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31 Jan 1974, Group 4, DoDD 5200.10; ONR ltr dtd 4 May 1977

ROCKETDYNE

A DIVISION OF NORTH AMERICAN AVIATION, INC.

R-3071-3

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(Unclassified Title)

RESEARCH ON FLUORINE OXIDIZERS, QUARTERLY PROGRESS REPORT FOR PERIOD ENDING 15 DECEMBER 1961

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Contract Nonr 3451 (00)
ARPA Order No. 23-61
Task 2, Item 1
Project No. 9100
G.O. 5983

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NO. OF PAGES 15 & v

REVISIONS

DATE 15 January 1962

DATE	REV. BY	PAGES AFFECTED	REMARKS

FORM R 18-G-1 (PLATE)

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FOREWORD

This report was prepared by the Chemical Synthesis Group of the Research Department at Rocketdyne. This research effort is supported by the Advanced Research Projects Agency under Contract Nonr 3451 (00); ARPA Order No. 23-61, Task 2, Item 1, Project Code No. 9100.

The responsible scientist for this work is Dr. Emil A. Lawton. Dr. Walter Maya, Dr. H. Frederick Bauer, and Mr. David F. Sheehan are fulltime associates. Analytical support was furnished by Dr. B. L. Tuffly and Mr. I. Lysyj. We wish to thank Mr. D. W. Moore, NOTS, China Lake, California, for taking the NMR spectra in this work.

ABSTRACT

The solids obtained from the reactions of the NF_3O-BF_3 complex with Cl_2O_7 and N_2O_4 were examined by NMR spectroscopy. No evidence was found for N-F compounds. Equally negative results were found for the reaction between $HClO_4$ and NF_3O. The solid obtained from the interaction of antimony pentafluoride and NF_3O was ~~shown to be~~ largely $NOSbF_6$.

No reaction was obtained between NF_3O and aqueous ~~potassium~~ KCN cyanide. Although no reaction occurred between NF_3O and an aqueous solution of the sodium salt of nitromethane, when the reaction was run in the absence of water, all the NF_3O was consumed. The products of this latter reaction have not yet been determined.

The isolation of pure Compound A (a new interhalogen) by ~~VPC~~ is being attempted. A small peak ~~has been~~ obtained in the chromatogram that may be ~~due to~~ Compound A, but its size has precluded identification. Compound B has ~~been~~ obtained from the electric discharge of mixtures of ~~nitrogen trifluoride~~ NF3 and ~~chlorine.~~ Cl. Compound B decomposes in glass to give SiF_4 and $FClO_3$, and is characterized by absorptions in the infrared ~~at 719, 713 and 707 cm^{-1}~~.

(Confidential Abstract)

* Vapor-phase chromatography

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ILLUSTRATIONS

DISCUSSION

CHEMISTRY OF TRIFLUORAMINE OXIDE

Reaction With Antimony Pentafluoride

The discovery that NF_3O forms a 1:2 complex with BF_3 (Ref. 1), led to an investigation of the reaction of NF_3O with antimony pentafluoride (Ref. 2). The principal interest was to determine if the reaction took the following course:

$$NF_3O + SbF_5 \longrightarrow NF_2OSbF_6$$

If the stable white solid formed in this reaction were the salt NF_2OSbF_6, it would constitute the first example of a stable NF_2O^+ ion. This ion has been postulated as the reactive intermediate in the additions of NF_3O to fluoro olefins (Ref 3).

When antimony pentafluoride was allowed to react with an excess of NF_3O at room temperature, a vigorous reaction occurred and a white solid was formed. Its infrared spectrum (Fig. 1) showed no evidence for a compound such as NF_2OSbF_6, but indicated it to be mainly $NOSbF_6$ with some possible nitrate impurity. Figure 2 shows the infrared spectrum of $NOSbF_6$ obtained from the reaction between NOCl and SbF_5 (Ref. 4), and comparison of the two spectra reveals them to be quite similar. Both spectra were taken in KCl pellets, prepared in a dry box.

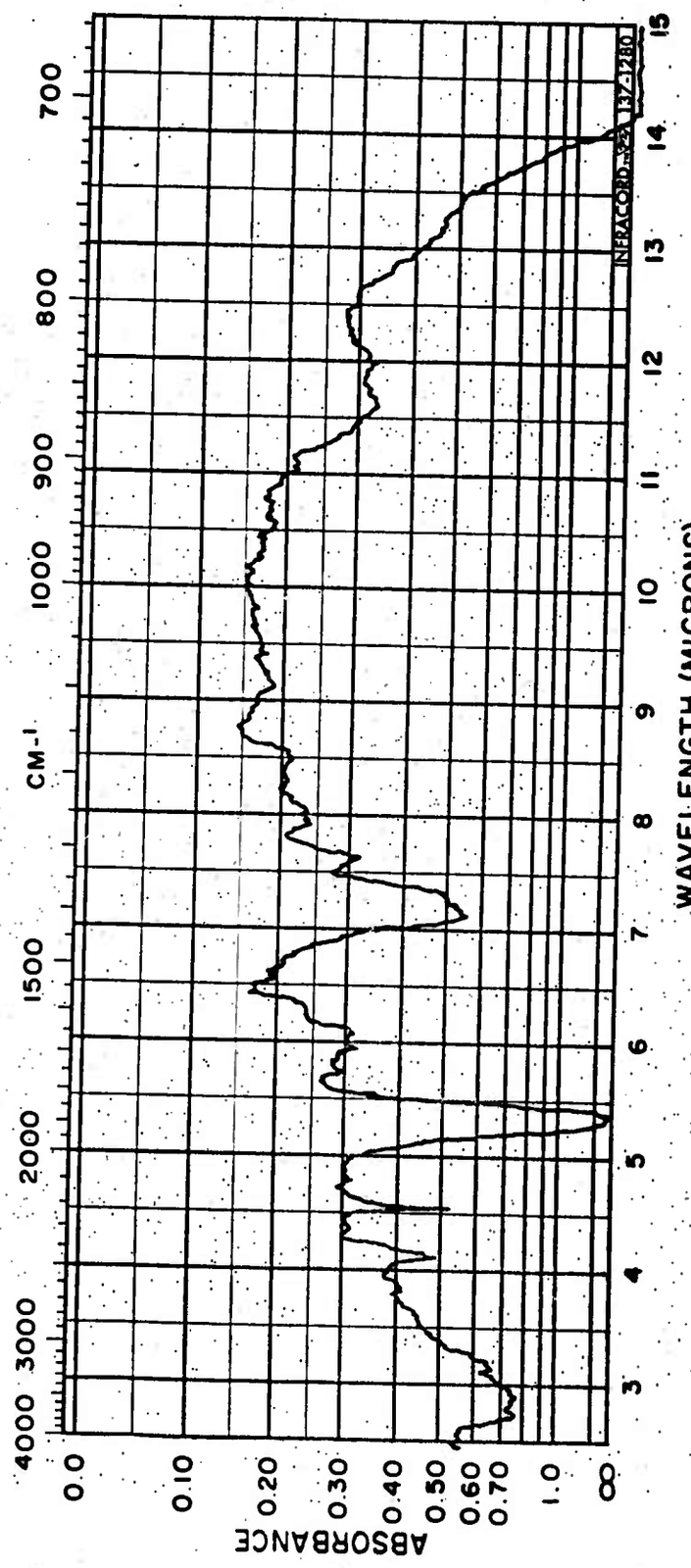


Figure 1. Solid From NF_3O and SbF_5

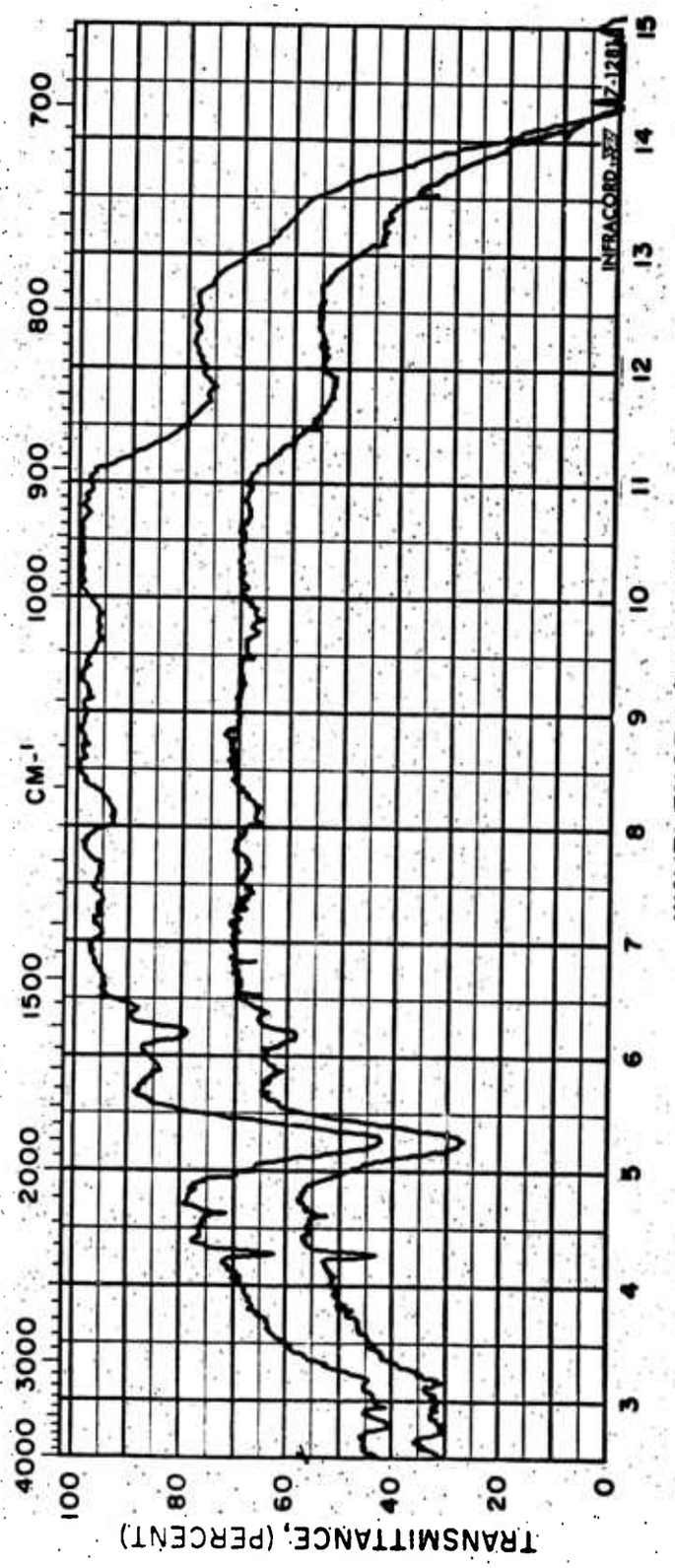


Figure 2: $NOSbF_6$ From NOCl and SbF_5

It was not possible to obtain a vapor-pressure composition diagram of the NF_3O-SbF_5 system because of the wide disparity of the physical properties of the two substances. Antimony pentafluoride melts at 7 C, while NF_3O has a boiling point of -89 C. Difficulty also was encountered in determining the stoichiometry of the reaction, both because the antimony pentafluoride tends to dissolve in the protective Fluorolube oil layer in the manometer; and because the white solids formed have about the same volatility as SbF_5. The amount of NF_3O consumed indicates reaction with two moles of SbF_5; however, it is impossible to draw any conclusions in view of the experimental uncertainties.

Reaction with Chlorine (VII) Oxide, Nitrogen Dioxide and Perchloric Acid

In the previous report (Ref. 1), the following reactions were attempted:

$$NF_3O + Cl_2O_7 \xrightarrow{BF_3} NF_2OClO_4 + FClO_3 \qquad (1)$$

$$NF_3O + BF_3 + N_2O_4 \longrightarrow NF_2ONO_3 + NOBF_4 \qquad (2)$$

$$NF_3O + HClO_4 \longrightarrow HF + NF_2OClO_4 \qquad (3)$$

White solids obtained from reactions 1 and 2, and a nonvolatile liquid from reaction 3 were incompletely characterized; there was a possibility that they may have contained N-F substances.

They have now been examined in the NMR, and no indications were found for the presence of N-F bonds. The only fluorine signal found was in the case of reactions 1 and 2, and were assignable to the BF_4^- ion.

Reaction With Potassium Cyanide

This reaction was attempted in an effort to extend the scope of the recently discovered addition of NF_3O to tetrafluoroethylene (Ref. 3). The following was the desired reaction, the formation of a C-O bond providing the driving force, as in the case of the addition to olefins:

$$CN^- + NF_3O \rightarrow NF_2OCN + F^-$$

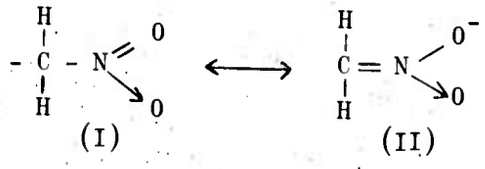
When the reaction was attempted between NF_3O and aqueous KCN, all the NF_3O was recovered. This reaction will be repeated using nonaqueous solvents and employing the NF_3O-BF_3 complex. The catalysis by BF_3 may be a necessary element in all these reactions.

Reaction With Nitromethane

The reaction between the sodium salt of nitromethane and NF_3O is being studied for the same reasons as in the KCN case. The following is the desired reaction:

$$CH_2NO_2Na + NF_3O \rightarrow NaF + F_2NOCH_2NO_2$$

The anion of nitromethane resonates between the two forms:



(I) (II)

and several reactions are known in which the anion behaves as the carbanion (I), such as the formation of nitroalkanes from the reaction with alkyl halides, and the synthesis of trichloronitromethane by reaction with hypochlorous acid (Ref. 5).

When carried out in aqueous solution, no reaction occurred. However, when nitromethane was used as solvent, all the NF_3O was consumed. This reaction is still under investigation to determine whether the desired addition took place.

NEW INTERHALOGENS

Compound A

During this quarter the main effort has been directed at obtaining pure Compound A. The synthetic procedure has been improved by employing conditions in the discharge that lead to increased gas ionization, thereby decreasing the amount of free chlorine obtained along with Compound A. Since BF_3 does not form a complex with Compound A, it has been used in the purification procedures to complex undesirable side products such as ClO_2F. Despite these improvements, Compound A has not yet been obtained in the pure state.

Purification of Compound A by gas chromategraphy was attempted in a column packed with halocarbon oil on Kel-F powder (Ref. 6). Found were SiF_4, Cl_2, ClO_2, $FClO_3$, and an unidentified fraction too small to manipulate. Since the peak may be due to ClO_2F or Compound A, it is not yet clear whether Compound A is actually decomposing on the column or not.

The infrared spectrum of Compound A shows, in addition to the absorptions at 732 cm^{-1} and 787 cm^{-1}, another absorption at 630 cm^{-1}. This latter absorptio has p, q and r branches which may be a result of an axial fluorine - chlorine stretching vibration A_1. While the parallel band for the axial fluorine - bromine stretch in BrF_5 (A_1 = 690 cm^{-1})(Ref. 7) is at a higher frequency than the perpendicular band (E = 645 cm^{-1}) in Compound A these absorptions are reversed with A_1 = 630 cm^{-1} and E = 732 cm^{-1}. This implies that if Compound A is ClF_5, the axial fluorine is further from the chlorine than are the other fluorines. The influence of the lone unshared electron pair in the proposed ClF_5 molecule would have a greater tendency to crowd all five fluorines on one side of the central atom than in BrF_5 because of increased steric crowding. The axial fluorine in ClF_5 interacting more strongly with the other four fluorines, would then be forced further from the chlorine. The reversal in the order of the A and the E stretching frequencies in BrF_5 and ClF_5 would not be unreasonable.

Four preliminary experiments with radio-frequency electrodeless discharge of NF_3 and Cl_2 in a glass reactor resulted in the formation of reproducible, but small amounts of Compound A and in one case FNO_3. The discharge could be maintained at pressures no greater than 5 mm and at relatively slow flowrates (a few cc/min). A radio-frequency generator of greater power output will be necessary to increase the operating pressure of the system.

Compound B

Compound B, previously considered as a possible binary N-F compound (Ref. 8), has been reproducibly made from NF_3 and Cl_2 along with Compound A. Compound B is the species previously referred to as the less stable of the two unknown compounds condensable at -142 C and is characterized by absorption in the infrared at 719, 713, and 707 cm^{-1} (Fig. 3). It reacts slowly with glass to give SiF_4 and ClO_3F. Compound B formed a BF_3 complex which could be easily separated from Compound A and other products. Thus, Compound B may be a new species containing chlorine and fluorine. The further investigation of Compound B has been temporarily set aside in favor of Compound A.

Because of the reactivity of Compounds A and B with glass, future work is planned in nonglass systems. To this end, an alumina and stainless-steel discharge cell is in fabrication and will be used in conjunction with a metal vacuum system. The use of high-purity alumina (99 percent Al_2O_3) is indicated by the need for a nonconducting cell material resistant to attack by fluorine.

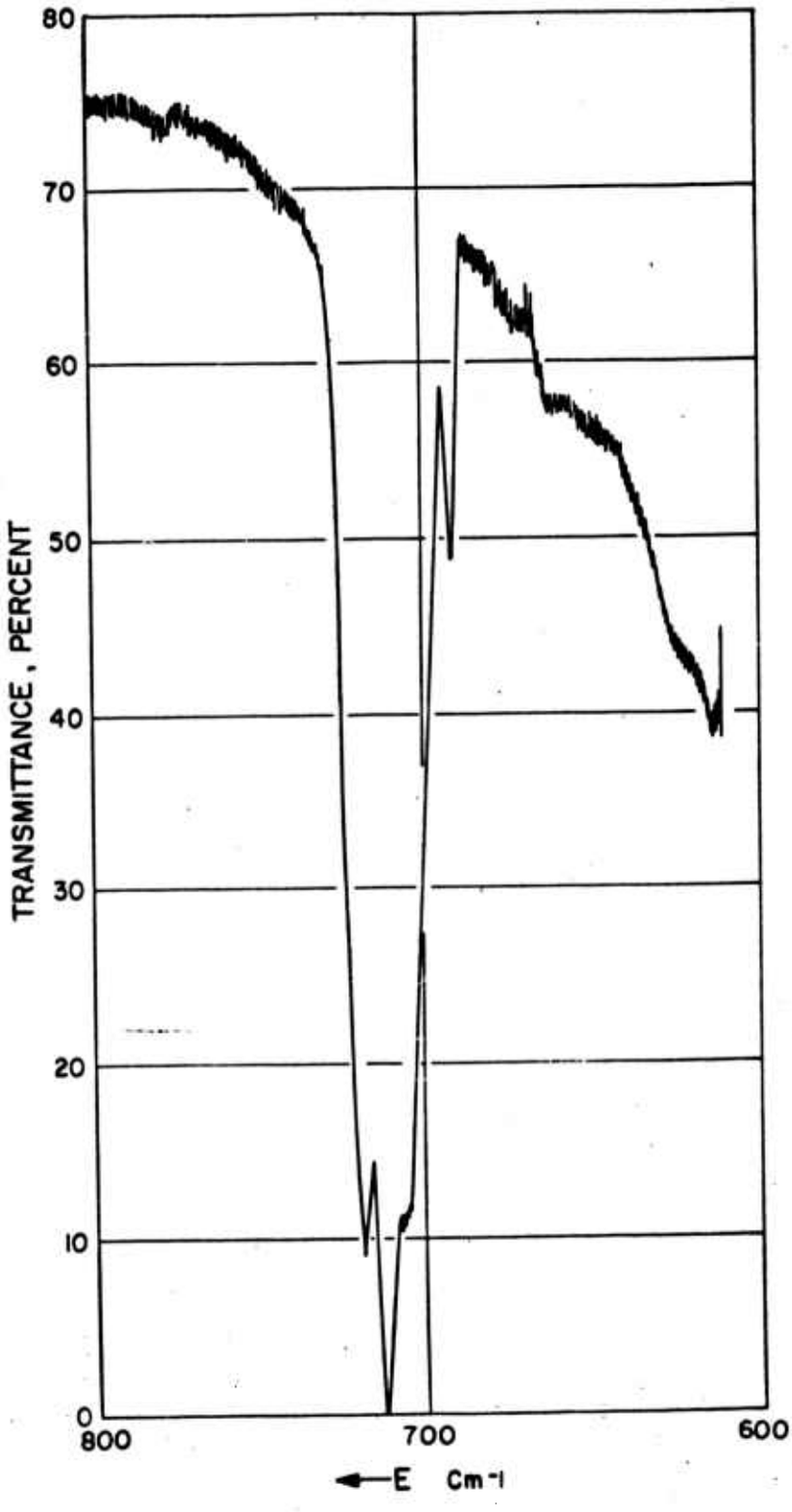


Figure 3. Infrared Spectrum of Compound 7

EXPERIMENTAL DETAILS

CHEMISTRY OF TRIFLUORAMINE OXIDE

Reaction With Antimony Pentafluoride

Antimony pentafluoride (1.7 mmols) was allowed to come into contact with an excess of NF_3O (373 cc) at room temperature. A vigorous reaction occurred, and a white solid was formed. The solid weighed less than the starting SbF_5 because of the absorption of the SbF_5 in the Fluorolube layer in the manometer and to the volatility of the solid. The NF_3O consumed in the reaction (0.8 mmols) corresponded to a 1:2 reaction with SbF_5. The infrared spectra of the solid is shown in Fig. 1 , taken in a KCl pellet. The solid was found to react with Nujol when ground in a dry box.

Reaction With Chlorine (VII) Oxide, Nitrogen Dioxide and Perchloric Acid

The experimental procedures were the same as described in the previous report (Ref. 1). The white solids were found to be somewhat soluble in nitromethane. Sulfur dioxide, carbon tetrachloride, and Cl_2O_7 did not dissolve the solids, while diethylether reacted with them.

Reaction With Potassium Cyanide

A solution containing 6.2 mmoles of KCN was allowed to stand overnight in contact with 1.8 mmoles of NF_3O. No reaction occurred, and all the NF_3O was recovered.

Reaction With Nitromethane

Trifluoramine oxide (29 cc) was left in contact with a solution containing an excess of nitromethane, made basic with NaOH, for two hours. Essentially all the NF_3O was recovered.

Nitromethane was left to stand for 24 hours in contact with NaOH. The clear yellow supernatant solution was then pipetted into an ampoule (2 ml), and exposed to 28 cc of NF_3O. After two hours, all the NF_3O had been consumed. The liquid is currently under investigation to determine if the desired reaction occurred.

NEW INTERHALOGENS

Compound A

A total of seven glow-discharge reactions employing NF_3 and Cl_2 were carried out. The samples submitted for gas chromatography were fractionated through a -112 C trap and condensed at -126 C. Only a single fractionation was carried out to minimize the reaction of Compound A with glass. Fractions recovered from the chromatographic column and identified were SiF_4, ClO_2, Cl_2, and $FClO_3$.

The preparation of Compound A by radio-frequency electrodeless discharge was carried out in a glass reactor at 800 volts and 90 ma. Both straight-tube and concentric-tube arrangements of the discharge cell were tested with no observable difference.

Compound B

Compound B was synthesized along with Compound A and separated from ClF, ClF_3, Compound A, ClO_2F, ClO_2, NF_3, Cl_2, and SiF_4 by the addition of excess BF_3 and fractionation through -80 C, -112 C, and -126 C traps. The -112 C trap contained some SiF_4, BF_3, and Compound B. However, neither BF_3 nor Compound B was observed in the -126 C trap.

About 5 cc of Compound B exploded while at -196 C in a U trap. The explosion was of sufficient force to destroy the U trap and the adjoining glass connections. The cause of the explosion is unknown.

SUMMARY AND CONCLUSIONS

The reaction of NF_3O with antimony pentafluoride yields a white solid, shown to be largely $NOSbF_6$, rather than NF_2OSbF_6.

The solids obtained from the reactions of the NF_3O-BF_3 complex with Cl_2O_7 and N_2O_4 have been shown by NMR and IR not to contain N-F compounds. Equally negative results were obtained for the reaction of NF_3O with $HClO_4$.

Trifluoramine oxide has been shown not to react with aqueous potassium cyanide. The reaction will be tried employing the NF_3O-BF_3 complex in a nonaqueous medium.

Trifluoramine oxide did not react with an aqueous solution of the sodium salt of nitromethane; however, a reaction did occur when nitromethane itself was used as a solvent. This reaction is being investigated to determine whether new NF_2O-type compounds have been synthesized.

Compound A has thus far eluded efforts to prepare it in the pure state. Compound A does not form a BF_3 complex, and BF_3 has been used to complex unwanted side products in the syntheses, such as ClO_2F. Purification by gas chromatography is under study. A small unknown fraction has been obtained in the VPC column that may be caused by Compound A, but the fraction has been too small to identify.

Compound B has been obtained by subjecting mixtures of NF_3 and Cl_2 to the glow discharge at -78 C. Compound B decomposes in glass to give $FClO_3$ and SiF_4. It absorbs in the IR at 719, 713, and 707 cm^{-1}. On one occasion, Compound B exploded with considerable force while in a U trap at -196 C. The cause for the explosion is not known.

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