the contamination was due to decomposition during storage.

A solution of the impure 1,2-bis(difluoramino)ethane was chromatographed on a preparative scale with automatic injection, and the fraction indicated as peak A in Figure 11 was collected. A repass of the collected material gave the single peak shown in Figure 12.

F. SYNTHESIS AND PURIFICATION OF 1,1-BIS(DIFLUORAMINO)HEPTANE

A sample of the title compound, containing 1-1.5% heptanal, was prepared previously (Ref 2) for thermochemical studies. The purity was found to be inadequate for this purpose and purification by preparative v.p.c. did not appear to be feasible. We have since confirmed the finding that columns sufficiently polar to effect a separation cause decomposition of the gem-bis(difluoramine).

The synthesis of this compound was repeated using the procedure already reported (Ref 2). The crude product was treated with concentrated sulfuric acid, in the same manner described in paragraph D above. The final product had an infrared absorption spectrum (Ref 1) which demonstrated the absence of any water or carbonyl function, and an elemental analysis which indicated purity of the order of 99.9%.

Anal. calcd. for $C_7H_{14}N_2F_4$: C, 41.58; H, 6.98; N, 13.85; F, 37.59
Found: C, 41.36; H, 7.25; N, 14.04; F, 37.45

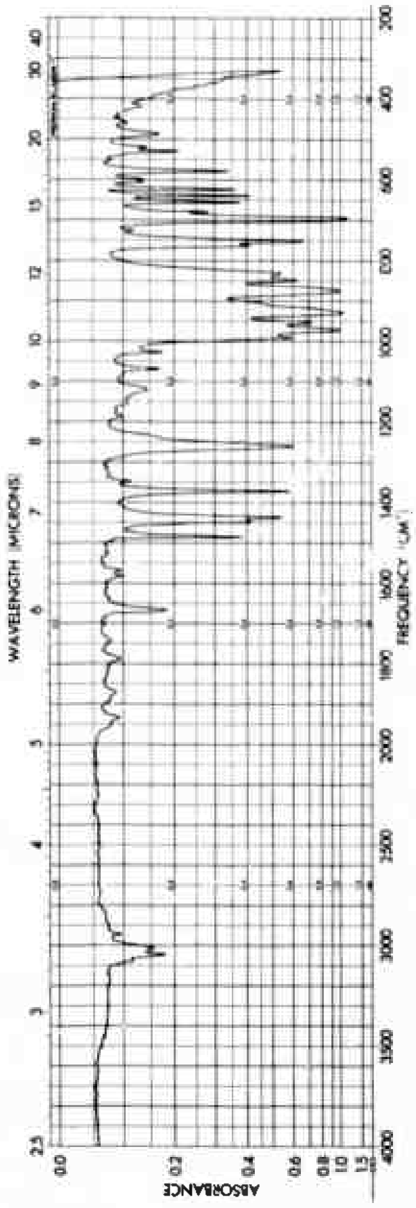


Figure 10. Infrared Spectrum of 1,1-Bis(difluoramino)phenylethane

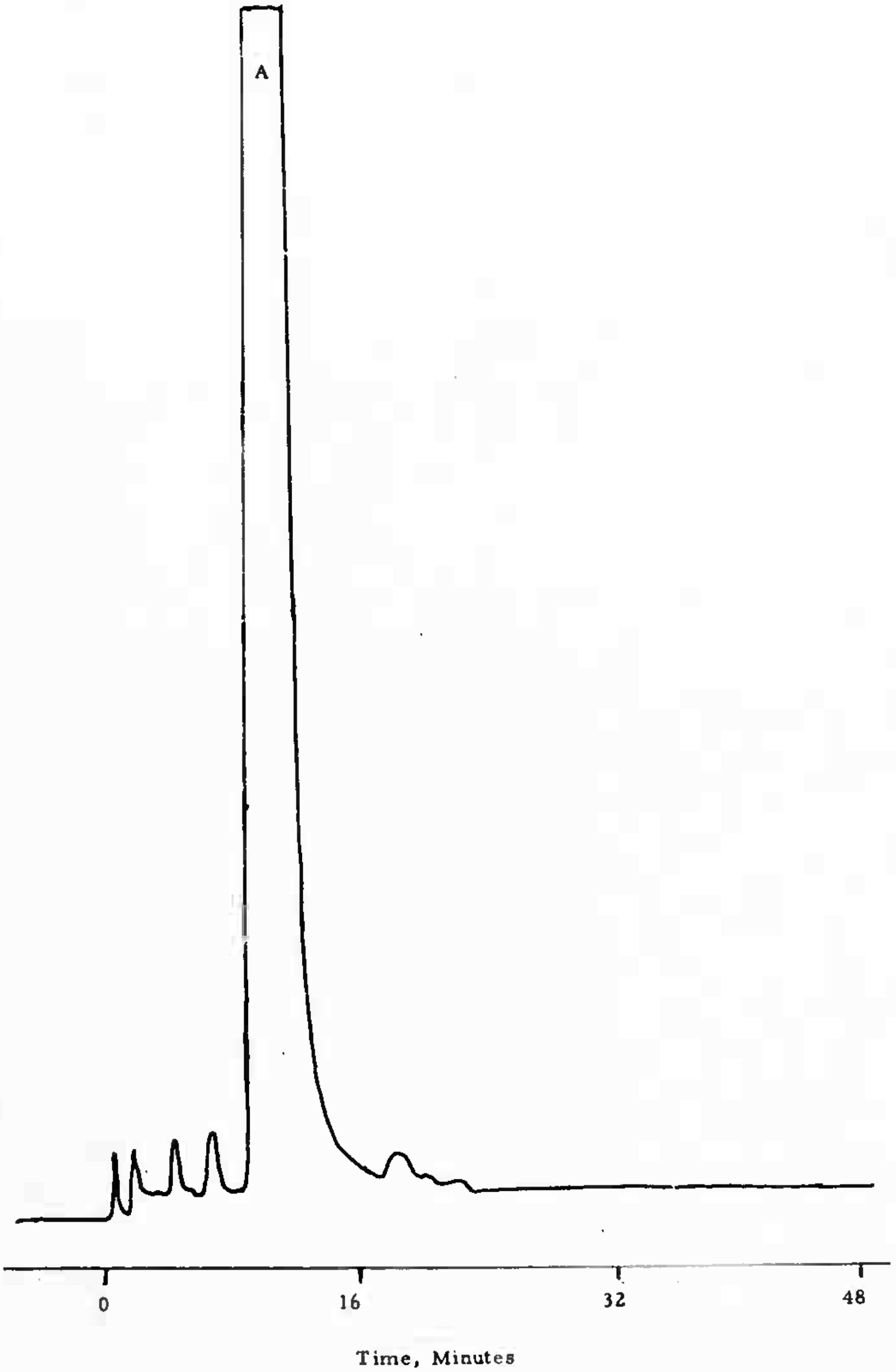


Figure 11. V.P.C. of 1, 1-Bis(difluoramino)ethane After 22 Months Storage

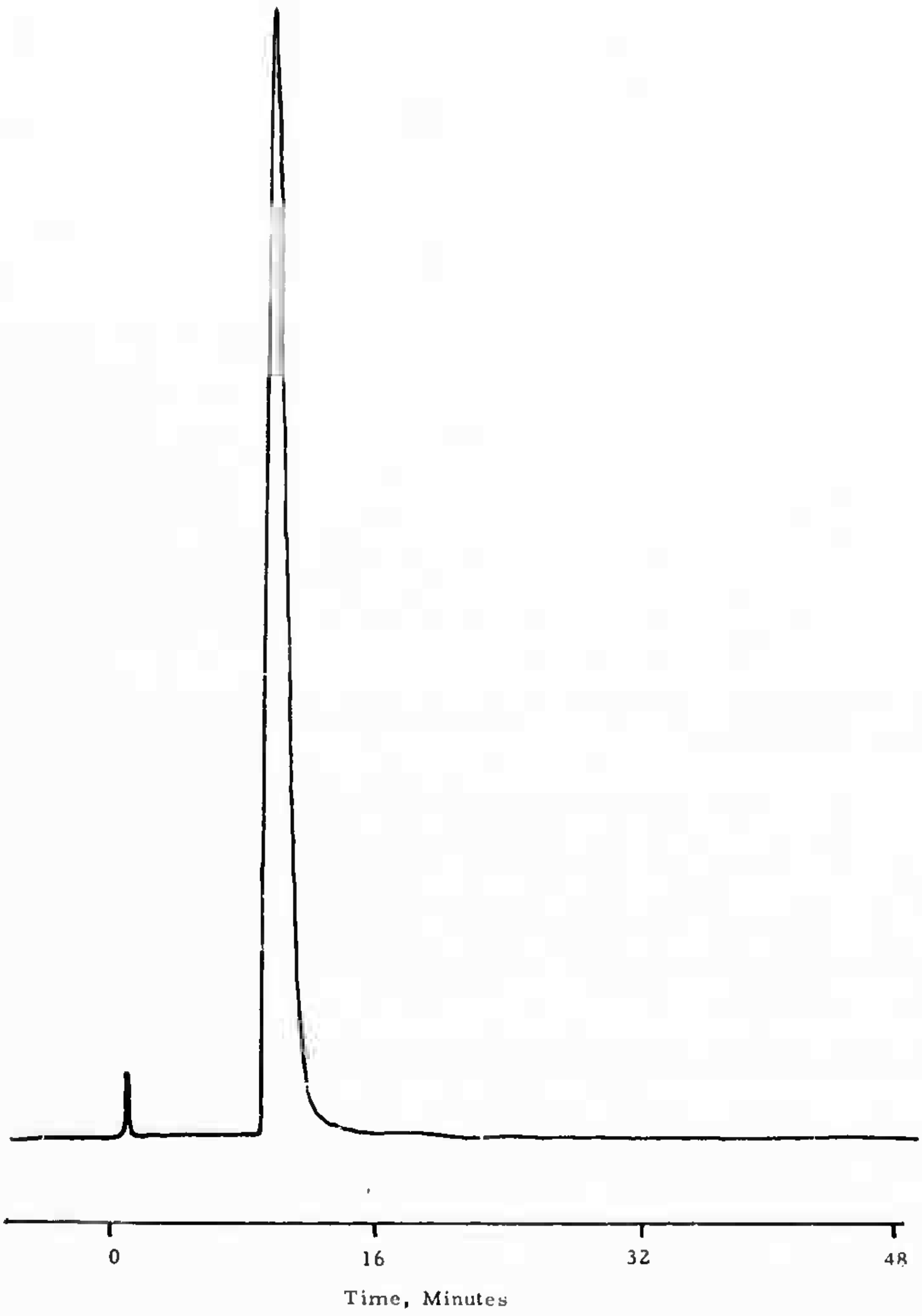


Figure 12. V.P.C. of Chromatographed 1,1-Bis(difluoramino)ethane

III. EXPERIMENTAL

A. 1-DIFLUORAMINO-2-FLUORIMINOCYCLOHEXANE

To 13.0 g. (0.0488 mole) of Amberlite IR-45 resin in 100 ml. CH_2Cl_2 was added dropwise 6.0 g. (0.0322 mole) of 1,2-bis(difluoramino)cyclohexane in 50 ml. CH_2Cl_2. The reaction mixture was refluxed for 6 hr., cooled and filtered. The filtrate was then evaporated to yield 4.3 g. of a crude liquid. Distillation of the crude product yielded 3 fractions: 2.99 g. boiling at 40-46°/3 mm., 0.50 boiling at 48-50°/3 mm., and 0.36 g. boiling at 54-56°/0.5 mm. The first and third fraction were characterized by their infrared spectra as 1,2-bis(difluoramino)cyclohexane and 1,2-difluoriminocyclohexane, respectively. The middle fraction had an infrared spectrum which showed absorptions attributable to both $-NF_2$ and $=NF$ groups, possibly in the same molecule.

B. ATTEMPTED REACTION OF N, N, N'-TRIFLUOROBENZAMIDINE WITH n-BUTANOL

To a mixture of 0.1 g. of urea and 0.16 g. (0.0021 mole) of n-butanol in 5 ml. of Freon-113 at 0° was added dropwise a solution of 0.34 g. (0.0021 mole) of N, N, N'-trifluorobenzamidine. After the reaction mixture was stirred for 2 hr. at 0°, it was allowed to warm to ambient temperature and stirred overnight. The reaction mixture was then filtered and the filtrate evaporated to yield a crude liquid which consisted of n-butanol and the starting formamidine.

C. BIS(DIFLUORAMINO)FLUORAMINOMETHOXYPENTANE

A mixture of 20 ml. Freon-113, 2.7 g. (0.031 mole) pentanol (Matheson Coleman and Bell), and 0.3 g. urea was placed in a Fisher-Porter reaction tube and degassed three times. The reactor was cooled to -120° and 1.12 l. of perfluoroguanidine measured at NTP (0.05 mole) was condensed in. After being allowed to warm up to 0°, the reactor was immersed in an ice bath and allowed to warm to 25° during 16 hr., with constant stirring. The remaining gas was then removed at 0°, and the reaction mixture was diluted with methylene chloride. The solution was stripped to yield 5.85 g. (86%) of crude product.

A v.p.c. of the crude product on Halocarbon oil gave a curve with 3 peaks of approximately equal areas. For this reason, and despite the fact that no break appeared in the boiling point (38-39°/5.0 mm.), the distillate was collected in 3 fractions. Each fraction gave a v.p.c. curve similar to that of the undistilled product. Material collected under the second peak was re-passed without change. The v.p.c. fraction represented by the third peak was converted on the column to a stable product having the same retention time as the original second peak.

D. 1,1-BIS(DIFLUORAMINE)PHENYLETHANE

To an aqueous solution containing 0.5 mole of difluorourea was added sulfuric acid. The liberated difluorourea was collected under Dry Ice reflux in a flask containing 7.0 ml. fuming sulfuric acid (104%). To this was added dropwise a solution of 6.17 g. (0.05 mole) of acetophenone in 20 ml. Freon-113. After the addition was complete, the mixture was stirred for an additional 0.5 hr. and the organic layer was separated, washed with water and aqueous bicarbonate and stripped of solvent. The crude product (2.8 g., 24% yield) was combined with that from several similar runs and distilled, b.p. 34°/0.06 mm.

E. 1,1-BIS(DIFLUORAMINO)HEPTANE

The difluoramine liberated from 1.0 mole of difluorourea was collected under Dry Ice reflux in a flask containing 7.0 ml. of 104% sulfuric acid. To this was added dropwise a solution of 5.10 g. (0.045 mole) heptanol (K and K Laboratory) in 10 ml. Freon-113. After 0.5 hr. of additional stirring, an additional 20 ml. of Freon-113 was added and the organic layer was separated.

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

IV. FUTURE WORK

- One additional attempt to obtain a satisfactory yield of cyclohexyldifluoramine, by the fluorination of ethyl N-cyclohexylcarbamate in acetonitrile solution, will be made.
- The conversion of bis(difluoramino)fluoraminomethoxypentane to the formamidine will be studied under a variety of conditions, with the intent of identifying the fragment eliminated.
- The N, N, N'-trifluoropentoxyformamidine obtained in these experiments will be utilizied as a model compound for reaction studies.

V. REFERENCES

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

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

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

5. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD AOR-ATS-63, Advanced Oxidizer Research (U), Section II, "Synthesis of Compounds for Structure-Sensitivity Study", February 1964.

SECTION II

TASK 53

INORGANIC OXIDIZER SYNTHESIS

Section II

Inorganic Oxidizer Synthesis

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

Report RMD 5043-Q3-65

RMD Project 5043, Task 53
Report Period: 1 July 1965 to
30 September 1965

Contract NONr 4364(00)
ARPA Order No. 417
Project Code 5910

FOREWORD

This section of the report summarizes the results of the synthesis of new inorganic oxidizers during the period from 1 July 1965 to 30 September 1965. This program was monitored by Mr. R. L. Hanson of the Office of Naval Research.

Personnel contributing to these studies were: A. R. Young (Project Supervisor), D. Moy and S. I. Morrow (Principal Investigators) and D. Kates, B. Fagan, and R. Crooker (Analytical Support).

ABSTRACT

Elemental analyses of the N_2F_4-AsF_5 adduct give a composition, $N_2F_4(AsF_5)_{1.33}$, indicating a mixture of adducts having 1:1 and 1:2 N_2F_4:AsF_5 ratios. Evidence presented previously that the adduct is ionic and contains the $N_2F_3^+$ cation still appears valid. The structure of the 1:2 adduct is possibly $N_2F_3^+As_2F_{11}^-$.

The reaction of N_2F_4 with $HAsF_6$ gives a solid N-F compound having X-ray and infrared spectra different than $N_2F_3AsF_6$. No reaction occurred when N_2F_4 was treated with $HClO_4$ in HF. Unsuccessful attempts were made to prepare $N_2F_3ClO_4$ by reacting $N_2F_3AsF_6$ with metal perchlorates in HF.

The reaction of O_2AsF_6 with $CsClF_4$ produces O_2 and Cl_2, as well as $CsAsF_6$, at about 0°C. The reaction of NO_2 with AsF_5 does not give a molecular adduct $NO_2 \cdot AsF_5$ as reported in the literature, but rather a mixture of $NOAsF_6$ and NO_2AsF_6.

CONTENTS

ILLUSTRATIONS

TABLES

I. INTRODUCTION

The concern of this portion of the Advanced Oxidizer Program is the study of the reactions of inorganic N-F and O-F compounds, the ultimate objective being the synthesis of new inorganic oxidizers. In previous work, we have shown that reactions of O_2F_2 and N_2F_2 in some cases yield ionic products containing the dioxygenyl (O_2^+) and fluorodiazonium (N_2F^+) ions, respectively. More recently, we have been studying adducts obtained by the reaction of N_2F_4 with AsF_5 which we believe to contain a new N-F cation, $N_2F_3^+$.

II. DISCUSSION

A. INORGANIC N-F CHEMISTRY

During the past quarter we continued our studies of adducts obtained by the reaction of N_2F_4 with AsF_5. We have interpreted previously reported analytical, infrared, and F^{19} n.m.r. data (Ref 1 and 2) to be in support of the formulation of the adduct isolable at room temperature as $N_2F_3^+ AsF_6^-$. Our most recent analysis of this product, however, is not in agreement with the elemental composition required by this formula. Indeed, our present analytical data suggest that the adduct is a mixture of compounds of compositions $N_2F_4 \cdot AsF_5$ and $N_2F_4 \cdot 2AsF_5$ In spite of this unexpected result, the evidence presented previously in support of the existence of $N_2F_3^+$ in the adduct still appears to be valid.

In addition to further analytical studies of $N_2F_4(AsF_5)_x$, we examined reactions of N_2F_4 with $H_2F^+AsF_6^-$ (AsF_5 dissolved in HF), of N_2F_4 with $HClO_4$ in HF, and of $N_2F_4(AsF_5)_x$ with metal perchlorates in HF. The reactions of N_2F_4 with $H_2F^+ AsF_6^-$ and of $N_2F_4(AsF_5)_x$ with $AgClO_4$ gave results which indicate that further study of these systems is warranted.

• CHARACTERIZATION OF $N_2F_4(AsF_5)_x$

1. Stoichiometry

Previous data (Ref 1 and 2) giving the quantities of reagents consumed at -80°C in runs with varying initial quantities of N_2F_4 and AsF_5 yielded an average composition of $N_2F_4(AsF_5)_{2.3 \pm 0.2}$ for the low temperature adduct. When the adduct is allowed to warm to room temperature, additional AsF_5 is recovered and determinations of the net reagents consumed yield an average composition of $N_2F_4(AsF_5)_{1.2 \pm 0.2}$ for the room temperature adduct. During this quarter, a sample of the adduct was pumped at ambient temperatures for three days in the hopes of removing the last traces of AsF_5, HF, and other volatile impurities. Independent

TABLE I

ELEMENTAL ANALYSIS OF $N_2F_4 (AsF_5)_x$

Element	Calcd. for $N_2F_4 \cdot AsF_5$	Calcd. for $N_2F_4 (AsF_5)_2$	Calcd. for $N_2F_4 \cdot (AsF_5)_{1.33}$	Found
F	62.42	59.93	61.31	62.15
N	10.23	6.31	8.37	8.39
As	27.35	33.76	30.22	30.56
Totals	100.00	100.00	100.00	101.10

analyses for arsenic, nitrogen, and fluorine were run on this sample. The results obtained indicate a composition $N_2F_4 (AsF_5)_{1.33}$ (see Table I). It appears, then, that the non-integral AsF_5/N_2F_4 molar ratios calculated previously are not due to the presence of physically adsorbed arsenic pentafluoride, but are more likely due to the presence of a mixture of adducts having different AsF_5/N_2F_4 molar ratios, as shown below,namely:

$$\underbrace{1/2\, N_2F_4 \cdot AsF_5 + 1/2\, NF_2AsF_5}_{\text{Mixture A}} = N_2F_4\ (AsF_5)_{1.33} = \underbrace{2/3\, N_2F_4 \cdot AsF_5 + 1/3\, N_2F_4(AsF_5)_2}_{\text{Mixture B}}$$

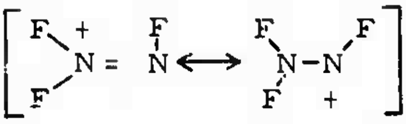
Since the room temperature adduct apparently is a mixture of compounds (assuming that our elemental analyses prove to be reproducible), we must consider whether the strength of our previous arguments (Ref 1) that the adduct contains the $N_2F_3^+$ cation is diminished. These arguments are based on the following results,namely:

— Material balance measurements gave a value of 1.2 for AsF_5/N_2F_4 in the room temperature adduct. It was assumed that more precise analytical procedures would indicate a value of 1.0.

— The reaction of NaF with $N_2F_4 (AsF_5)_x$ liberated substantial quantities of NF_3 and N_2F_2 in addition to N_2F_4, which would be the only product expected if the adduct were molecular and of composition $AsF_5/N_2F_4 = 1.0$.

— The F^{19} n.m.r. of $N_2F_4 (AsF_5)_x$ showed three non-equivalent fluorine on nitrogen peaks of equal intensity.

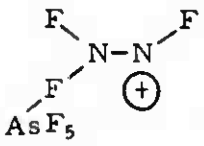
We believe that the obervance of NF_3 and N_2F_2 as products of the reaction of NaF with $N_2F_4\ (AsF_5)_x$ still provides strong support for the presence of a new ionic species, such as $N_2F_3^+$, in the adduct. Even if $N_2F_4\ (AsF_5)_x$ were a mixture of molecular adducts such as $N_2F_4 \cdot AsF_5$, NF_2AsF_5, and $N_2F_4 \cdot 2\ AsF_5$, we believe that N_2F_4 would be the sole gas liberated upon reaction with NaF. As shown previously (Ref 1), the presence of N_2F_2 and NF_3 in the products of the NaF reaction can be easily rationalized if one assumes an ionic constitution for $N_2F_3\ (AsF_5)_x$ in which the cation is $N_2F_3^+$ (Equation 1).



$$+ F^- \longrightarrow N_2F_4 + NF_3 + NF \qquad (1)$$

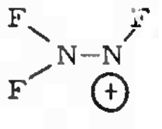
Similarly, the argument for the presence of $N_2F_3^+$ based on the F^{19} n.m.r. spectra still appears to be valid. An ion such as $N_2F_3^+$, having restricted rotation about the N-N Bond, would produce (as was observed) a spectrum showing three non-equivalent fluorine atoms of equal intensity. On the other hand, although there would indeed be three groups of non-equivalent fluorine atoms in a mixture of molecular adducts such as $N_2F_4 \cdot AsF_5$ and NF_2AsF_5, it is doubtful that one could observe an n.m.r. signal in such a system, since NF_2AsF_5 would be paramagnetic. The other possible molecular mixture $(N_2F_4 \cdot AsF_5 + N_2F_4 \cdot 2AsF_5)$ would, at the most, have only two groups of non-equivalent N-F fluorine atoms.

Thus, we can still feel fairly confident that the N_2F_4 - AsF_5 product is an ionic adduct containing the $N_2F_3^+$ ion. The non-integral values obtained for AsF_5/N_2F_4 ratio in the adduct in our analyses might be explained by the presence of structures such as I and II in addition to pure $N_2F_3^+AsF_6^-$. During the next quarter we shall attempt to establish the reliability of our



AsF_6^-

I



As_2F_{11}

II

elemental analysis and, if possible, to isolate pure $N_2F_3^+\ As\ F_6^-$.

2. Infrared Spectrum of N_2F_4 $(AsF_5)_x$

We have continued studies of the infrared spectra of $N_2F_4(AsF_5)_x$ because we have obtained varying results (Ref 1 and 2) depending upon the method used in the preparation of infrared samples. During this quarter, we obtained an exceptionally well-resolved spectrum on a sample prepared by pressing finely divided $N_2F_4(AsF_5)_x$ between AgCl windows (Figure 1). This spectrum is in agreement with previous spectra (Ref 1)obtained by this powder technique. In addition to a doublet at 500 cm^{-1} and the (ν_3) AsF_6^- absorption at 695 cm^{-1}, there are strong absorptions at 920 cm^{-1}, 1110 cm^{-1}, and 1295 cm^{-1} and weak bands at 820 cm^{-1}, 990 cm^{-1}, 1420 cm^{-1}, and 1500 cm^{-1}. Spectra obtained by the powder technique have been consistently more complex than a spectrum obtained on a film of N_2F_4 $(AsF_5)_x$ which was prepared by allowing AsF_5 and N_2F_4 to react on a AgCl window at -80°C (Ref 2). The latter spectrum shows only four peaks, namely: 700 cm^{-1} (AsF_6^-), 830 cm^{-1}, 920 cm^{-1}, and 1100 cm^{-1}. No satisfactory explanation for the difference in spectra obtained by the two techniques can be given at present. It is possible, however, that in the case of the powder spectra impurities are introduced during the sampling process (reaction with moisture) giving rise to the higher frequency bands (1295 cm^{-1}, 1420 cm^{-1}, 1500 cm^{-1}). Or it may be that the complexity of the powder spectrum (Figure 1) is simply due to the fact that $N_2F_4(AsF_5)_x$ is a mixture of adducts. Additional efforts will be expended during the next quarter on the identification of the absorption bands observed in the spectrum of $N_2F_4(AsF_5)_x$. It is anticipated that these efforts will contribute significantly to our knowledge of the structure of the adduct.

• REACTIONS OF $N_2F_4(AsF_5)_x$ WITH METAL PERCHLORATES

Reactions of $N_2F_4(AsF_5)_x$ with $KClO_4$ and with $AgClO_4$ were attempted during this quarter. These reactions were conducted in an "H"-shaped Kel-F apparatus using HF as a solvent medium. In the reaction with $KClO_4$, equimolar quantities of the solid reagents were mixed and placed in one leg of the "H"-tube. Upon distilling HF on the solid mixture, a pale yellow solution formed but a portion of the solid remained undissolved. The solution was decanted to the second leg and all volatiles were removed from the tube, leaving white solid residues in both legs. Only trace amounts of gaseous reaction products were observed, including NF_3, ClO_3F, ClO_2, and N_2O. The solids in both legs gave essentially the same X-ray and infrared spectra. The X-ray pattern indicates the presence of $KAsF_6$ and $NOClO_4$. Similarly, the infrared spectrum (NaF pellet) shows an absorption at 2080 cm^{-1} which might be attributed to NO^+. However, there were also

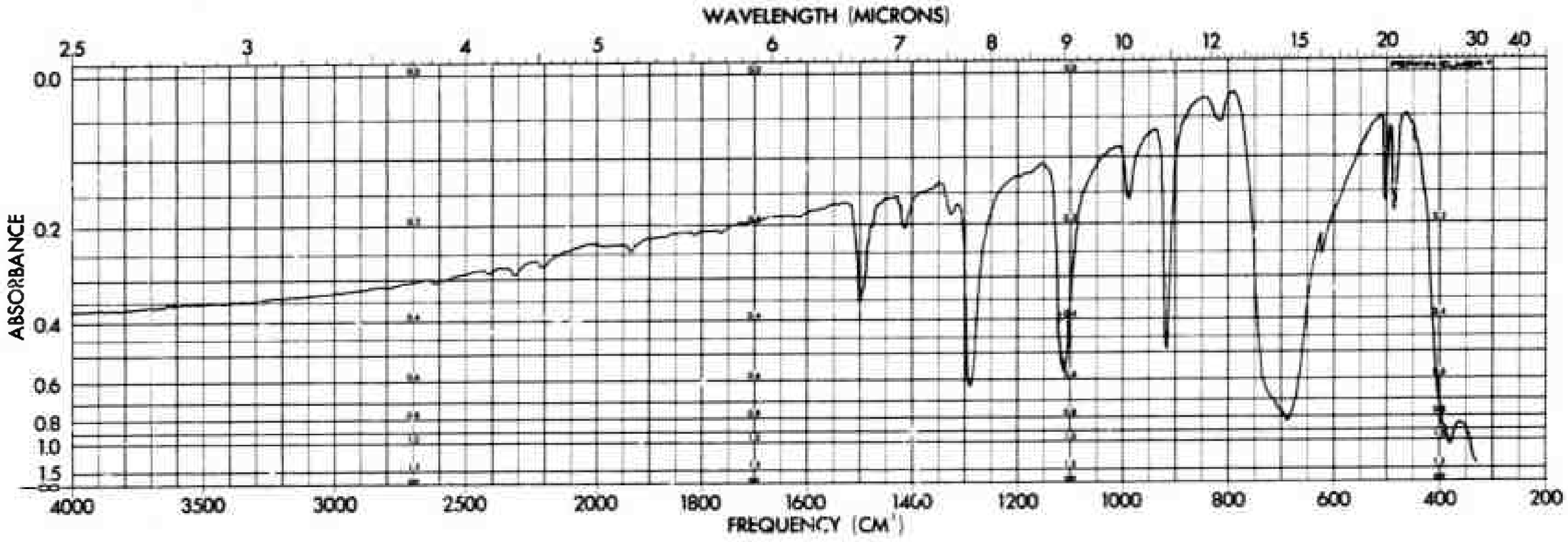


Figure 1. Infrared Spectrum of $N_2F_4(AsF_5)_x$ Powder on AgCl

absorptions at 930 cm $^{-1}$ and 850 cm $^{-1}$ which might be due to N-F. The strongest bands in the spectrum were at 1050 cm $^{-1}$ (ClO_4^-) and 700 cm $^{-1}$ (AsF_6^-). At this point, we are not certain whether $NOClO_4$ is an initial product of the reaction of N_2F_4 $(AsF_5)_x$ with $KClO_4$ or whether it is obtained by the decomposition of an N-F perchlorate during the preparation of X-ray and infrared samples.

We made an attempt to investigate further the reaction of $N_2F_4(AsF_5)_x$ with ClO_4^-, using $AgClO_4$ as the source of the perchlorate ion. The change in perchlorate reagent was made because we expected to be better able to isolate a pure N-F perchlorate due to the insolubility of $AgAsF_6$ in HF (Equation 2).

$$N_2F_3AsF_6 + AgClO_4 \xrightarrow[HF]{?} AgAsF_6 \downarrow + N_2F_3ClO_4 \qquad (2)$$

However, we were unsuccessful in evaluating this reaction because the presence of an impurity (probably H_2O) in the HF caused the $N_2F_3AsF_6$ to decompose, liberating N_2O, NF_3, and trans-N_2F_2. Further studies of the reaction of $N_2F_4(AsF_5)_x$ with metal perchlorates in HF presently are being conducted.

- THE ATTEMPTED REACTION OF N_2F_4 WITH PERCHLORIC ACID IN HF

We recently attempted the preparation of $N_2F_3AsF_6$ by reacting N_2F_4 with a solution of AsF_5 in hydrogen fluoride. We obtained a solid product which we assumed to be $N_2F_3AsF_6$. Reasoning that the reaction proceeded as shown in Equations 3 and 4, we attempted to carry out an analogous reaction using the $HClO_4$ as the protonating agent shown in Equations 5 and 6.

$$AsF_5 + 2\,HF \longrightarrow H_2F^+ + AsF_6^- \qquad (3)$$

$$N_2F_4 + H_2F^+ \xrightarrow{?} 2\,HF + N_2F_3^+ \qquad (4)$$

$$HClO_4 + HF \xrightarrow{?} H_2F^+ + ClO_4^- \qquad (5)$$

$$N_2F_4 + H_2F^+ \xrightarrow{?} 2HF + N_2F_3^+ \qquad (6)$$

N_2F_4 was condensed onto a solution of $HClO_4$ in HF and allowed to remain in contact with the solution for two weeks, after which the N_2F_4 was recovered virtually quantitatively. The failure of this reaction to proceed as predicted (Equations 5 and 6) led us to further investigate the solid we had obtained by the action of N_2F_4 on $HAsF_6$. As described in the next paragraphs, the solid proved to be an N-F compound, but of apparently completely different composition and structure than the adduct obtained by reacting N_2F_4 with AsF_5 in the absence of HF.

- THE REACTION OF N_2F_4 WITH $HAsF_6$

Since AsF_5 is such a strong acid (fluoride ion acceptor), it exists solely as AsF_6^- when dissolved in HF. It, therefore, occurred to us that if $N_2F_4(AsF_5)_x$ were a molecular addition compound no reaction should take place upon addition of N_2F_4 to a solution of $HAsF_6$ in HF. Molecular AsF_5 could only be made available in such a system by displacing the strong base F^- from AsF_6^-. If, on the other hand, a reaction did occur producing N_2F_4-$(AsF_5)_x$ this would be strong chemical evidence that this material is ionic (Equations 3 and 4).

When we allowed N_2F_4 to remain in contact with a solution of AsF_5 in HF for three days, we found upon stripping the solvent that a pale yellow solid product was obtained. The yellow color was due to the presence of a small amount of $Ni(AsF_6)_2$ (Ref 3) formed by the action of $HAsF_6$ on the Monel portions of the reactor. In spite of its yellow color, the solid appeared to be identical to the adduct obtained by reaction of N_2F_4 with AsF_5 in the absence of HF. For example, it reacted violently with water, producing oxides of nitrogen. However, as mentioned in the previous section, we decided to examine the solid more carefully to see if it were, indeed, identical to $N_2F_4(AsF_5)_x$. To our surprise, we obtained results from elemental analysis, infrared analysis, and X-ray analysis indicating that the product is different from the N_2F_4-AsF_5 adduct in both structure and composition. The data obtained are presented in Table II (emission spectrum), Table III (elemental analysis), Table IV (X-ray) and in Figure 2 (infrared spectrum).

TABLE II

EMISSION SPECTRUM OF N_2F_4-$HAsF_6$ PRODUCT

Element	Intensity
As	High
Ni	Low
Cu	Trace
Mn	Trace
Fe	Faint Trace

Legend: High, more than 10%; Medium, 1 - 10%; Low, 0.1 - 1%
Trace, 0.01 - 0.1%

TABLE III

ELEMENTAL ANALYSIS OF N_2F_4-$HAsF_6$ PRODUCT

Element	Found	Calculated for $N_2F_4(AsF_5)_{1.33}$
As	35.66	30.22
F	59.76	61.31
N	1.43	8.47
	96.85	100.00

TABLE IV

X-RAY PATTERN OF N_2F_4-$HAsF_6$ PRODUCT

N_2F_4-$HAsF_6$ Product		Principal Lines of $N_2F_4(AsF_5)_x$	
d, Å	I/I_o	d, Å	I/I_o
6.78	50	5.37	50
*5.73	3	4.45	100
5.26	10	3.38	100
*4.80	25	2.71	20
4.11	100	2.30	15
*3.98	10		
*3.51	50		
3.19	25		
*3.06	2		
*2.88	7		
2.75	4		
2.64	1		
2.57	4		
2.35	1		
2.25	2		
*2.16	8		
*1.77	10		
1.72	12		
1.57	4		
1.45	2		
1.38	8		
1.32	2		

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* These lines also are present in the diffraction pattern of $Ni(AsF_6)_2$, according to a private communication from Dr. A. E. Pavlath of Stauffer Chemical Company, Richmond, Calif.

The infrared spectrum (Figure 2) is particularly interesting, for although it shows absorptions at 920 cm^{-1}, 1120 cm^{-1}, and 1295 cm^{-1}, similar to those found in $N_2F_4(AsF_5)_x$ (Figure 1), it does not show a single ν_3 absorption for AsF_6^- at 700 cm^{-1}. The absorption in the region of 700 cm^{-1}

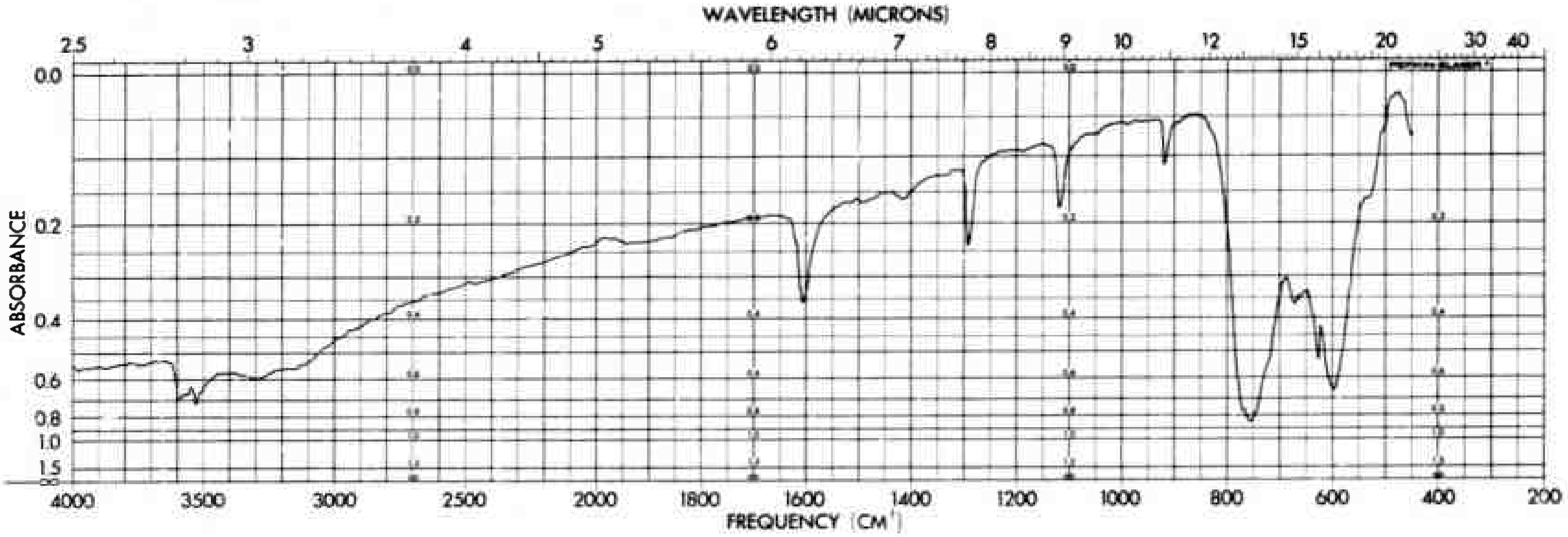

Figure 2. Infrared Spectrum of the Reaction Product of N_2F_4 with $HAsF_6$ (Powder Technique)

is split into four bands occurring at 755 cm^{-1}, 665 cm^{-1}, 630 cm^{-1} and 600 cm^{-1}. There is also a peak at 1600 cm^{-1} which does not appear in $N_2F_4(AsF_5)_x$. The complex band observed in the 700 cm^{-1} region of Figure 2 indicates considerable distortion of the AsF_6^- octahedra in this product. The nature of this distortion remains to be determined.

Even though our data show (Tables I and II) that elements other than N, As, and F were present in this product, we believe the data also show that the predominant component is a compound made up of these three elements, and that it is not the same as the adduct obtained from N_2F_4 and AsF_5. We have constructed an all-plastic reactor (including a Teflon valve) for future runs involving the reaction of N_2F_4 with $HAsF_6$ in order to avoid contamination by metal hexafluoroarsenates. We hope to characterize the pure product during the next quarter.

- ATTEMPTED REACTION OF $N_2F^+AsF_6^-$ WITH $CsClF_4$

The preparation of N_2FClF_4 was attempted this quarter via a solid state reaction of N_2FAsF_6 with $CsClF_4$ (Equation 7). $CsClF_4$ (0.74 mmole) and N_2FAsF_6 (0.68 mmole) were mixed in a Kel-F tube at -78°C in vacuo. The

$$N_2FAsF_6 + CsClF_4 \longrightarrow CsAsF_6 + N_2FClF_4 \qquad (7)$$

apparatus was attached to a mass spectrometer and the gases evolved were monitored at -78°C, -55°C, and 0°C. There was no appreciable gas evolution until the reactor reached 0°C, whereupon considerable pressure developed. The gases observed in the mass spectrometer were N_2O, N_2, and O_2, indicating that a leak had occurred in the system. Further attempts to determine whether N_2F^+ and ClF_4^- are compatible will be made during the next quarter.

B. DIOXYGENYL SALT CHEMISTRY

We have previously investigated the reaction of O_2AsF_6 and NO_2ClO_4 in the hope of preparing O_2ClO_4 (Ref 1 and 5) and concluded that the principal reaction occurring in this system was the formation of oxides of chlorine (most probably Cl_2O_6), NO_2AsF_6, and possibly $NO_2 \cdot AsF_5$. We have now determined that the reported preparation of $NO_2 \cdot AsF_5$ (Ref 5) was probably erroneous since reactions of NO_2 with AsF_5 in various initial ratios yield a mixture of ionic adducts, $NOAsF_6$ and NO_2AsF_6. We have also continued the study of the O_2AsF_6-$CsClF_4$ reaction (Ref 2) during the current report period.

- REACTION OF O_2AsF_6 WITH $CsClF_4$

We continued to study the reaction of O_2AsF_6 with $CsClF_4$ because of the favorable ΔH_f value of -21 kcal/mole (Ref 2) calculated for the hypothetical salt, O_2ClF_4. The desired reaction is:

$$O_2AsF_6 + CsClF_4 \longrightarrow O_2ClF_4 + CsAsF_6 \qquad (8)$$

Two experiments were carried out in which O_2AsF_6 and $CsClF_4$ were mixed together in a Kel-F reactor for several hours in a vacuum. In the first experiment, the amount of gases evolved during the reaction (O_2, Cl_2, and possible F_2) was only about half as great as expected if all of the O_2AsF_6 had been converted to O_2ClF_4, i.e.:

$$O_2ClF_4 \longrightarrow O_2 + 1/2\ Cl_2 + 2F_2 \qquad (9)$$

Despite this encouraging result, indicating that some O_2ClF_4 might have been left in the solid residue, hydrolyses of the solid residue failed to produce any oxygen. Dioxygenyl salts, such as O_2ClF_4, produce oxygen and ozone under these conditions. X-ray analysis of the solid product showed that it was a mixture of $CsAsF_6$ and unreacted $CsClF_4$.

In the second experiment, an effort was made to determine whether there was an unstable intermediate formed in this reaction. The reactants were stirred in vacuo at -78°, whereupon traces of Cl_2 and O_2 in a ratio of 3:1 were evolved. Gas evolution upon standing overnight was negligible. The mixture was then stirred at 0°. A mixture of O_2 and Cl_2 in a ratio of 1.6:1.0 was evolved. The amount of gases evolved again was only about a third of that expected if O_2ClF_4 had been formed and then decomposed. However, X-ray analyses of the solid product gave only the diffraction pattern of $CsAsF_6$. It is difficult to get a clear picture of events in this system due to the fact that expected decomposition products of O_2ClF_4, ClF, ClF_3, and F_2 cannot be distinguished by the mass spectrometer. However, it does appear that O_2ClF_4 (if it forms) is unstable and decomposes at 0°C or below.

- REACTION OF NO_2 WITH AsF_5

Prior work on the reaction of NO_2ClO_4 and O_2AsF_6 led us to suspect that the molecular adduct, $NO_2 \cdot AsF_5$, might have been a component of the solid products, in addition to NO_2AsF_6. We postulated that the following reaction might have taken place (ClO_3F was one of the reaction products):

$$NO_2AsF_6 + \cdot ClO_3 \longrightarrow ClO_3F + NO_2 \cdot AsF_5 \qquad (10)$$

This suggested the presence of $NO_2 \cdot AsF_5$, which has been reported by Aynsley et al. (Ref 5), and might account for unknown X-ray lines in the product. When we originally tried to prepare $NO_2 \cdot AsF_5$ (Ref 2) by allowing NO_2 and AsF_5 to react in a vacuum, $NOAsF_6$ was obtained instead. We have explored this reaction further under varied conditions in the hope of obtaining $NO_2 \cdot AsF_5$. In every run we obtained a product which was predominantly $NOAsF_6$, containing varying amounts of NO_2AsF_6. We, therefore, feel that the reported existence of a molecular adduct, $NO_2 \cdot AsF_5$, is erroneous (Ref 5). The X-ray powder patterns of the products contained only one significant line at 3.85 Å that could not be attributed to either $NOAsF_6$ or NO_2AsF_6. The infrared spectra showed the ν_3 absorption of AsF_6^- at 700 cm^{-1} and absorptions in the 2200-2400 cm^{-1} region where NO^+ and NO_2^+ have been reported to absorb (Ref 6). We postulate the following reaction (Equation 11) to account for the observed reaction products of the NO_2-AsF_5 reaction:

$$10\ NO_2 + 12\ AsF_5 \longrightarrow 5\ NO_2AsF_6 + 5\ NOAsF_6 + As_2O_5 \qquad (11)$$

This reaction is analogous to one reported for the NO_2-BF_3 reaction (Ref 6, Equation).

$$6\ NO_2 + 8\ BF_3 \longrightarrow 3\ NO_2BF_4 + 3\ NOBF_4 + B_2O_3 \qquad (12)$$

III. EXPERIMENTAL

A. REACTION OF N_2F_4 WITH $HAsF_6$

Approximately 25 ml of hydrogen fluoride was treated with $N_2F_4(AsF_5)_x$ in order to remove last traces of water and other reactive impurities. The HF was then distilled to a Kel-F test tube fitted with a Monel valve and cooled to -196°C. Roughly 4 mmoles of arsenic pentafluoride were condensed on the frozen HF, the valve was shut off and the tube was allowed to warm to room temperature in order to form a dilute solution of $HAsF_6$ in HF. The tube was recooled to -196°C and approximately 1 millimole N_2F_4 was condensed in it. The valve was closed and the tube was warmed to -80° C, and a clear solution was observed. Over a period of several hours at -80°C, a white precipitate formed in the tube. This was assumed to be $N_2F_3AsF_6$.

Three days later, after the tube had been standing at ambient temperature, it was decided to examine the solid product (completely dissolved at room temperature) more thoroughly. The HF was distilled to a receiver cooled to -196°C leaving a yellow solid residue in the reaction tube. This was pumped for several hours and then removed from the tube under dry N_2 for analysis. The yellow solid was quite reactive with water, producing flames and brown fumes (NO_2). Samples were examined by means of emission spectroscopy, elemental analysis, X-ray spectroscopy and infrared spectroscopy (Discussion Section, Tables II, III, and IV, and Figure 2). The results of these analyses showed that the solid contained metal hexafluoroarsenate impurities (predominantly $Ni(AsF_6)_2$) and that, although it was an N-F compound, it was not identical to the adduct obtained by the reaction of N_2F_4 with AsF_5.

B. ATTEMPTED REACTION OF N_2F_4 WITH $HClO_4$ IN HF

Approximately 5 ml of anhydrous HF was dried over $N_2F_4(AsF_5)_x$ and distilled to a Kel-F tube fitted with a Monel valve. Four mmoles of anhydrous $HClO_4$ (prepared by dropping 70% $HClO_4$ into concentrated H_2SO_4) were condensed into the tube containing the HF at -196°C. The tube was warmed to room temperature in order to form a solution of $HAsF_6$ in HF. The tube was then recooled to -196°C and 0.5 mmole N_2F_4 was condensed into it. The system was then warmed to -80°C and maintained so for 10 days. The tube was then opened up to a vacuum line and pumped through two Kel-F traps at -80°C and -196°C, respectively. Roughly 0.5 mmole of unreacted N_2F_4 collected in the -196°C trap.

C. REACTION OF $N_2F_4(AsF_5)_x$ WITH $KClO_4$ IN HF

A 0.365 gm sample of an approximately 1:1 N_2F_4-AsF_5 adduct (1.34 mmoles) was mixed with 0.200 gm $KClO_4$ (1.44 mmoles) in one leg of an "H"-shaped Kel-F reactor. The reactor was evacuated through a Monel valve and ball joint assembly, and 5 ml anhydrous HF was distilled onto the solid mixture at -196°C. The system was warmed to -78°C and agitated for two hr. During this period, a significant amount of solid remained undissolved in the HF but the HF solution became yellow. The tube was allowed to stand at -78°C for two days, and then volatile materials were removed by distilling from the reactor at -78°C to a trap at -196°C.

The material collected in the -196°C was predominantly HF. However, about 10%, or 0.2 mmoles, was shown by infrared to be a mixture of NF_3, ClO_3F, ClO_2, and N_2O. A portion of the yellow solution was then decanted to the second leg of the "H"-tube and the HF was completely distilled from the reactor. The solid residue from the yellow solution was white and showed the following infrared absorption (obtained on a sample pressed between AgCl plates):

1230	w. sharp	
1150-1030	s. broad	ClO_4^-
980	w. sharp	
855	w. sharp	
700	s. sharp	AsF_6^-
630	w. sharp	ClO_4^-

In order to obtain a better spectrum, a sample was mixed with dry NaF and a pellet was pressed. This exhibited the following absorptions:

2090 cm^{-1}	(NO^+ ?)
1050 cm^{-1}	ClO_4^-
930 cm^{-1}	
850 cm^{-1}	
700 cm^{-1}	AsF_6^-

The X-ray diffraction pattern of solid isolated from the HF solution was as follows:

d, Å	I/I_o	$KAsF_6$ (Ref 4) d^o, Å
*5.64	10	---
4.83	90	4.82
*4.48	30	---
*3.91	15	---
3.70	100	3.68
*3.61	30	---
*3.54	30	---
*3.37	10	---
*3.19	90	3.16
*2.92	20	2.92
*2.87	30	---
*2.55	15	---
2.42	5	2.40
*2.30	3	2.29
*2.25	1	---
*2.17	20	---
2.15	10	2.12
2.03	70	2.00
*1.90	2	---
1.85	7	1.84

---

* Diffraction lines present in pattern of $NOClO_4$

An attempt was made to obtain nitrogen content of the solid by hydrolysis. A 90 mg sample was weighed into a dry glass (under N_2) tube fitted with a stopcock ball joint assembly. However, the solid immediately began to evolve NO_2. The tube was rapidly evacuated and water distilled onto the solid at -196°C. Upon warming to room temperature, the solid went into solution with vigorous gassing. The gas (4.5 mg) was nitric oxide.

D. ATTEMPTED REACTION OF $N_2F_4(AsF_5)_x$ WITH $AgClO_4$ IN HF

A 0.255 gm of $AgClO_4$ and 0.284 gm of $N_2F_4(AsF_5)_x$ were weighed into separate legs of the "II" reactor. The tube was evacuated and 5 ml of dry HF was distilled onto the $N_2F_4(AsF_5)_x$ at -196°C. Upon warming the tube to room temperature, the $N_2F_4(AsF_5)_x$ went into solution with vigorous gas evolution.

Approximately 1 mmole of a mixture of NF_3, N_2F_2, and N_2O was formed in the process. The experiment was discontinued because of the ohvious decomposition of the adduct.

E. REACTION OF N_2FAsF_6 WITH $CsClF_4$

A 59.0 cc volume Kel-F, metal reactor with a small vacuum gauge attached to it was used in this experiment. A 0.18 gm sample of $CsClF_4$ was loaded into a swivel-side arm. The 0.16 gm of N_2FAsF_6 was placed in the bottom of the reactor along with a Teflon coated stirring bar. The $CsClF_4$ was dropped into the reactor under vacuum conditions at -78°C. No significant rise in pressure was noted when this was done, but traces of gases were detected by the mass spectrometer which had the following composition: Cl_2 65%, O_2 28%, CO_2 3%, and ClO_3F 4%. The reactor was held at -78° overnight. The next morning the pressure was $\leq$25 mm. These gases were pumped out and the reactor was warmed to -55° and held there for 1 hr. No gases were detected by the mass spectrometer. The reactor was then warmed to 0°C and within 5 minutes, during which the reagents were being stirred, the pressure rose to $\cong$250 mm. The composition of this gas as determined by mass spectroscopy was N_2O, N_2, and O_2. The ratio of N_2:O_2 was similar to that in air. No NF^+ or ClF^+ fragments were detected. These gases were removed and the reactor was allowed to stand several days in a vacuum at room temperature. A 0.34 mmole mixture of gas was then found in the reactor, which had the composition 50% O_2, 15% N_2O, 35% N_2. Again the presence of air was indicated.

The solid residue from the reaction is being analyzed.

F. REACTION OF O_2AsF_6 WITH $CsClF_4$

A 59.0 cc volume metal, Kel-F reactor with a vacuum gauge was used for this reaction. A 0.25 gm sample of $CsClF_4$ was loaded into the swivel-side arm and 0.22 gm of O_2AsF_6 was loaded into the bottom of the reactor along with a Teflon covered magnetic stirring bar. The reactants were mixed in vacuo at -78°, whereupon only a trace of gas was evolved. This was composed of Cl_2 and O_2 in the ratio of 3:1. The mixture was next stirred at 0°C. A 1.0 mmole quantity of gas was generated, which was composed of O_2:Cl_2 in a ratio of 1.6:1.0. A trace of ClO_3F was also detected. The solid product, which was a dark, fused mass, weighed 0.20 gm. Its X-ray powder pattern was in agreement with that of $CsAsF_6$.

G. REACTION OF NO_2 WITH AsF_5

A typical experiment was carried out in a glass reactor which had a volume of about 150 cc. In this particular instance, 0.2139 gm of NO_2 was condensed into the lower half of the reactor at -196°. Then 0.7805 gm of AsF_5 reagent (58.2% AsF_5, the rest BF_3 and SiF_4) was condensed onto the frozen NO_2 at -196°. The stoichiometric ratio of NO_2:AsF_5 was 1.75:1.00. The reactor was then placed in an unsilvered Dewar flask, and prechilled with liquid N_2. The open part of the Dewar was packed with glass wool and the reactor was allowed to warm from -196°to room temperature. Due to the fact that the Dewar was prechilled, this took place slowly. Reaction was observed to take place vigorously at about 25°C. Both white and yellow solids formed in the reactor. The yellow material formed in the bottom. A 7.6 mg quantity of O_2 was evolved. This was removed while the reactor was kept at -78°C. When the reactor was warmed to -56° and held there for an hour, 36.8 mg of a mixture of NO_2, SiF_4, and traces of HNO_3 were removed. The reactor was warmed to room temperature. Nitrogen dioxide was evolved from the yellow solid as it turned white and began to crumble to a powder. The weight of gas evolved was 35.1 mg. Infrared analysis showed this was NO_2 with a trace of HNO_3. The weight of the white solid left after removal of all of the gases was 0.8709 gm. This represented 149% of the weight of $NOAsF_6$ expected from the quantity of AsF_5 used. A sample of the adherent white solid was removed from the walls and analyzed by X-ray spectroscopy. It was a mixture of $NOAsF_6$ with lesser amounts of NO_2AsF_6. A strong "d" line at 3.86 A could not be identified with either; however, a sample of powdery white material from the bottom of the flask, which was a decomposition product of the yellow material, also was analyzed by X-ray. Its composition was the same as that from the walls. Some of the solid product was analyzed by infrared spectroscopy by smearing it onto AgCl plates. Bands were observed at: 2370 cm^{-1} (NO^+ or NO_2^+), 895, 695 (AsF_6^-), and 584 cm^{-1}.

IV. REFERENCES

1. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q1-65, Advanced Oxidizer Research, 31 March 1965 (C)

2. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q2-65, Advanced Oxidizer Research, 30 June 1965 (C)

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SECTION III

TASK 55

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

SECTION III

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

C. J. Grelecki
W.J. Cruice

Report RMD 5043-Q3-65

RMD Project 5043, Task 55
Report Period: 1 July 1965
to 30 September 1965

Contract No. NOnr 4364(00)
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FOREWORD

This section of the advanced oxidizer report summarizes work carried out during the period from 1 July 1965 to 30 September 1965 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).

ABSTRACT

The presence of ammonium perchlorate as a decomposition product of hydroxylammonium perchlorate was found to be dependent on the removal of oxidizing species from the system and, hence, non-stoichiometric. The oxidation of ammonium perchlorate by anhydrous perchloric acid at elevated temperatures was demonstrated.

CONTENTS

I. INTRODUCTION

The objective of this program is to study the kinetics of the thermal reactions of high energy solid oxidizers in order to understand the mechanism by which they decompose. Work previously reported includes a detailed literature search, results of experimental work on the vapor pressure and thermal decomposition of anhydrous perchloric acid, determination of the temperature coefficients of the reactions of hydrazinium monoperchlorate, hydroxylammonium chloride, and hydroxylammonium perchlorate, determination of the reaction stoichiometry of hydrazinium monoperchlorate, studies on the reaction stoichiometry of hydroxylammonium perchlorate, and results of some preliminary experiments on hydrazinium diperchlorate.

Destructive distillation experiments have been performed on high purity hydroxylammonium perchlorate and the results compared with the results of closed-system experiments of the kind previously reported. Basic exploratory studies have been conducted to determine whether ammonium perchlorate can be oxidized by perchloric acid at temperatures comparable to those where hydroxylammonium perchlorate decomposes.

This report includes a summary of experimental work done in the third quarter of 1965 and a brief outline of projected work for the following quarter.

II. SUMMARY

During this report period, the thermal decomposition of hydroxylammonium perchlorate was found to produce ammonium perchlorate only if the volatile products were constantly removed. The stoichiometry for decomposition of free hydroxylamine was found to be inapplicable, indicating definite oxidation of some intermediate which normally decomposes spontaneously to yield ammonia. The oxidation of ammonium perchlorate by anhydrous perchloric acid to yield nitrous oxide was demonstrated, although the normal decomposition of the acid is the preferred reaction. Additional experiments directed toward discovery of the stoichiometry and mechanism of the reaction are under way.

III. EXPERIMENTAL

A. PROCEDURES

1. Stoichiometry Experiments

The methods used in these experiments have been discussed in detail in Reference 1.

2. Ammonium Perchlorate — Perchloric Acid Systems

Thermal decomposition experiments were performed on mixtures of ammonium perchlorate and, alternately, perchloric acid dihydrate, hydroxylammonium perchlorate, and anhydrous perchloric acid. The additive was introduced into a preweighed Sickle gauge (Ref 2) containing a weighed amount of ammonium perchlorate. The gauge was set into liquid nitrogen, evacuated immediately, and sealed. The sealed gauge plus the fragment removed in sealing then were reweighed and the weight of additive determined. The balance of the experiment proceeded in the manner previously referenced.

B. MATERIALS

1. Hydroxylammonium Perchlorate

The production of hydroxylammonium perchlorate is detailed in Reference 1.

2. Anhydrous Perchloric Acid

The production of anhydrous perchloric acid is detailed in Reference 2.

3. Perchloric Acid

Baker 72% perchloric acid (ACS) was employed as perchloric acid dihydrate for the purposes of this experiment. The actual assay was 71.1% $HClO_4$, corresponding to a 2.27 molar ratio of H_2O to $HClO_4$.

4. Ammonium Perchlorate

The ammonium perchlorate used in these experiments was Matheson, Coleman and Bell reagent grade, assayed at RMD at over 99% purity.

IV. RESULTS AND DISCUSSION

A. STOICHIOMETRY EXPERIMENTS

1. Destructive Distillation of Hydroxylammonium Perchlorate

Hydroxylammonium perchlorate was maintained at 180°C for periods of approximately 18 hr; the system was continually evacuated through a liquid nitrogen trap at a pressure of 0.05 mm Hg. The reactant initially melted and rapid gassing was observed. However, after a period of time, the sample was observed to congeal, forming a white solid. This solid residue accounted for 20% of the starting mass; it was composed of 42.5% hydroxylammonium perchlorate, 39.1% ammonium perchlorate and 18.0% perchloric acid dihydrate. The remaining 0.4% was assumed to be additional water.

If the stoichiometry

$$4HONH_2 \longrightarrow 2NH_3 + N_2O + 3H_2O$$

were to apply, however, the residue would account for at least 44% of the starting material, based on pure ammonium perchlorate. Therefore, the above stoichiometry cannot apply to this reaction without further reservations. The products isolated from the cold traps were found to be nitrous oxide, hydrogen chloride, and another strong acid. There was not enough of the latter to permit adequate identification, but it appears to have been perchloric acid.

B. AMMONIUM PERCHLORATE — PERCHLORIC ACID SYSTEMS

As previously stated (Ref 1), products of the decomposition of hydroxylammonium perchlorate in sealed systems are nitrous oxide, hydrogen chloride and chlorine in the vapor phase. The condensed residue is a colorless liquid which may solidify slightly above ambient temperature. No ammonia has been detected in this residue, and it was supposed that the ammonia predicted by the above stoichiometry might be oxidized by perchloric acid produced in the reaction.

In order to verify this assumption, a number of thermal decomposition experiments were performed on ammonium perchlorate mixtures containing (alternately) hydroxylammonium perchlorate, perchloric acid dihydrate, and anhydrous perchloric acid. No decomposition was observed when a mixture of ammonium perchlorate and perchloric acid dihydrate was maintained at 150°C for an extended period.

An approximately equimolar mixture of ammonium perchlorate and hydroxylammonium perchlorate was maintained at 150°C for 150 minutes. Examination of the residue showed a slight increase in the total mass of ammonium perchlorate. Less hydroxylammonium perchlorate was consumed than would have been consumed in such an experiment performed on pure hydroxylammonium perchlorate.

Mixtures of ammonium perchlorate and anhydrous perchloric acid were run at 55°C, 70°C, and 100°C. At the lower temperatures, the molar ratios employed were (AP:$HClO_4$) 5:1 and 3:1 respectively, whereas at 100°C the molar ratio was approximately 1:2. At 55°C, normal decomposition products of anhydrous perchloric acid were obtained in the vapor phase, although the rate of pressure rise was lower than that observed for the pure acid. At 70°C, traces of N_2O were detected in the vapors and at 100°C (where the mixture decomposed instantaneously), 2% N_2O was detected. Thus, oxidation of the ammonia moiety of ammonium perchlorate by perchloric acid at elevated temperatures is definitely possible.

C. GENERAL DISCUSSION

The following specific facts concerning the thermal decomposition reaction of hydroxylammonium perchlorate are now fairly well established:

— The reaction in a closed system proceeds to nitrous oxide, hydrogen chloride and chlorine, and a strongly acidic liquid. No ammonium perchlorate is produced.

— The reaction in a constant vacuum proceeds to nitrous oxide, hydrogen chloride and chlorine, and a solid containing ammonium perchlorate, perchloric acid dihydrate and unreacted hydroxylammonium perchlorate. The amount of ammonium perchlorate produced does not correspond to the stoichiometry proposed for simple decomposition of free hydroxylamine.

— The kinetic data do not indicate competing reactions; the value of the activation energy indicates that the rate-controlling step in the early stages of the reaction is not the same as in hydrazinium mono- or diperchlorate or anhydrous perchloric acid. Likewise, it is not the same as in the decomposition of free hydroxylamine.

Thus it appears that the difference in end-product residue between the sealed system and the evacuated system is due to the removal of oxidizing species in the evacuated system. The reaction proceeds through some intermediate which may be oxidized to yield only nitrous oxide or may decompose spontaneously to yield nitrous oxide and ammonia. Such reactions should be first order with respect to oxidizing species and with respect to intermediate in the first case, and first order with respect to intermediate only in the second. Since the concentration of oxidants is high in the closed system but low in the evacuated system, the spontaneous decomposition should occur to a much higher degree in the evacuated system (as is the case). It appears that the rate constant for oxidation is greater than that for spontaneous decomposition, since no ammonia at all is found in the closed system.

V. FUTURE WORK

Additional work on the stoichiometry and mechanism of thermal decomposition of hydroxylammonium perchlorate is required. Specific objectives for the following report period include:

— Complete thermal decomposition of samples of hydroxylammonium perchlorate to obtain mass balance,

— Reexamination and integration of experimental results and information in the literature to propose a mechanism of decomposition.

VI. REFERENCES

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2. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-64-F, Advanced Oxidizer Research, Section IV, 14 December 1964 (C)

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13. ABSTRACT

Task 51 - Further experiments on the dehydrofluorination of secondary alkyldifluoramines are described. A new partially dehydrofluorinated product, 1-difluoramino-2-fluoriminocyclohexane, was obtained by treating bis(difluoramino)cyclohexane with basic ion exchange resin for a limited time. Bis(difluoramino)fluoraminomethoxypentane was synthesized by the addition of pentanol to perfluoroguanidine.

Task 53 - Elemental analyses of the N_2F_4-AsF_5 adduct gave a composition, $N_2F_4(AsF_5)_{1.33}$, indicating a mixture of adducts having 1:1 and 1:2 N_2F_4:AsF_5 ratios. The structure of the 1:2 adduct possibly is $N_2F_3^+ As_2F_{11}^-$. (U)

The reaction of O_2AsF_6 with $CsClF_4$ produced O_2 and Cl_2, as well as $CsAsF_6$, at about 0°C The reaction of NO_2 with AsF_5 does not give a molecular adduct $NO_2 \cdot AsF_5$ as reported in the literature, but rather a mixture of $NOAsF_6$ and NO_2AsF_6. (U)

Task 55 - The presence of ammonium perchlorate as a decomposition product of hydroxylammonium perchlorate was found to be dependent on the removal of oxidizing species from the system and, hence, non-stoichiometric.

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14 KEY WORDS	LINK A		LINK B		LINK C	
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Dehydrofluorination						
Alkyldifluoramines						
Pentanol						
Perfluoroguanidine						
Adduct						
Ammonium Perchlorate						
Anhydrous Perchloric Acid						
Hydroxylammonium Perchlorate						

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