| AD NUMBER |
| --- |
| AD353118 |
| CLASSIFICATION CHANGES |
| TO: unclassified |
| FROM: confidential |
| LIMITATION CHANGES |
| TO:<br>Approved for public release, distribution unlimited |
| FROM:<br>Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; JUN 1964. Other requests shall be referred to Office of Naval Research, Arlington, VA 22203. |
| AUTHORITY |
| 31 Jul 1976, DoDD 5200.10; ONR ltr 16 Feb 1979 |

AD 353118

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA

# DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY PRACTICABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

REPORT NO. 0235-01-20 (QUARTERLY)
PERIOD COVERED: 1 APRIL-30 JUNE 1964

# RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT TO

## OFFICE OF NAVAL RESEARCH

AND

## ADVANCED RESEARCH PROJECTS AGENCY

CONTRACT Nonr 2655(00)
ARPA ORDER NO. 170, AMENDMENT NO. 6
PROJECT CODE 4910

JULY 1964
COPY NO. CP-61-9



*CHEMICAL PRODUCTS DIVISION*
AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

## NOTICE

REPRODUCTION IN WHOLE OR IN PART IS PERMITTED FOR ANY PURPOSE OF THE UNITED STATES GOVERNMENT.

## United States Patent Office Secrecy Order

**NOTICE**

The Aerojet-General Corporation has filed patent applications in the U. S. Patent Office to cover inventions disclosed in this publication, and the Commissioner of Patents has issued a secrecy order thereon.

Compliance with the provisions of this secrecy order requires that those who receive a disclosure of the secret subject matter be informed of the existence of the secrecy order and of the penalties for the violation thereof.

The recipient of this report is accordingly advised that this publication includes information which is now under a secrecy order. It is requested that he notify all persons who will have access to this material of the secrecy order.

Each secrecy order provides that any person who has received a disclosure of the subject matter covered by the secrecy order is

> "in nowise to publish or disclose the invention or any material information with respect thereto, including hitherto unpublished details of the subject matter of said application, in any way to any person not cognizant of the invention prior to the date of the order, including any employee of the principals, but to keep the same secret except by written permission first obtained of the Commissioner of Patents."

Although the original secrecy order forbids disclosure of the material to persons not cognizant of the invention prior to the date of the order, a supplemental permit attached to each order does permit such disclosure to:

> "(a) Any officer or employee of any department, independent agency, or bureau of the Government of the United States.
>
> "(b) Any person designated specifically by the head of any department, independent agency or bureau of the Government of the United States, or by his duly authorized subordinate, as a proper individual to receive the disclosure of the above indicated application for use in the prosecution of the war.
>
> "The principals under the secrecy are further authorized to disclose the subject matter of this application to the minimum necessary number of persons of known loyalty and discretion, employed by or working with the principals or their licensees and whose duties involve cooperation in the development, manufacture or use of the subject matter by or for the Government of the United States, provided such persons are advised of the issuance of the secrecy order."

No other disclosures are authorized, without written permission from the Commissioner of Patents. Public Law No. 239, 77th Congress, provides that whoever shall "willfully publish or disclose or authorize or cause to be published or disclosed such invention, or any material information with respect thereto," which is under a secrecy order, "shall, upon conviction, be fined not more than $10,000 or imprisoned for not more than two years or both." In addition, Public Law No. 700, 76th Congress, provides that the invention in a patent may be held abandoned, if it be established that there has been a disclosure in violation of the secrecy order.

It must be understood that the requirements of the secrecy order of the Commissioner of Patents are in addition to the usual security regulations which are in force with respect to activities of the Aerojet-General Corporation. The usual security regulations must still be observed notwithstanding anything set forth in the secrecy order of the Commissioner of Patents.

July 1964

Report No. 0235-01-20
(Quarterly)

# RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

By

K. Baum
J. M. Cavallo
V. Grakauskas
M. P. Mascari

Analytical Support

C. L. Deuel
K. Inouye
H. M. Nelson

A Report To

OFFICE OF NAVAL RESEARCH
and
ADVANCED RESEARCH PROJECTS AGENCY

Contract Nonr 2655(00)
ARPA Order No. 170, Amendment No. 6
Project Code 4910



Von Karman Center

AEROJET-GENERAL CORPORATION

A Subsidiary of The General Tire & Rubber Company

## ABSTRACT

The reaction of 1-nitro-1-nitrosocyclohexane with difluoramine in the presence of the boron trifluoride complex of phosphoric acid gave nitrocyclohexane and 1-nitro-1-(fluoroazoxy)cyclohexane. The uncatalyzed reaction of alkyl nitrites with difluoramine gave the corresponding alcohols. 1-Chloro-1-nitrobutane was nitrosated, and the unstable product was treated with difluoramine in fuming sulfuric acid to give 1-chloro-1,1-bis(difluoramino)butane.

Evidence was obtained showing that N-fluoroformamide is produced in the direct fluorination of formamide (no solvent). Fluorination in solventless systems was extended to methyl- and ethylformamide where, in addition to alkyldifluoramines previously isolated in aqueous fluorination, the corresponding mono-N-fluoro derivatives were obtained. Subsequently these mono-N-fluoro derivatives, and also N-acetyl-N-fluoro-n-butylamine were obtained, although in very low yields, in the aqueous fluorination of the corresponding N-alkylamides.

Fluorination in the absence of a solvent was also extended to a cyclic amide, 2-pyrrolidinone, where 3-difluoraminobutyryl fluoride was obtained in addition to N-fluoro-2-pyrrolidinone.

The fluorination of aqueous 2-oxazolidone gave its N-fluoro derivative and 2-difluoraminoethanol.

It was shown that fluoroammonium perchlorate is insensitive to impact below 40-45 cm/2-kg wt. Several 30 to 50-mg batches of analytically pure material were prepared.

## CONTRACT FULFILLMENT STATEMENT

This is the twentieth in a series of quarterly technical summary reports submitted in partial fulfillment of the contract. It covers the period 1 April through 30 June 1964.

AEROJET-GENERAL CORPORATION

L. R. Rapp /eprischer

L. R. Rapp, Manager
Chemical Products Division

CONTENTS

CONTENTS (cont.)

## I. INTRODUCTION

The objective of this program is to develop new methods of preparing high-energy materials for military applications.

## II. TECHNICAL DISCUSSION

### A. REACTIONS OF DIFLUORAMINE (K. Baum)

#### 1. Discussion

Work was continued toward the preparation of a 1,1,1-tris(difluoramino)alkane through replacement of nitro, nitroso, and halo groups by difluoramine. It was previously demonstrated* that 1,1-dibromo-1-nitrobutane reacted with difluoramine in fuming sulfuric acid to give 1-bromo-1,1-bis(difluoramino)butane, whereas 1,1-dichloronitrobutane gave 1,1-dichloro-1-difluoraminobutane. This study has been extended to the halonitro-nitroso derivatives.

1-Chloro-1-nitrobutane was synthesized in high yield by an extension of the procedure developed by Levering** for preparing 1-chloro-1-nitroethane. The chlorination of the sodium salt of nitrobutane was conducted in the presence of sodium chloride, and the product was removed as it was formed. A similar procedure was used to prepare 1-bromo-1-nitrobutane.

To prepare 1-chloro-1-nitro-1-nitrosobutane, 1-chloro-1-nitrobutane was dissolved in aqueous alkali at 0-5°C and sodium nitrite and sulfuric acid were added. A dark-blue oil separated, which, however, was too unstable for vacuum distillation. In one case the material fumed off after standing for several

---

*Aerojet-General Report 0235-01-19, April 1964, p. 1 (Confidential).

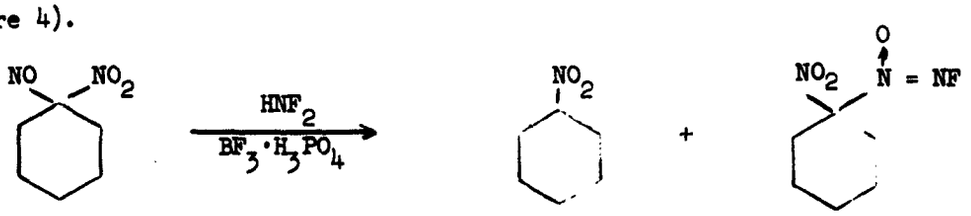
**D. R. Levering, J. Org. Chem., 27, 2930 (1962).

minutes at room temperature. Subsequently the nitrosation product was dissolved in pentane as soon as it was formed, and was stored at -80°C until it was reacted with difluoramine. When this blue oil was reacted with refluxing difluoramine in fuming sulfuric acid, 1-chloro-1,1-bis(difluoramino)butane was formed, as evidenced by elemental analysis, infrared spectrum (Figure 1), and proton (Figure 2) and fluorine (Figure 3) NMR spectra. These spectra are similar to those of 1-bromo-1,1-bis(difluoramino)butane.*

One attempt was made to react the nitrosation product of 1-bromo-1-nitrobutane with difluoramine. The product, however, was a complex mixture. This work will be repeated using different reaction conditions.

The reaction of 1-nitro-1-nitrosocyclohexane with difluoramine in fuming sulfuric acid has been shown to give 1,1-bis(difluoramino)cyclohexane.** This reaction was repeated using a milder catalyst, the boron trifluoride complex of phosphoric acid, instead of sulfuric acid. An intermediate, such as 1-nitro-1-difluoraminocyclohexane, might thus be isolated. No general method for the preparation of this class of compounds is known.

When a mixture of 1-nitro-1-nitrosocyclohexane, difluoramine, and the boron trifluoride complex of phosphoric acid was allowed to reflux for 45 min, two products were isolated: nitrocyclohexane and 1-nitro-1-(fluoroazoxy)cyclohexane. The latter compound was identified by elemental analysis and its infrared spectrum (Figure 4).

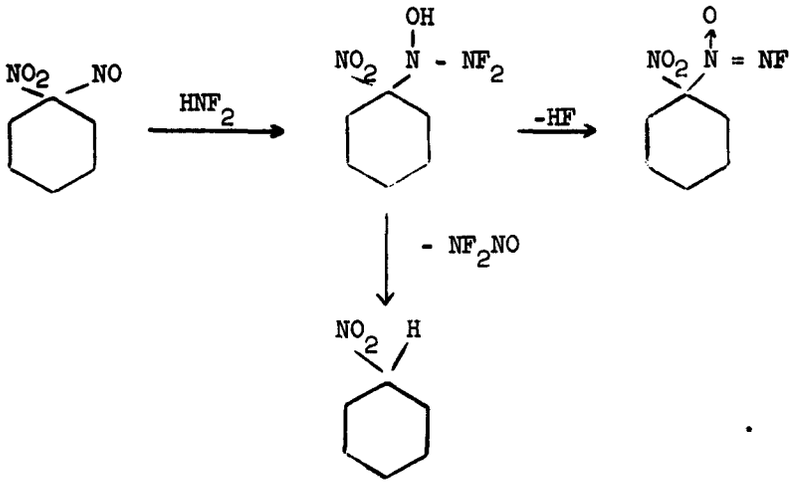



These products might be formed from a common intermediate, the nitrosodifluoramine adduct. The loss of HF would give the fluoroazoxy compound,

*Aerojet-General Report 0235-01-19, April 1964, Figs. 1-3 (Confidential).

**Ibid., p. 3 (Confidential).

whereas elimination of $NONF_2$ would give nitrocyclohexane. The latter reaction is essentially the nitrosation of difluoramine by 1-nitro-1-nitrosocyclohexane. The mechanisms of these reactions, and the function of the acid catalyst, if any, are unknown.




The formation of fluoroazosy compounds from nitroso compounds and difluoramine has been reported previously only with the use of basic catalysts.*

Alkyl nitrites might be expected to react with difluoramine either as alkylating agents, giving alkyldifluoramines, or as nitrosating agents, giving alcohols and $NF_2NO$. The former course would be useful in the preparation of propellant ingredients. When n-octyl nitrite was added to refluxing difluoramine, with no catalyst, a transient purple color formed, indicative of $NF_2NO$. When the difluoramine was removed, n-octanol remained. Similarly, t-butyl nitrite gave t-butanol.

$$R - ONO + HNF_2 \longrightarrow ROH + NF_2NO$$

*Rohm & Haas Co., Quarterly Progress Report on ARPA Projects, Report No. P-61-21, October 25, 1961, p. 2 (Confidential).

2. Experimental

a. Reaction of 1-Nitro-1-nitrosocyclohexane with Difluoramine

Difluoramine (27 g) was refluxed over 5 g (0.0316 mole) of 1-nitro-1-nitrosocyclohexane, giving a homogeneous solution. The boron trifluoride complex of phosphoric acid (2 ml) was added dropwise, and the mixture was allowed to reflux for 45 min. Methylene chloride (80 ml) was added and the excess difluoramine was allowed to escape. The lower (catalyst) layer was discarded, and the methylene chloride solution was dried over sodium sulfate and distilled to remove the solvent. The residue was vacuum-distilled to yield 1.50 g (0.0112 mole, 39.4% yield) of nitrocyclohexane, b.p. 30°C/3 mm, which was identified by comparing its infrared spectrum with that of an authentic sample. Further distillation gave 3.22 g (0.0168 mole, 53.4% yield) of 1-nitro-1-(fluoroazoxy)cyclohexane, b.p. 69°C/3 mm.

Anal. Calcd. for $C_6H_{10}N_3O_3F$: C, 37.7; H, 5.23; N, 22.0; F, 9.95.
Found: C, 38.1; H, 5.57; N, 21.7; F, 10.0.

b. Reaction of Octyl Nitrite with Difluoramine

Octyl nitrite (5.0 g, 0.0314 mole) was added dropwise to approximately 27 g of refluxing difluoramine. A purple color appeared, but disappeared after about 1/2 hour. After 4 hours, the excess difluoramine was removed. Vacuum distillation of the residue gave 3.14 g (0.024 mole, 77% yield) of n-octanol, b.p. 54°C/1 mm, identified by its infrared spectrum.

c. 1-Chloro-1-nitrobutane

Nitrobutane (20.0 g, 0.194 mole) was dissolved, with swirling and heating on a steam bath, in 120 ml of water containing 8.0 g (0.194 mole) of 97% sodium hydroxide. Sodium chloride (10 g) was added and the solution was cooled in an ice bath. Chlorine was bubbled slowly through the solution, without agitation, while the temperature was maintained at 0-5°C. A liquid, heavier than water, separated. The chlorination was periodically interrupted whenever several ml of this liquid accumulated, and it was removed with a dropper. When no additional liquid separated, the combined product was dried over sodium sulfate and distilled to give 22.5 g (0.164 mole, 84.5% yield) of 1-chloro-1-nitrobutane, b.p. 45°C/6 mm, $n_D^{25}$ 1.4310.

Anal. Calcd. for $C_4H_8NO_2Cl$: C, 34.9; H, 5.82; N, 10.17.
Found: C, 34.8; H, 5.72; N, 9.85.

d. 1-Bromo-1-nitrobutane

A mixture of 10 g (0.097 mole) of 1-nitrobutane and 70 ml of water containing 0.097 mole of sodium hydroxide was heated at 50°C until solution was complete. Sodium bromide (20.0 g) was then added, and the solution was cooled to 0°C. Liquid bromine (15.5 g, 0.097 mole) was added dropwise while the solution was kept at 0-5°C. A red oil separated, and was removed with a dropper whenever several ml accumulated. The combined product was distilled to give 14.5 g (0.080 mole, 82% yield) of 1-bromo-1-nitrobutane, b.p. 36°C/1.1 mm, $n_D^{25}$ 1.4613.

Anal. Calcd. for $C_4H_8NO_2Br$: C, 26.4; H, 4.40; N, 7.70.
Found: C, 26.1; H, 4.58; N, 7.60.

e. 1-Chloro-1-nitro-1-nitrosobutane

1-Chloro-1-nitrobutane (5.0 g, 0.0364 mole) was added to a solution of 1.64 g (0.041 mole) of sodium hydroxide at 0-5°C and the mixture was stirred and maintained at this temperature until solution was complete (about 2 hours). Sodium nitrite (3.79 g, 0.055 mole) was added and the solution was cooled with an ice-acetone bath (-8°C) while 20 ml of 25% sulfuric acid was added dropwise. The rate of addition was such as to maintain the solution temperature at 0-5°C, although at one point it rose to 10°C. A dark-blue oil formed, and was added by means of a separatory funnel to 25 g of pentane. The weight of the crude nitroso compound was 6.2 g. The pentane solution was stored at -80°C until it was reacted with difluoramine. A dark oil separated at this temperature.

A similar preparation of the nitroso compound resulted in decomposition during an attempted distillation. The product of another preparation fumed off after standing at room temperature for several minutes without a solvent.

f. Reaction of 1-Chloro-1-nitro-1-nitrosobutane with Difluoramine

This product was warmed to room temperature and was added, with stirring, to a refluxing mixture of 10 ml of 20% fuming sulfuric acid and 27 g of difluoramine. Refluxing was continued for 4 hours. The mixture was drained onto

100 ml of crushed ice, which was then allowed to melt. The pentane layer was separated, and the aqueous layer was extracted with two 50-ml portions of methylene chloride. The combined organic solutions were distilled. Vacuum distillation of the residue that remained after the solvent was removed yielded 0.82 g of colorless liquid, b.p. 33-34°C/35 mm. Gas chromatography indicated that the material contained three minor impurities. The major peak was trapped and characterized as 1-chloro-1,1-bis(difluoramino)butane.

Anal. Calcd. for $C_4H_7N_2F_4Cl$: C, 24.7; H, 3.60; N, 14.4.
Found: C, 24.9; H, 3.89; N, 13.8.

Two attempted fluorine analyses resulted in explosions. The infrared spectrum (Figure 1) and proton and fluorine NMR spectra (Figures 2 and 3, respectively) compare closely with those of 1-bromo-1,1-bis(difluoramino)butane.

The NMR spectra were obtained using a Varian microcell with carbon tetrachloride solution containing TMS (tetramethylsilane) and $CFCl_3$ as internal references. The proton spectrum contains an irregular triplet at 1.01 ppm, assigned to the terminal methyl group, $-CH_2\underline{CH_3}$. The multiplet with maximum intensity at 107 cps, corresponding at least roughly to the expected sextet, is assigned to the $CH_2\underline{CH_2}CH_3$ methylene group. The multiplet with maximum intensity at 134 cps is assigned to the $Cl(NF_2)_2C\underline{CH_2}$- methylene group. The $F^{19}$ spectrum consists of an AB quartet (chemical shifts of -30.42 and -37.35 ppm, coupling constant 609 cps).

B. DIRECT FLUORINATION (V. Grakauskas)

1. Discussion

It has been shown that the fluorination of aqueous monoalkylamides gives the corresponding difluoramines.* The presence of N-alkyl-N-fluoroamide intermediates in these fluorination reactions has been suggested** but the intermediates have not been isolated. The fluorination of amides was studied more thoroughly during this quarter with the objective of synthesizing the corresponding N-monofluoro derivatives. These N-fluoroamides would be desirable intermediates for the preparation of fluoroammonium salts.

*Aerojet-General Report 2099 (Summary), November 1961, p. 21 (Confidential).
**Ibid., p. 22.

The possibility of synthesizing N-fluoroformamide itself, HCONHF, was investigated first because of the potential utility of the compound as an intermediate for the preparation of fluoroammonium perchlorate:

$$HCONHF + HClO_4 \longrightarrow NH_3F^{\oplus}ClO_4^{\ominus} + CO$$

It has already been shown that the fluorination of aqueous formamide gives N,N-difluorourea* and therefore, fluorination in aqueous solution did not appear promising; i.e., it seemed unlikely that a variation of reaction conditions would change the course of the reaction. Instead, pure formamide was fluorinated at 0-3°C. The fluorination proceeded smoothly and fluorine was readily consumed. A solid material gradually accumulated as the reaction progressed. This solid was removed by filtration at the end of the fluorination and identified as cyanuric acid. The clear filtrate on standing at 0-5°C gradually deposited more cyanuric acid. The rate of the formation of cyanuric acid increased significantly when an aliquot of the fluorination mixture was allowed to warm to room temperature. Another aliquot of the mixture was examined by NMR; the $F^{19}$ NMR spectrum indicated the presence of hydrogen fluoride and a doublet at -65.91 ppm suggesting -NHF structure. This doublet signal was tentatively assigned to N-fluoroformamide. When the solution in the NMR sample tube warmed to 25-28°C, the intensity of the doublet signal gradually weakened and cyanuric acid deposited. On the basis of the above observations, it is concluded that formamide undergoes fluorination giving relatively unstable fluoroformamide, which then gradually decomposes to cyanuric acid:

$$HCONH_2 + F_2 \longrightarrow HCONHF + HF$$

$$HCONHF \xrightarrow{-HF} HNCO$$

$$3\ HNCO \longrightarrow \text{cyanuric acid}$$

When the formation of fluoroformamide had been tentatively established, attempts were made to fluorinate formamide in the presence of perchloric acid with the objective of hydrolyzing fluoroformamide to fluoroammonium perchlorate in situ. These attempts, however, were unsuccessful. When the fluorination was

*Aerojet-General Report 2730 (Summary), October 1963, p. 24 (Confidential).

carried out in an excess of perchloric acid, fluorine passed through the reaction mixture without reacting. When the ratio of the reagents was reversed, i.e., a small amount of perchloric acid was added to formamide, the fluorination proceeded in the same manner as with pure formamide. At the end of the run, the fluorination mixture contained fluoroformamide but no fluoroammonium salt, as determined by its $F^{19}$ NMR spectrum. Thus, in this case perchloric acid did not interfere with the fluorination of formamide, but also did not hydrolyze fluoroformamide.

The fluorination of formamide, presently under further investigation, supplied several important general clues concerning the fluorination of nitrogenous organic compounds and provided the basis of this quarter's direct fluorination studies. First of all, it became evident that even in the absence of an inert solvent, nitrogenous organic compounds can be selectively fluorinated with elementary fluorine instead of being "burned" to $CF_4$. It also suggested that in a solventless system organic nitrogenous compounds with long hydrocarbon chains might also undergo selective direct fluorination on nitrogen instead of an uncontrollable attack on the hydrocarbon portion of the molecule. These suppositions were found to be correct, as shown later in the discussion.

When the fluorination of formamide provided evidence that N-fluoroamide derivatives can be synthesized, the fluorination of monoalkylamides was investigated with the expectation that their N-fluoro derivatives might be less sensitive to decomposition, and thus possibly could be isolated and characterized. The fluorination of aqueous ethylformamide was studied next:

$$C_2H_5NHCHO + F_2 \longrightarrow C_2H_5NFCHO \xrightarrow{F_2} C_2H_5NF_2$$

A volatile liquid was isolated from the fluorination mixture and the compound was identified as N-fluoro-N-formylethylamine on the basis of its elemental analysis, its infrared spectrum (Figure 5), and its proton (Figure 6) and fluorine (Figure 7) NMR spectra. The yield of the material was only 5%. A considerable amount of ethyldifluoramine was also produced in this fluorination, suggesting that under these reaction conditions N-fluoro-N-formylethylamine undergoes fluorination at a faster rate than the starting material.

The fluorination of ethylformamide in the absence of a solvent was also investigated. The fluorination was carried out at -40 to -45°C and the reaction was accompanied by frequent localized fires in the reaction flask; fluorine, however, was readily consumed. At the end of the run, the reaction mixture was fractionated to remove, first, a mixture of hydrogen fluoride and ethyldifluoramine, and then N-fluoro-N-formylethylamine. The yield of the latter amounted to 50%, a significant improvement over the aqueous fluorination. Owing to the proximity of the boiling points of hydrogen fluoride and ethyldifluoramine, the mixture was not separated and the yield of ethyldifluoramine was not established.

N-Fluoro-N-formylethylamine was converted to N-fluoroethylammonium bisulfate by reacting it with an excess of concentrated sulfuric acid:

$$C_2H_5NFCHO + H_2SO_4 \xrightarrow[\Delta]{} C_2H_5NH_2F^{\oplus}HSO_4^{\ominus} + CO$$

The reaction was slow at room temperature, but was carried to completion in 45-60 min at 65-70°C. No attempts were made to isolate the pure salt. Its presence in sulfuric acid solution was confirmed by proton (Figure 8) and fluorine (Figure 9) NMR spectra. The slow hydrolysis of N-fluoro-N-formylethylamine is in agreement with the observed stability of fluoroformamide in formamide-perchloric acid solution at 0-3°C.

The fluorination of methylformamide (no solvent) was investigated next. The reaction was analogous to that of the ethyl derivative, except that fewer localized fires occurred. N-Fluoro-N-formylmethylamine was identified on the basis of its elemental analysis, its infrared spectrum (Figure 10), and its proton (Figure 11) and fluorine (Figure 12) NMR spectra.

Similarly to the corresponding ethyl derivative, N-fluoro-N-formylmethylamine reacted with concentrated sulfuric acid to give N-fluoromethylammonium bisulfate, $CH_3NH_2F^{\oplus}HSO_4^{\ominus}$, identified in sulfuric acid solution by its proton (Figure 13) and fluorine (Figure 14) NMR spectra.

One unsuccessful attempt was made to generate N-fluoromethylamine in situ from its salt and oxidatively couple it to N,N'-difluoro-N,N'-dimethylhydrazine:

$$CH_3NH_2F^{\oplus} + H_2O \longrightarrow [CH_3NHF] + H_3O^{\oplus}$$

$$2[CH_3NHF] \xrightarrow{[OX]} CH_3NFNFCH_3$$

If it proceeded, this reaction would be analogous to the preparation of tetrafluorohydrazine from difluoramine. Aqueous ferric ammonium sulfate was chosen as the oxidizing agent. The desired product was not obtained, and due to the small-scale experiment no other reaction products could be identified. Little emphasis should be placed on this sole "test-tube" experiment. The results simply mean that the desired hydrazine derivative was not obtained under these reaction conditions. In the absence of additional experimental work at this time, the reaction is presented here as a possibility that others may wish to investigate.

To extend the scope of amide fluorination reactions, aqueous n-butylacetamide was fluorinated:

$$CH_3CONHC_4H_9 + F_2 \longrightarrow CH_3CONFC_4H_9 \xrightarrow{F_2} C_4H_9NF_2$$

No attempt was made to isolate butyldifluoramine. A small amount of a higher-boiling product was isolated and the material was identified as N-acetyl-N-fluoro-n-butylamine on the basis of its elemental analysis, its infrared spectrum (Figure 15), and its proton (Figure 16), and fluorine (Figure 17) NMR spectra.

Fluorination in the absence of a solvent was extended to a cyclic amide, 2-pyrrolidinone. Two products were isolated: N-fluoro-2-pyrrolidinone, previously obtained in the aqueous fluorination of 2-pyrrolidinone,* and 3-difluoraminobutyryl fluoride:

*Aerojet-General Report 0235-01-15, January 1963, p. 13 (Confidential).


The latter compound was identified on the basis of its elemental analysis, its infrared spectrum (Figure 18), and its proton (Figure 19) and fluorine (Figure 20) NMR spectra. Due to the high freezing point of 2-pyrrolidinone, the fluorination in this case was started at 25-27°C and the reaction temperature was gradually lowered to 5-7°C as the concentration of the reaction products in the solution increased, and thus lowered the freezing point of the starting material. The fluorination was accompanied by frequent localized fires at the tip of the gas-inlet tube, producing some carbonaceous material.

In related work, the fluorination of aqueous 2-oxazolidone was investigated. In this case both N-fluoro-2-oxazolidone and 2-difluoraminoethanol were obtained:


N-Fluoro-2-oxazolidone was identified on the basis of its elemental analysis, its infrared spectrum (Figure 21), and its proton (Figure 22) and fluorine (Figure 23) NMR spectra. 2-Difluoraminoethanol was previously synthesized.* The main objective was to synthesize N-fluoro-2-oxazolidone and, therefore, the fluorination was stopped at a 1:1 molar ratio of fluorine to substrate. From the results it appears that at a 2:1 molar ratio of the reagents, this method would be a better and simpler route to 2-difluoraminoethanol than the previously reported two-step synthesis starting with N-2-hydroxyethylamides.**

In a continuing search for useful solvents that will withstand fluorine, dimethylformamide was considered as a good ionizing medium, possessing

*Aerojet-General Report 2730 (Summary), October 1963, p. 25 (Confidential).
**Ibid.

good solubility characteristics, and probably inert to the action of fluorine, at least in the presence of reactive substrates. A control run was carried out and it was found that fluorine was readily consumed by dimethylformamide. There was very little firing at -40 to -50°C, and the resulting straw-yellow fluorination mixture readily oxidized potassium iodide. The solution retained the oxidizing properties for at least several days when stored at -80°C. However, when the mixture was allowed to warm to room temperature it gradually turned dark, gassed, and rapidly lost its oxidizing power. The oxidizing species present in the solution has not yet been identified, but may be due to dimethylfluoramine:

$$(CH_3)_2NHCHO + F_2 \longrightarrow (CH_3)_2NF + HCOF$$

The oxidizing species apparently is unstable at ambient temperatures and decomposes with the elimination of hydrogen fluoride. This path of decomposition has been previously observed in the fluorination of aqueous dimethylformamide where methylamine was isolated:*

$$[(CH_3)_2NF] \xrightarrow{-HF} CH_2{=}NCH_3 \xrightarrow{H_2O} HCHO + CH_3NH_2$$

2. Experimental

a. Fluorination of Formamide

Formamide (Eastman, White Label), 200 g, was fluorinated at 0-3°C with elementary fluorine (diluted with nitrogen, 1:5) until 17 liters of fluorine was consumed (3.0 hours). Fluorine was readily consumed and a white solid gradually accumulated in the reaction flask. At the end of the run the reaction mixture was filtered and the filtrate was kept at 0-2°C. The filter cake was washed with some formamide, then with ethanol and ether. The white solid, m.p. > 305°C, amounted to 7.0 g. A sample of the material was crystallized from water and a sample of the crystallized material was submitted for infrared analysis. Its infrared spectrum was found to be identical with that of an authentic sample of cyanuric acid.

*Aerojet-General Report 2099 (Summary, November 1961, pp. 21-22 (Confidential).

A sample of the cold filtrate was examined by NMR. The fluorine NMR spectrum indicated the presence of hydrogen fluoride and another signal, a doublet which was assigned to the -NHF structure. The originally clear solution gradually turned turbid when it warmed up in the NMR sample tube. At the same time the intensity of the -NHF signal gradually decreased. The white solid was identified as cyanuric acid.

In another experiment, a solution of 4.5 g (0.1 mole) of formamide in 63 g (~0.5 mole) of 72% perchloric acid was subjected to fluorination at 0 to -5°C. Fluorine consumption was very poor. After passing in 2.5 liters of fluorine, a sample of the fluorination mixture was examined by NMR. No NF species was detected.

This experiment was repeated using "reverse" ratio of reagents. Fluorine (diluted with nitrogen, 1:5), 3 liters, was passed at 0-5°C into a solution of 13.5 g (0.1 mole) of 72% perchloric acid in 135 g (3.0 mole) of formamide. In this run, fluorine was consumed readily. An aliquot of the fluorination mixture was examined by NMR. The fluorine NMR spectrum indicated the presence of hydrogen fluoride and fluoroformamide, but no fluoroammonium ions.

b. N-Fluoro-N-formylethylamine

A solution of 73 g (1.0 mole) of ethylformamide in 350 ml of water was fluorinated at 0-5°C until 22 liters of fluorine was consumed. During the course of fluorination, 4.5 ml of ethyldifluoramine accumulated in a -80°C trap connected in series with the reactor. At the end of the run the fluorination mixture was extracted with three 50-ml portions of methylene chloride, followed by five 50-ml portions of diethyl ether. All extracts were combined, dried, and worked up to give 5.0 g of a colorless liquid, b.p. 20-21°C/25 mm, $n_D^{25}$ 1.3930, which was identified as N-fluoro-N-formylethylamine.

Anal. Calcd. for $C_3H_6NFO$: C, 39.55; H, 6.64; N, 15.38; F, 20.86.
Found: C, 39.6; H, 6.8; N, 15.4; F, 21.1.

The infrared spectrum of the material is shown in Figure 5.

The 60-mc proton and 56.4-mc fluorine NMR spectra were obtained using a $CDCl_3$ solution with TMS and $CFCl_3$ as internal references. The assignments are as follows.

The proton spectrum (Figure 6) is readily rationalized on the basis of the suggested structure. The triplet at 1.31 ppm is assigned to the methyl group, $CH_3CH_2$-. The doublet (splitting 31.2 cps) of quartets at 3.84 ppm is assigned to the $CH_3CH_2$- methylene group. The doublet (splitting 13.3 cps) at 8.53 ppm is assigned to the aldehyde proton, -NFCHO. The chemical shift of the extraneous weak signal at 2.01 ppm corresponds closely to that of acetonitrile.

On the basis of the coupling observed in the proton NMR spectrum, the fluorine NMR spectrum (Figure 7) would be expected to consist of a triplet (31.2 cps) of doublets (13.3 cps). However, only a broad, unresolved signal at +81.7 ppm is observed. There seems to be no obvious explanation for the form of the signal. Quadruple broadening by nitrogen is unlikely, since well-resolved multiplets have been observed for many analogous N-fluorocarbamates. The signal would be complicated by cis-trans isomerisms, but there is no evidence of this in the proton spectrum. In any case, the chemical shift is consistent with the -NFCO- structure.

In another experiment, ethylformamide, 100 g, was fluorinated at -40 to -45°C with elementary fluorine (diluted with nitrogen, 1:5) until 7.2 liters of fluorine was consumed (2.5 hours). Fluorine was readily consumed, but occasional firings were observed, mainly at the end of the gas-inlet tube. At the end of the run the fluorination mixture was subjected to aspirator vacuum (25 mm) and allowed to warm up from -40 to +20°C. A mixture of hydrogen fluoride and ethyldifluoramine was removed from the solution and the products were collected in a -80°C trap. The mixture amounted to ca. 10 ml. When it was poured into 40 ml of cold water, ca. 4 ml of water-insoluble liquid remained which evaporated when the aqueous mixture was warmed to 30°C. The compound must be ethyldifluoramine.

After removal of hydrogen fluoride and ethyldifluoramine, the fluorination mixture was subjected to a 0.3-mm vacuum at 25°C to remove N-fluoro-N-formylethylamine. The distillate was condensed in a -80°C trap and the crude material amounted to 13 g. The product was redistilled to give 12.0 g (ca. 50% yield) of a colorless liquid, b.p. 20-21°C/25 mm, $n_D^{25}$ 1.3925. Its infrared spectrum was identical in all respects with that of analytically pure N-fluoro-N-formylethylamine.

The fluorination of ethylformamide in the absence of a solvent was repeated several times with similar results.

c. N-Fluoroethylammonium Bisulfate

N-Fluoro-N-formylethylamine, 0.4 g, was added at 20-25°C with stirring to 2.0 g of concentrated sulfuric acid, but little or no reaction was noticed. The solution was gradually warmed to 65-70°C (gas evolution began at 40-45°C), and the reaction was completed at this temperature in 45 min. The presence of the fluoroammonium salt in sulfuric acid solution was established on the basis of NMR spectra.

The 60-mc proton (Figure 8) and 56.4-mc fluorine (Figure 9) NMR spectra were obtained using concentrated sulfuric acid solution. The proton signals are referred to sulfuric acid signal in ppm positive upfield. The fluorine spectrum is referred to external TFA. The assignments are as follows:

H'. The triplet at +9.83 ppm is assigned to the $CH_3CH_2$- methyl group. The pair (splitting 28.3 cps) of multiplets at +7.46 ppm is assigned to the $CH_3CH_2$- methylene. This signal would be expected to be a doublet (coupling to the fluorine) of triplets (coupling to the $-NH_2$- protons) of quartets (coupling to the $CH_3$ protons). While all of the 24 lines are not resolved, the signal is clearly of the expected form. The pair (42.2 cps) of broadened triplets at +0.22 ppm is assigned to the $-CH_2NH_2F^{\oplus}$ protons. The weak, sharp signal at +8.81 ppm is unassignable, and is apparently due to an impurity or a decomposition product.

$F^{19}$. The fluorine spectrum consists of a single multiplet, a triplet (42.5 cps) of triplets (28.7 cps) at -15.51 ppm. It is assigned to the $-CH_2NH_2F^{\oplus}$ fluorine. The coupling constants are in excellent agreement with those observed in the proton spectrum.

It should be noted that the practice of using sulfuric acid as an internal standard for proton spectra has been shown to be unsatisfactory, and the proton spectrum will be reobtained with tetramethylammonium ion as an internal standard.

d. N-Fluoro-N-formylmethylamine

Methylformamide, 100 g, was fluorinated with elementary fluorine (diluted with nitrogen, 1:5) at -20 to -25°C until 15 liters of fluorine

was consumed (2.5 hours). At the end of the run the reaction mixture was subjected to aspirator vacuum (25 mm) at 10-15°C to remove hydrogen fluoride and methyldifluoramine. The product was removed from the unreacted methylformamide at 20-25°C/0.2 mm and condensed in a -80°C trap. The material was redistilled to give 8.0 g of a colorless liquid, b.p. 76-77°C, $n_D^{25}$ 1.3800, which was found (gas chromatograph) to be 93-95% pure N-fluoro-N-formylmethylamine. An analytical sample was purified by gas chromatography.

Anal. Calc. for $C_2H_4NFO$: C, 31.17; H, 5.23; N, 18.18; F, 24.66.
Found: C, 31.3; H, 5.4 N, 18.0; F, 24.1

The infrared spectrum of the material is shown in Figure 10.

The 60-mc proton (Figure 11) and 56.4-mc fluorine (Figure 12) NMR spectra were obtained using a $CDCl_3$ solution with TMS and $CFCl_3$ added as internal references. The assignments are as follows:

H'. The doublet (splitting 26.2 cps) at 3.45 ppm is assigned to the methyl group. The broadened doublet (splitting 13.0 cps) at 8.58 ppm is assigned to the aldehyde proton. The latter signal appears rather weak, but an average of the integrals gave a ratio of 0.99:3.00 for the strengths of the two signals. This is within the expected experimental error.

$F^{19}$. The fluorine spectrum consists of a single broadened signal at +67.1 ppm. On the basis of the coupling observed in the proton spectrum, one would expect a quartet (26.2 cps) of doublets (13.0 cps). The situation may be complicated by the existence of cis and trans conformations with slightly different chemical shifts. A similar behavior was noted for the corresponding ethyl derivative (see Figure 7).

After removal of the first "crop" of N-fluoro-N-formylmethylamine, the unreacted methylformamide was subjected to further fluorination at -30 to -40°C, and 11 liters of fluorine was passed into the solution. The reaction mixture was worked up in the same manner as above. After removal of 11-12 g of hydrogen fluoride-methyldifluoramine mixture, 13 g of N-fluoro-N-formylmethylamine was obtained.

e. N-Fluoromethylammonium Bisulfate

N-Fluoromethylammonium bisulfate was prepared from N-fluoro-N-formylmethylamine and concentrated sulfuric acid in the same manner as described for the corresponding ethyl derivative (see paragraph B,2,c, above). The pure salt was not isolated; its presence in sulfuric acid solution was demonstrated by NMR spectra.

The 60-mc proton (Figure 13) and 56.4-mc fluorine (Figure 14) NMR spectra were obtained using concentrated sulfuric acid solution. In the proton spectrum the signal positions are referred to sulfuric acid signal, position upfield. An external TFA reference was used for the fluorine spectrum. The assignments are as follows:

H'. The pair (splitting 28.3 cps) of unresolved triplets at +7.96 ppm is assigned to the methyl group. The pair (splitting 41.0 cps) of partially resolved quartets is assigned to the -NH- protons. The weak, broadened signal at 3.12 ppm has no obvious assignment and is apparently due to an impurity.

$F^{19}$. The fluorine spectrum consists of a single multiplet, a triplet (splitting 41.9 cps, coupling to the -NH- protons) of quartets (splitting 28.1 cps, coupling to the methyl group protons) at -29.17. The observed coupling constants are in good agreement with those of the proton spectrum.

The proton and fluorine NMR spectra are consistent with each other and with the $CH_3NH_2F^{\oplus}$ structure.

f. Attempted Preparation of N,N'-Difluoro-N,N'-dimethylhydrazine

N-Fluoromethylammonium bisulfate was prepared from 2.0 g of N-fluoro-N-formyl methylamine and 10.0 g of concentrated sulfuric acid as described under paragraph e, above. The resulting sulfuric acid solution of the salt was placed in a dropping funnel and was added dropwise with stirring at 5-10°C to a solution of 15 g (0.03 mole) of ferric ammonium sulfate, $\left[Fe(NH_4)(SO_4)_2 \cdot 12\ H_2O\right]$, in 70 ml of distilled water. The reactor, flushed with nitrogen, was connected in series with 0 and -80°C traps. No visible reaction occurred either at 5-10°C or when the reaction mixture was warmed to 25-30°C. No products were found in the cooling traps.

g. N-Acetyl-N-fluoro-n-butylamine

A solution of 86.5 g (0.75 mole) of n-butylacetamide in 450 ml of water was fluorinated at 0-5°C until 17 liters of fluorine was consumed. The reaction mixture was extracted with three 50-ml portions of methylene chloride, and the combined extracts were dried, filtered, and concentrated to remove the solvent and n-butyldifluoramine. The residual material was distilled to give 2.0 g of a colorless liquid, b.p. 45-6°C/25 mm, which contained 70-75% of N-acetyl-N-fluoro-n-butylamine as determined by gas chromatography. An analytical sample was separated by gas chromatography.

Anal. Calcd. for $C_6H_{12}NFO$: C, 54.12; H, 9.08; N, 10.52; F, 14.27.

Found: C, 54.0; H, 9.1; N, 10.8; F, 14.6.

The infrared spectrum of N-acetyl-N-fluoro-n-butylamine is shown in Figure 15.

The 60-mc proton (Figure 16) and 56.4-mc fluorine (Figure 17) NMR spectra were obtained using a carbon tetrachloride solution with TMS and $CFCl_3$ added as internal references. The assignments are as follows:

H'. The irregular triplet at 0.95 ppm is assigned to the n-butyl methyl group, $-CH_2\underline{CH_3}$. The pair (splitting 33.8 cps) of triplets at 3.73 ppm is assigned to the methylene group bonded to nitrogen, $-NF\underline{CH_2}CH_2-$. The complex multiplet with maximum intensity at 92 cps is then assigned to the remaining methylene groups, $-CH_2\underline{CH_2}\underline{CH_2}CH_3$. The doublet (splitting 7.6 cps) at 2.12 ppm is assigned to the $\underline{CH_3}CO-$ methylene group. The 7.6-cps splitting arises from an unusually long-range coupling to the -NF- fluorine, as is confirmed by the fluorine NMR spectrum.

$\underline{F^{19}}$. The fluorine spectrum consists of a triplet (splitting 33.8 ±0.5 cps) of poorly resolved quartets (splitting 7.3 ±1.0 cps) at +66.37 ppm. It is assigned to the $CH_3CON\underline{F}CH_2-$ fluorine. The triplet splitting rises from coupling to the adjacent methylene group. The quartet splitting can only result from coupling to three equivalent protons and must be attributed to the $CH_3CO-$ methyl group. The good agreement of the coupling constants obtained from the proton and fluorine spectra confirms the assignment.

The proton and fluorine NMR spectra are consistent with each other and with the suggested structure.

h. Fluorination of 2-Pyrrolidinone (No Solvent)

2-Pyrrolidinone (Eastman, Practical Grade), 140 g, was fluorinated with elementary fluorine (diluted with nitrogen, 1:5) until 11.5 liters (0.5 mole) of fluorine was consumed (2.5 hours). The fluorination was started at 24-26°C and the reaction temperature was gradually lowered to 0-5°C. Frequent firing occurred in the reactor during the course of fluorination, and the reaction mixture gradually turned dark due to the formation of carbonaceous combustion products. Most of the hydrogen fluoride escaped from the reactor during the course of fluorination. At the end of the run, the reaction mixture was subjected to 0.1-0.2 mm vacuum. After removal of a gaseous forerun of 20-35°C, N-fluoro-2-pyrrolidinone was distilled at 40-75°C bath temperature. The crude material was redistilled to give 12.5 g of pure N-fluoro-2-pyrrolidinone, b.p. 38-9°C/0.2 mm, $n_D^{25}$ 1.4385. Its physical properties and infrared spectrum were identical with those previously reported.*

The forerun, of N-fluoro-2-pyrrolidinone distillation, amounting to ca. 1.5 g was redistilled. The distillate came over as a gas at 20°C/0.2 mm and was condensed in a -80°C trap. The distillate was found (gas chromatograph) to be 95-97% pure 3-difluoraminobutyryl fluoride. An analytical sample was obtained by gas chromatography.

Anal. Calcd. for $C_4H_6NF_3O$: C, 34.05; H, 4.29; N, 9.93; F, 40.39.
Found: C, 34.2; H, 4.23; N, 10.05; F, 39.2.

The infrared spectrum of 3-difluoraminobutyryl fluoride is shown in Figure 18; in general, it is similar to that of 3-difluoraminobutyryl chloride.**

The 60-mc proton (Figure 19) and 56.4-mc fluorine (Figure 20) NMR spectra were obtained using a carbon tetrachloride solution with TMS and $CFCl_3$ added as internal references and employing a Varian microcell. The assignments are as follows:

*Aerojet-General Report 0235-01-15, January 1963, p. 18 (Confidential).
**Aerojet-General Report No. 2381 (Summary), October 1962, Fig. 20 (Confidential).

H'. The triplet (splitting 28.9 cps) of triplets at 3.58 ppm is assigned to the $NF_2\underline{CH_2}$- methylene group. The quintet at 2.08 ppm is assigned to the $-CH_2\underline{CH_2}CH_2$ - methylene group. The triplet at 2.68 ppm is assigned to the $-CH_2\underline{CH_2}COF$ methylene group.

$\underline{F^{19}}$. The fluorine NMR spectrum consists of a poorly resolved triplet at -54.16 ppm assigned to the $N\underline{F_2}CH_2$- fluorines, and a singlet at -43.87 ppm assigned to the -C<u>O</u>F fluorine. The triplet appears to be relatively weak, but an average of ten integrals gave a ratio of 2.02:1.00 for the intensity of the two signals as required by the assignment.

The proton and fluorine NMR spectra are consistent with each other and with the $NF_2(CH_2)_3COF$ structure.

i. N-Fluoro-2-oxazolidone

A solution of 42 g (0.5 mole) of 2-oxazolidone in 250 ml of water was fluorinated at 0-5°C until 11.5 liters (0.5 mole) of fluorine was consumed. The reaction mixture was extracted with five 30-ml portions of methylene chloride, followed by five 30-ml portions of diethyl ether.

The methylene chloride extracts were worked up to give 20 g of a colorless liquid, b.p. 51-4°C/0.3 mm, $n^{25}$ 1.41.20. An analytical sample of the material was obtained by redistilling an aliquot of the crude product, b.p. 47-8°C/0.1 mm, $n_D^{25}$ 1.4165.

Anal. Calcd. for $C_3H_4NFO_2$: C, 34.28; H, 3.84; N, 13.33; F, 18.08.
Found: C, 34.6; H, 4.1; N, 13.2; F, 18.2.

The infrared spectrum of N-fluoro-2-oxazolidone is shown in Figure 21.

The 60-mc proton (Figure 22) and 56.4-mc fluorine (Figure 23) NMR spectra were obtained using $CDCl_3$ solution with TMS and $CFCl_3$ added as internal references. The assignments are as follows:

H'. The differences in the chemical shifts of the two-ring methylene groups are relatively small and much second-order splitting is evident. However, the spectrum has roughly the form of a triplet with maximum intensity at 264 cps assignable to the $-CH_2\underline{CH_2}O$- methylene group, and a pair of triplets with maximum intensities at 224 and 242 cps assignable to the $-CH_2\underline{CH_2}NF$ methylene group.

$F^{19}$. The fluorine NMR spectrum consists of a triplet (splitting 15.4 cps) at +69.48 ppm assignable to the $-CH_2\underline{N}FCO-$ fluorine.

The proton spectrum is somewhat ambiguous as a result of the small differences in chemical shift, but the proton and fluorine spectra are generally consistent with each other and with the suggested structure.

The forerun obtained in the N-fluoro-2-oxazolidone distillation was redistilled to give 1.5 g of a colorless liquid, b.p. 40-42°C/25 mm, $n_D^{25}$ 1.3680, which was identified (infrared spectrum) as 2-difluoraminoethanol, synthesized previously.* The ethereal extracts were worked up to give additional 2.5 g of 2-difluoraminoethanol.

C. FLUOROAMMONIUM PERCHLORATE (V. Grakauskas)

The preparation of fluoroammonium perchlorate from isopropyl N-fluorocarbamate and 72% perchloric acid has been previously reported.** During this quarter, several 30 to 50-mg batches of the compound were prepared following the same procedure, with one small modification. The excess of perchloric acid was removed at 35-42°C, which significantly speeded up the concentration step. The material was used to determine its impact sensitivity. On the basis of a limited number of determinations, it was found that fluoroammonium perchlorate is not sensitive to impact (bare anvil, 2-kg wt) below 40-45 cm in a dry argon atmosphere; one positive firing occurred at 50 cm. To be certain that the salt did not become desensitized by the absorption of some moisture during the process of impact-sensitivity determination, a portion of the material was saved (same sample) and analyzed. Its elemental analysis (found: C, 0.35; H, 2.3; N, 10.0; F, 14.4) indicated that the salt was analytically pure; therefore, the impact-sensitivity data is valid.

Although not exhaustive, the impact-sensitivity determination shows that fluoroammonium perchlorate can be handled safely in this respect. Work is now planned to synthesize several 100-mg batches of the salt to determine its sensitivity to static charge and to friction before the preparation of gram quantities required for determination of its heat of formation is attempted.

---

*Aerojet-General Report 2730 (Summary), October 1963, p. 33 (Confidential).

**Aerojet-General Report 0235-01-19, April 1964, p. 24 (Confidential).

## III. PERSONNEL

The experimental synthesis work was performed by K. Baum, J. M. Cavallo, V. Grakauskas, and M. P. Mascari. Analytical support was provided by C. L. Deuel (gas chromatography), K. Inouye (microanalysis), and H. M. Nelson (NMR and infrared analysis).

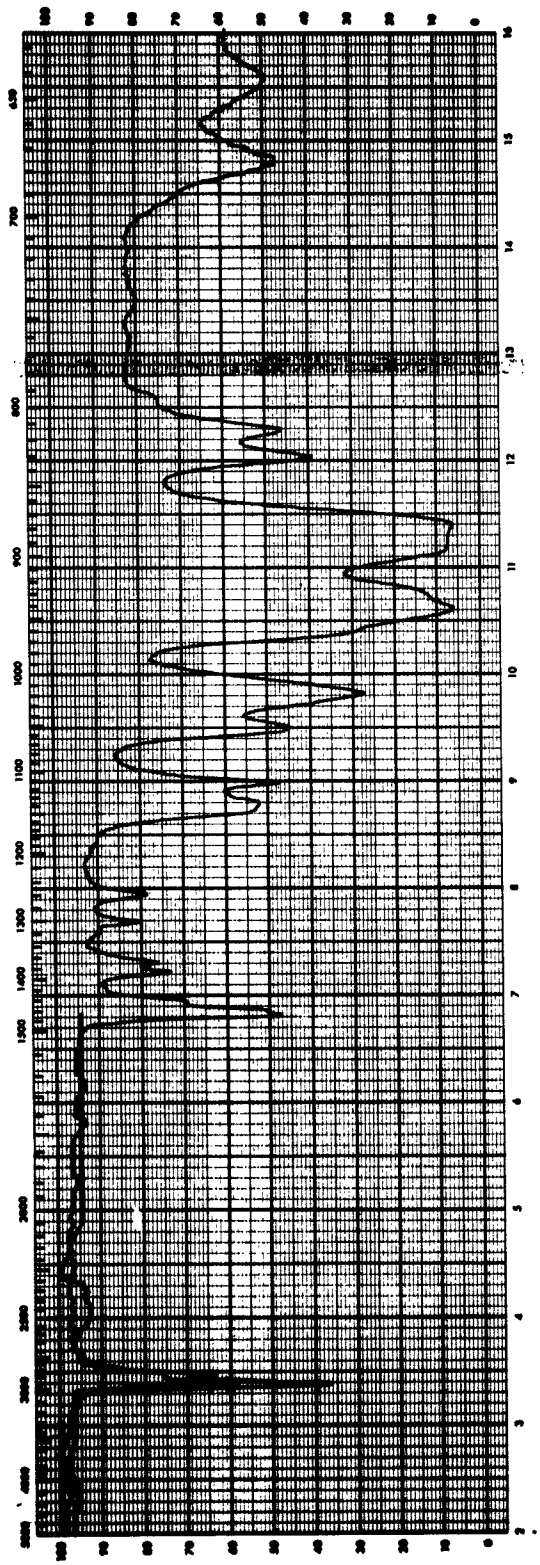


Fig. 1 Infrared Spectrum of 1-Chloro-1,1-bis(difluoramino)butane

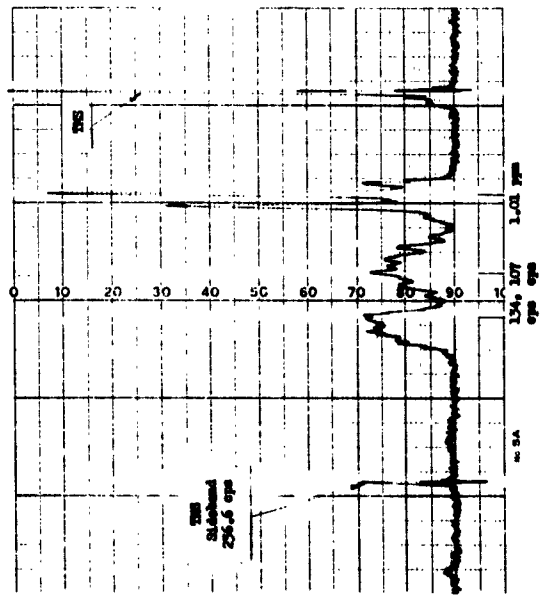


Fig. 2 Proton NMR Spectrum of 1-Chloro-1,1-bis(difluoramino)butane

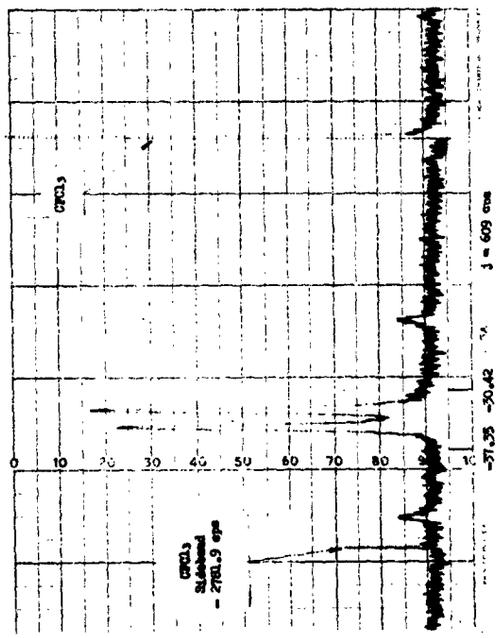



Fig. 3 Fluorine NMR Spectrum of 1-Chloro-1,1-bis(difluoramino)butane

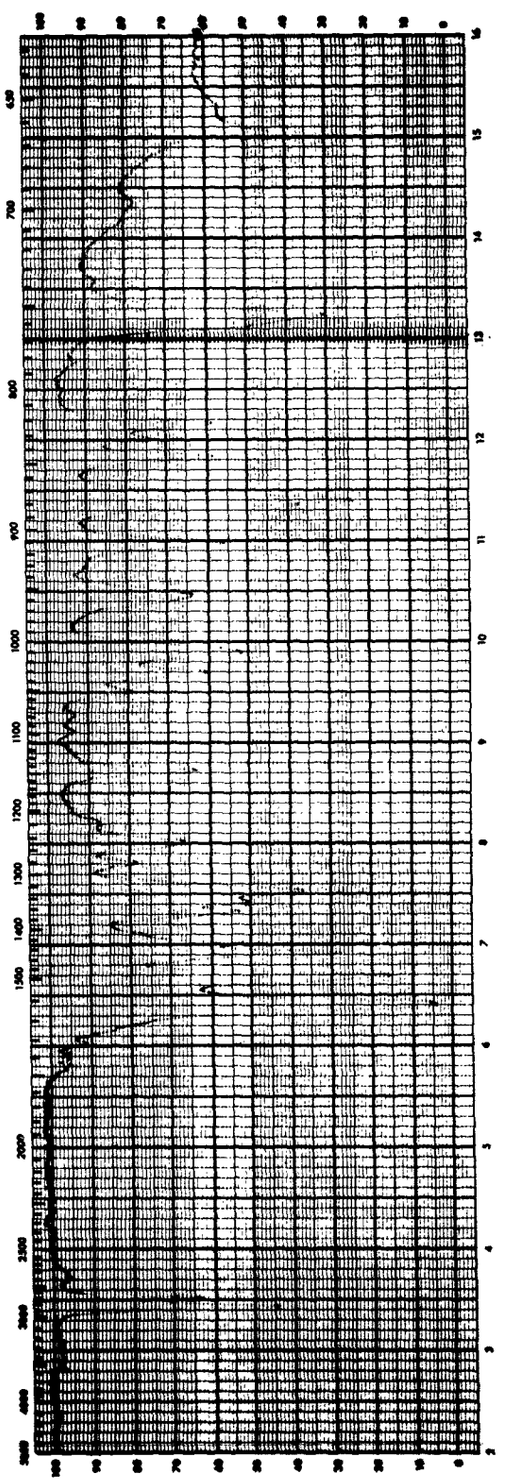


Fig. 4 Infrared Spectrum of 1-Nitro-1-fluoroazoxycyclohexane

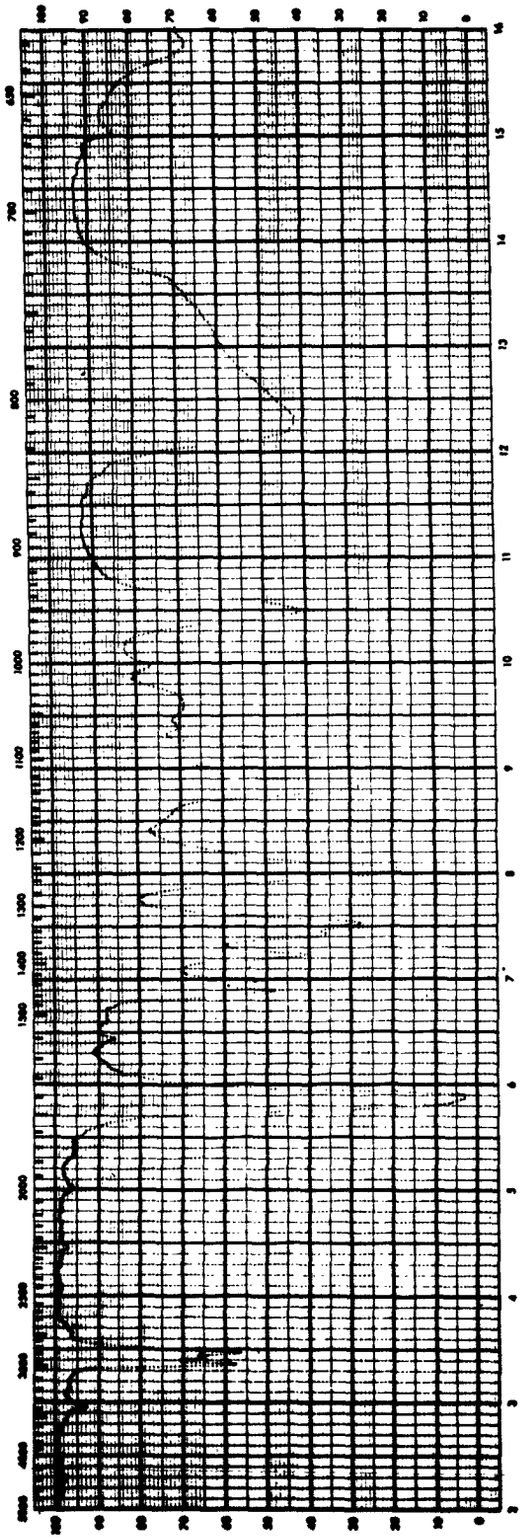


Fig. 5 Infrared Spectrum of N-Fluoro-N-formylethylamine

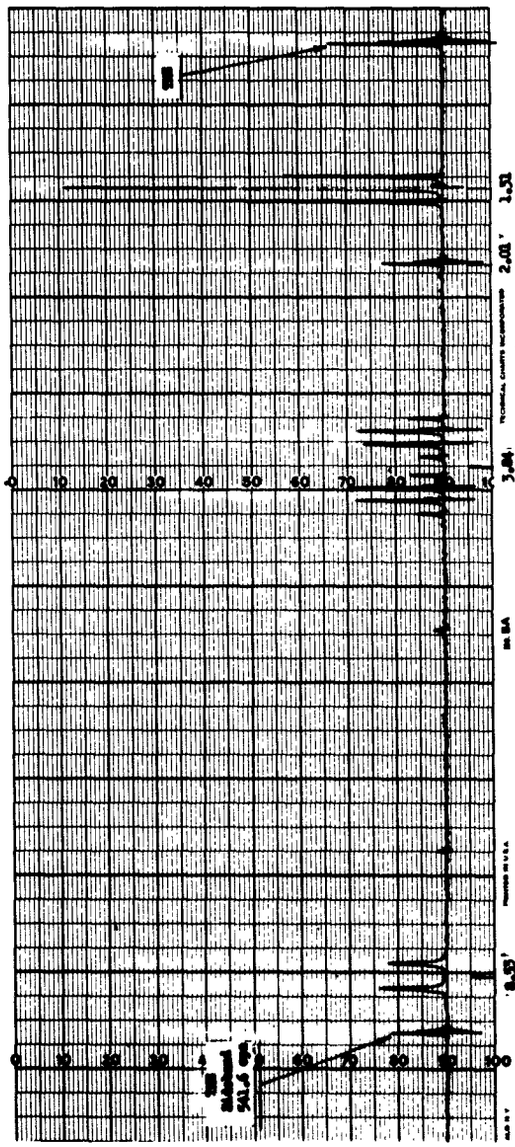


Fig. 6 Proton NMR Spectrum of N-Fluoro-N-formylethylamine

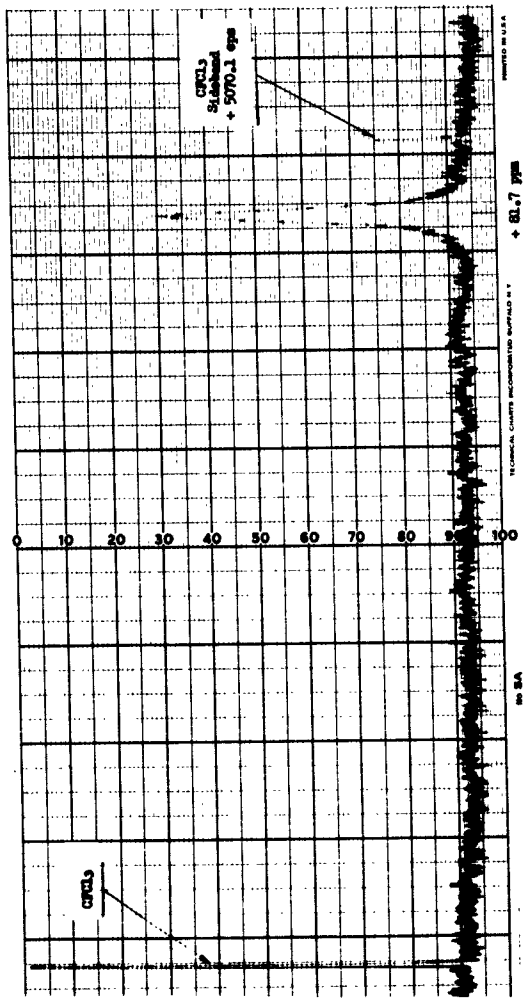


Figure 7. Fluorine NMR Spectrum of N-Fluoro-N-formylethylamine

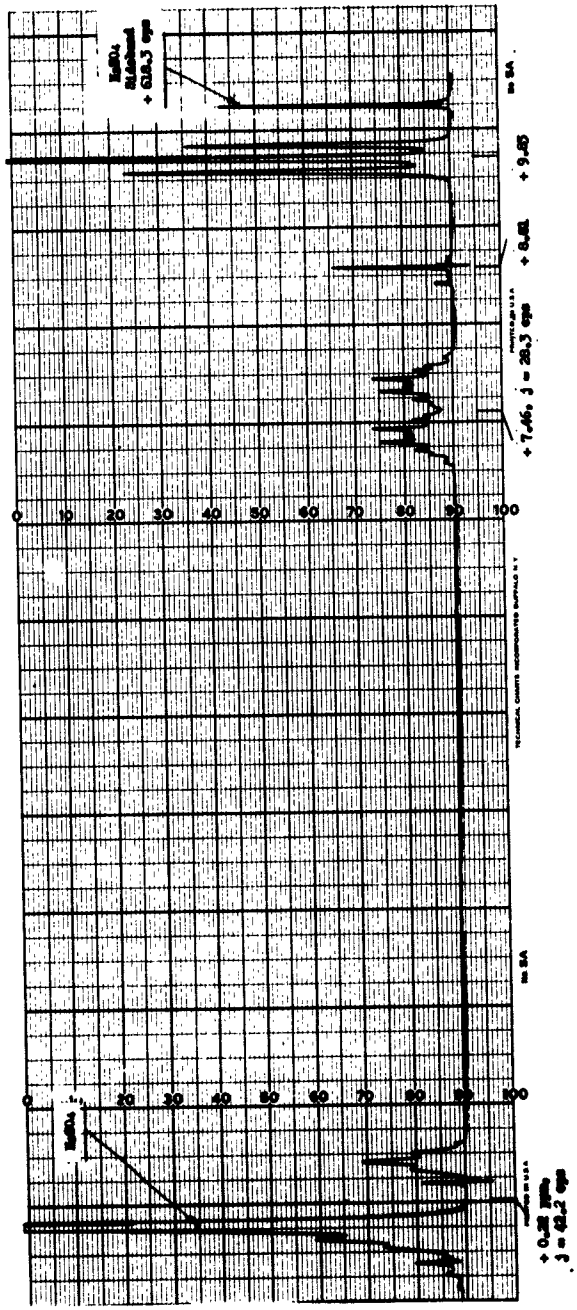


Figure 8. Proton NMR Spectrum of N-Fluoroethylammonium Bisulfate

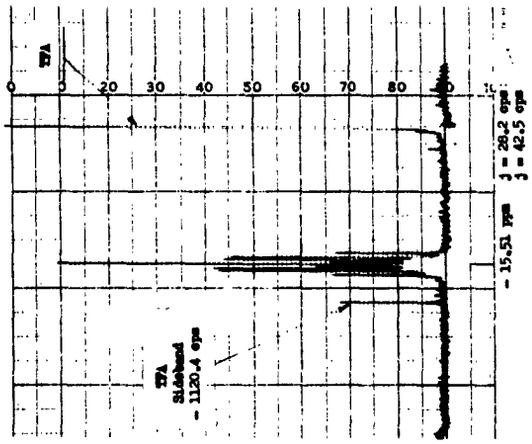



Figure 9. Fluorine NMR Spectrum of N-Fluoroethylammonium Bisulfate

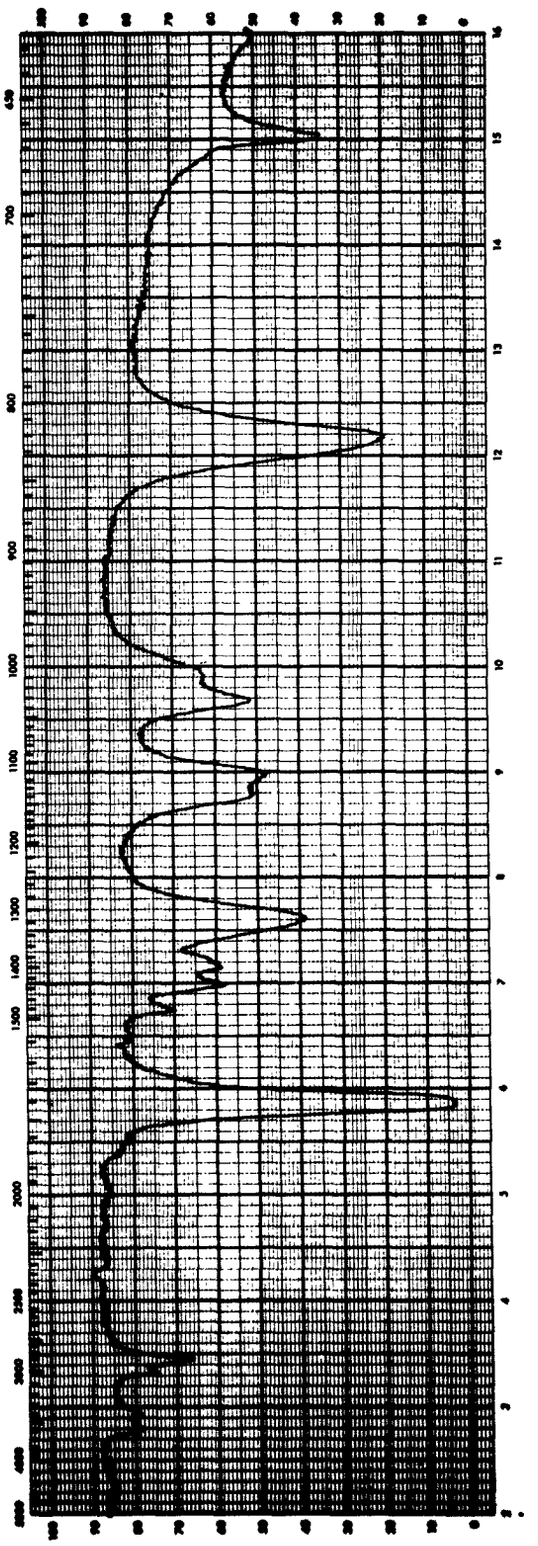


Figure 10. Infrared Spectrum of N-Fluoro-N-formylmethylamine

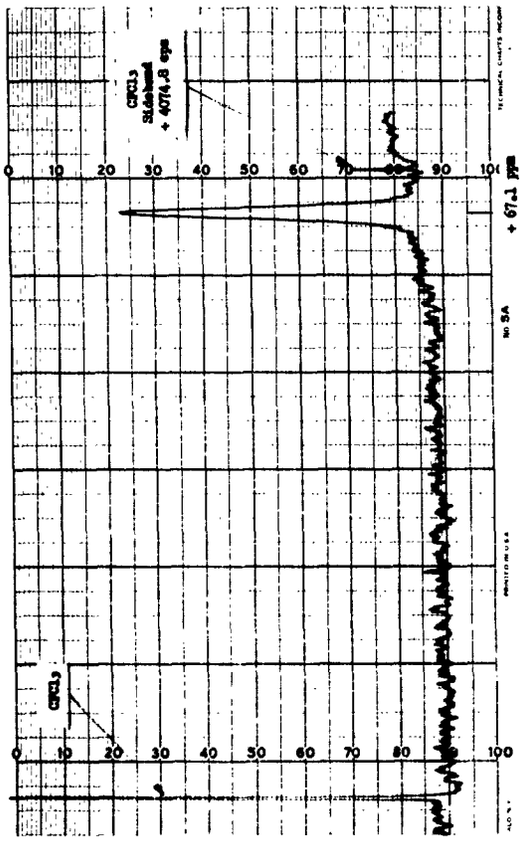


Figure 11. Proton NMR Spectrum of N-Fluoro-N-formylmethylamine

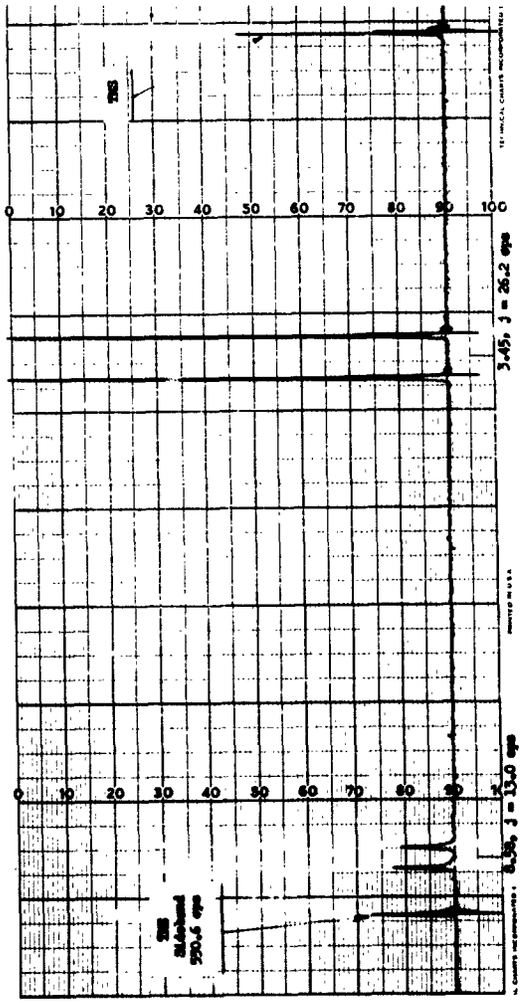


Figure 12. Fluorine NMR Spectrum of N-Fluoro-N-formylmethylamine

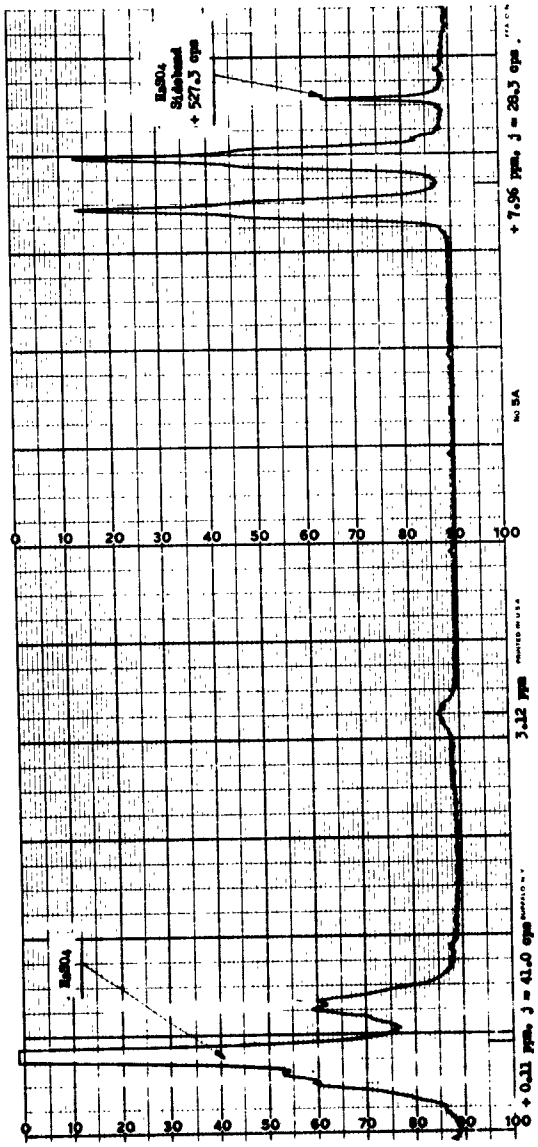


Figure 13. Proton NMR Spectrum of N-Fluoromethylammonium Bisulfate

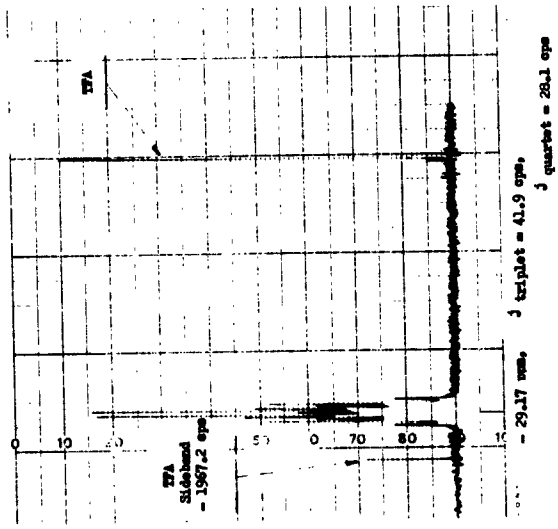


Figure 14. Fluorine NMR Spectrum of N-Fluoromethylammonium Bisulfate

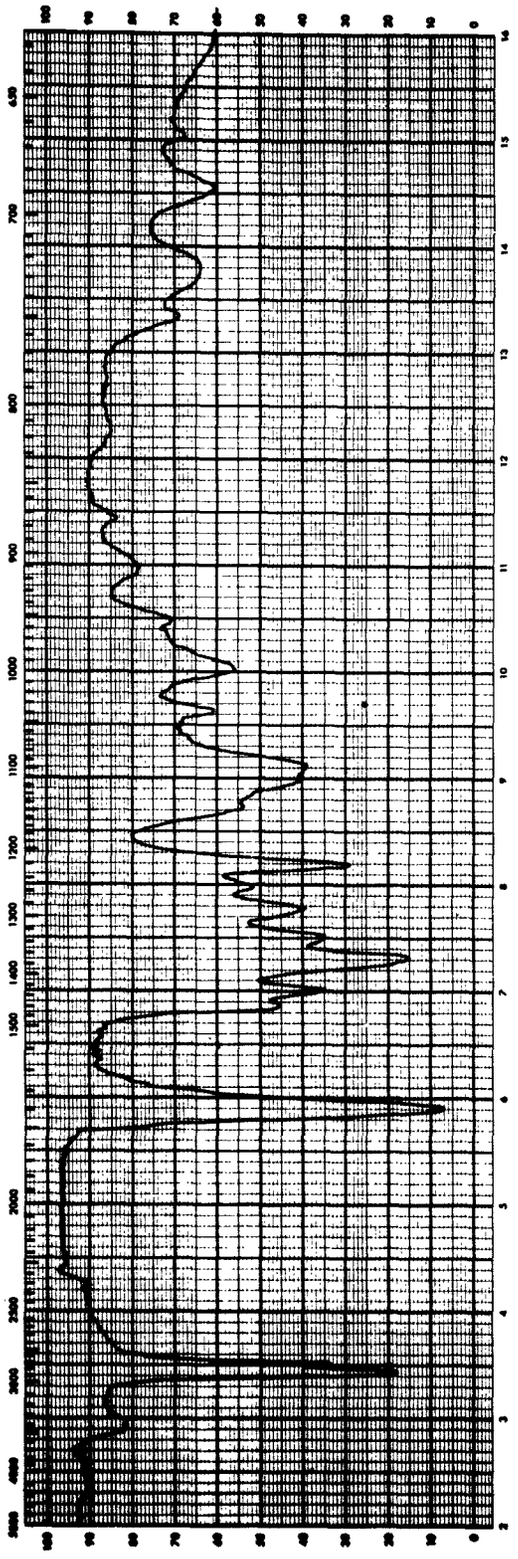


Figure 15. Infrared Spectrum of N-Acetyl-N-fluoro-n-butylamine

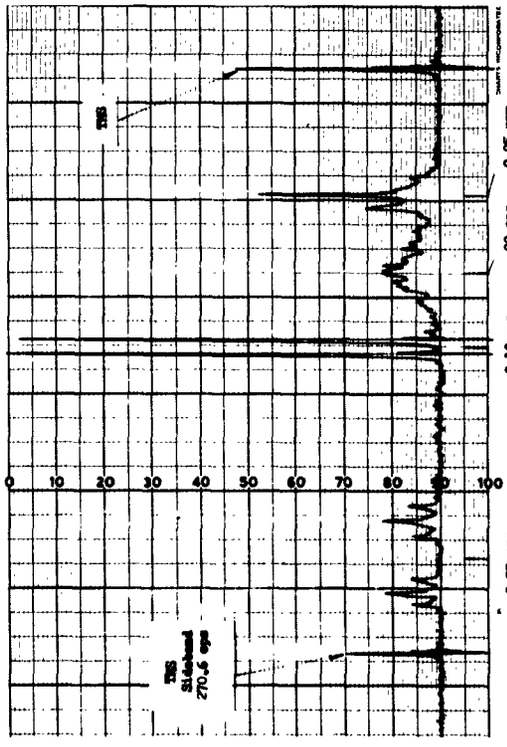



Figure 16. Proton NMR Spectrum of N-Acetyl-N-fluoro-n-butylamine

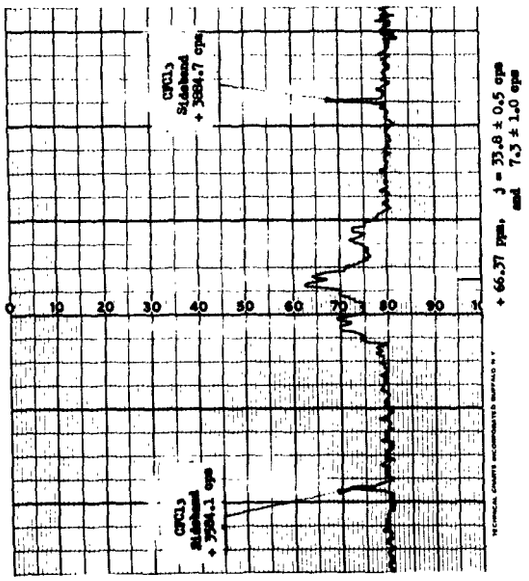



Figure 17. Fluorine NMR Spectrum of N-Acetyl-N-fluoro-n-butylamine

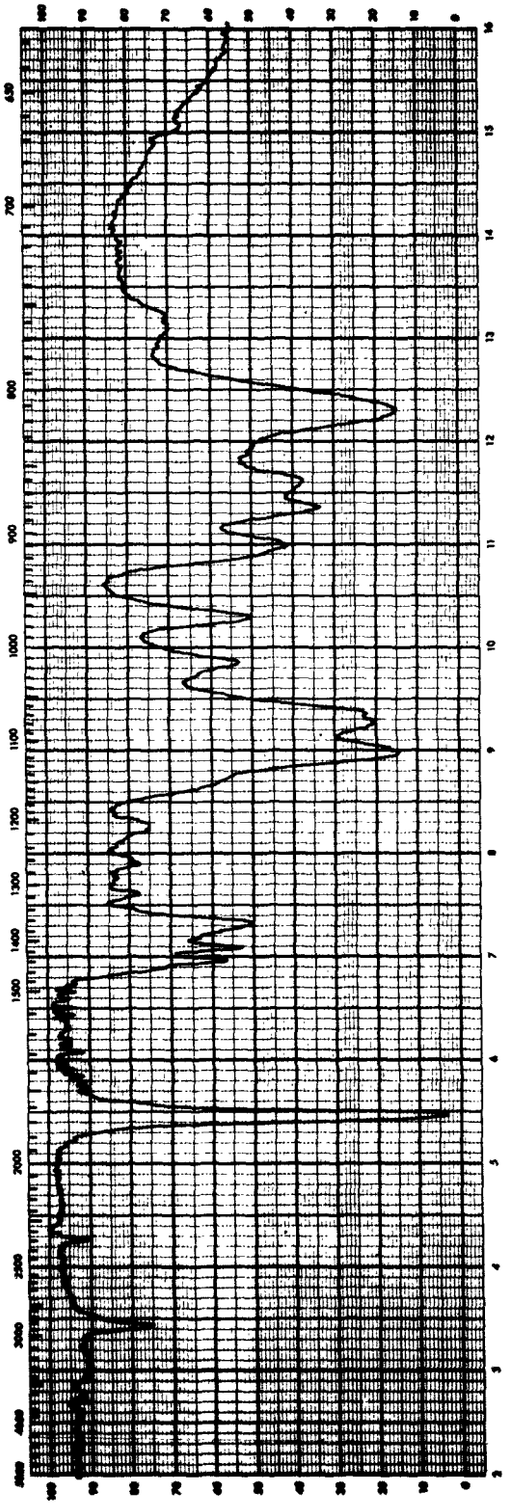


Figure 18. Infrared Spectrum of 3-Difluoraminobutyryl Fluoride

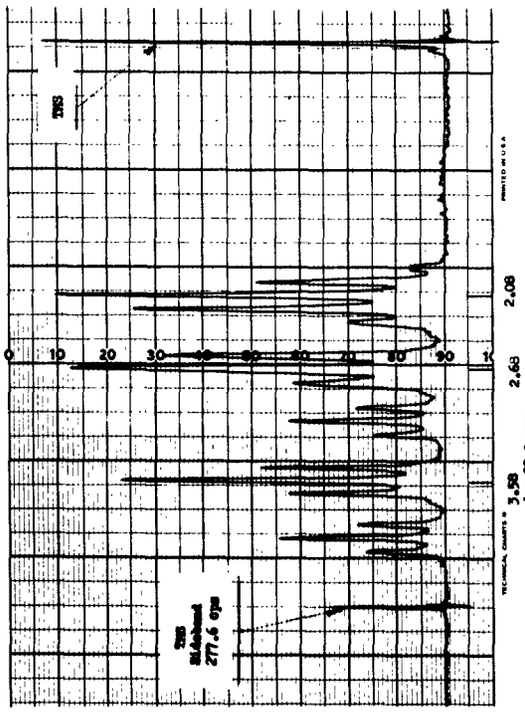



Figure 19. Proton NMR Spectrum of 3-Difluoraminobutyryl Fluoride

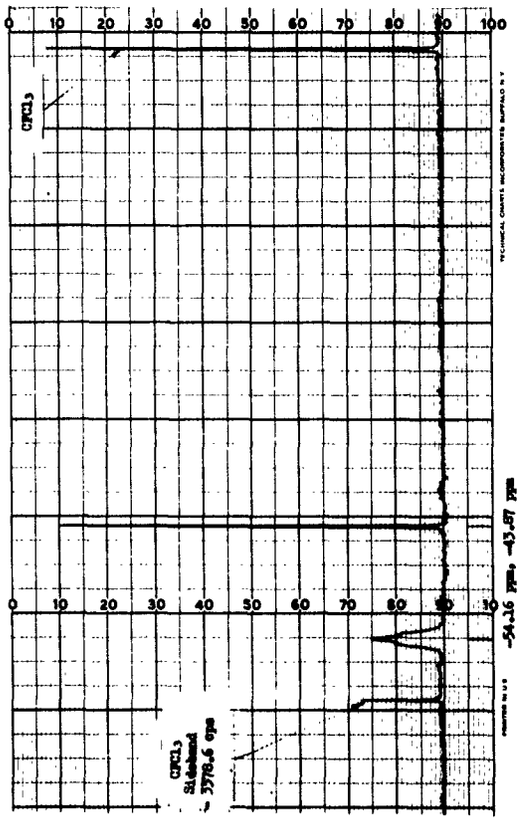



Figure 20. Fluorine NMR Spectrum of 3-Difluoraminobutyryl Fluoride

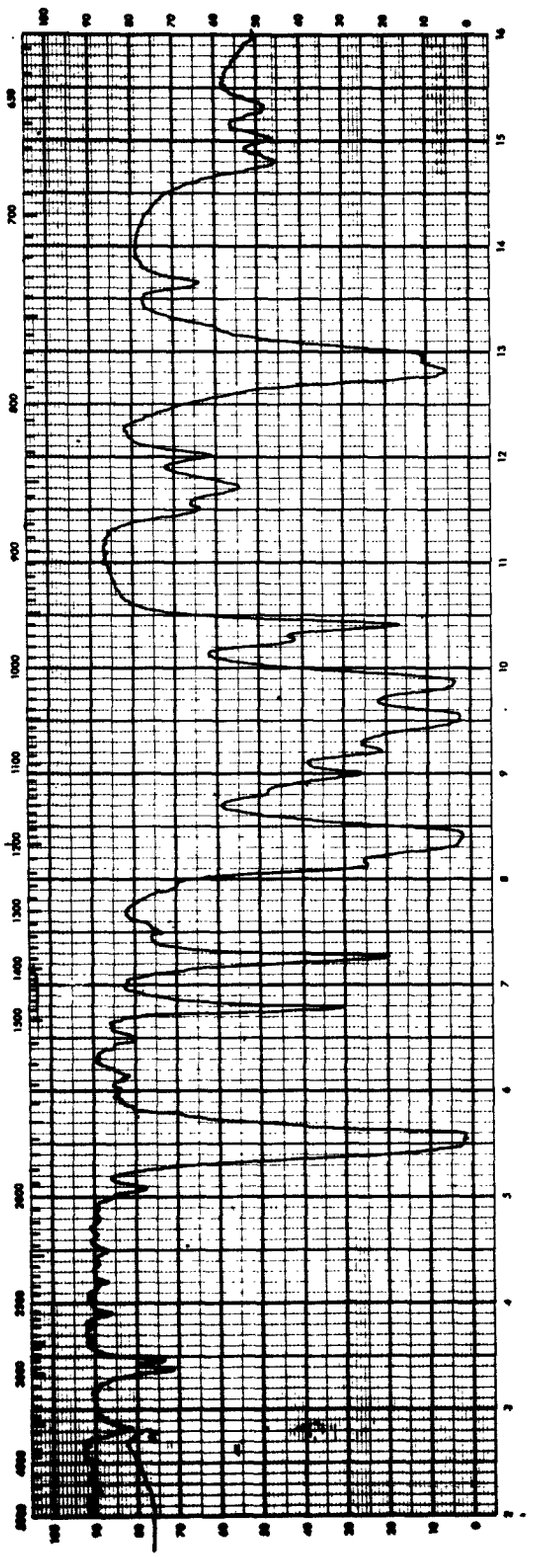


Figure 21. Infrared Spectrum of N-Fluoro-2-oxazolidone

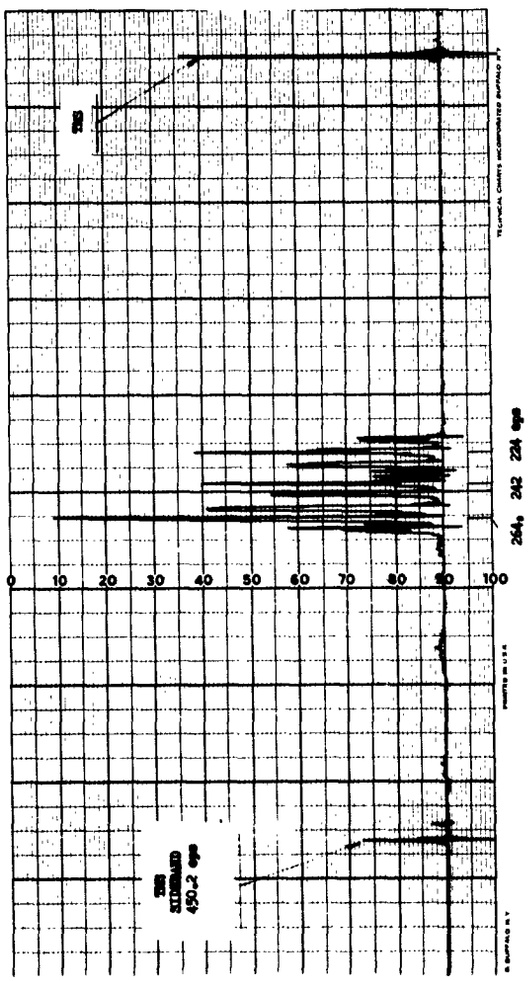
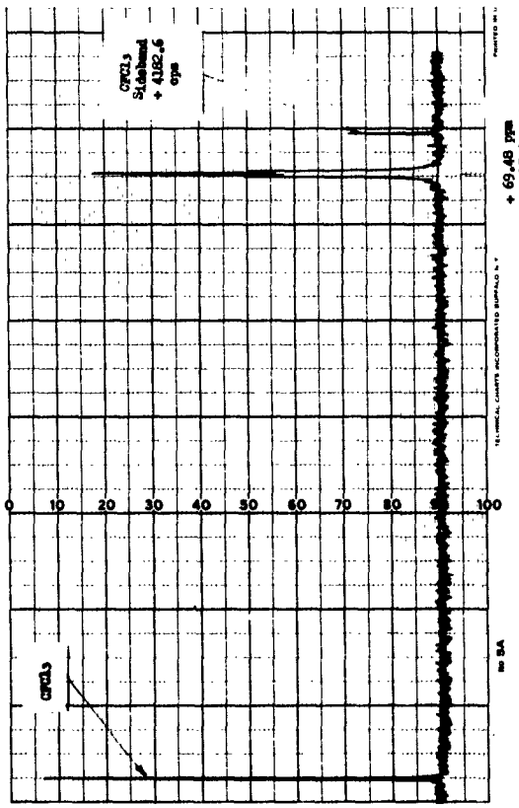



Figure 22. Proton NMR Spectrum of N-Fluoro-2-oxazolidone




Fluorine NMR Spectrum of N-Fluoro-2-oxazolidone

Report No. 0235-01-20

DISTRIBUTION LIST

| | No. of Copies |
|---|---|
| Chief, Office of Naval Research<br>Department of the Navy<br>Washington 25, D.C.<br>Attn: Power Branch - Code 429 | 11 |
| BuWepsRep., Azusa | 1 |
| Director<br>Advanced Research Projects Agency<br>The Pentagon<br>Washington 25, D.C.<br>Attn: Technical Information Officer | 6 |
| Dr. D. V. Sickman<br>Naval Ordnance Laboratory<br>White Oak, Silver Spring, Maryland | 1 |
| Commanding Officer<br>Army Chemical Center, Maryland<br>Attn: Technical Library | 1 |
| Los Alamos Scientific Laboratory<br>Los Alamos, New Mexico<br>Attn: Technical Library | 2 |
| Chief Scientist<br>Office of Naval Research<br>1030 East Green Street<br>Pasadena, California | 1 |
| Dr. T. L. Brownyard<br>Bureau of Naval Weapons<br>Department of the Navy<br>Attn: Code RRE-5<br>Washington 25, D.C. | 1 |
| Dr. E. E. Gruber<br>Head, Plastics Research<br>General Tire & Rubber Co.<br>Research Laboratory<br>Akron, Ohio | 1 |

DISTRIBUTION LIST (cont.)

| | No. of Copies |
|---|---|
| Stanford Research Institute<br>Menlo Park, California<br>Attn: Marion Hill | 1 |
| CPIA List as required | |
| Internal | 27 |