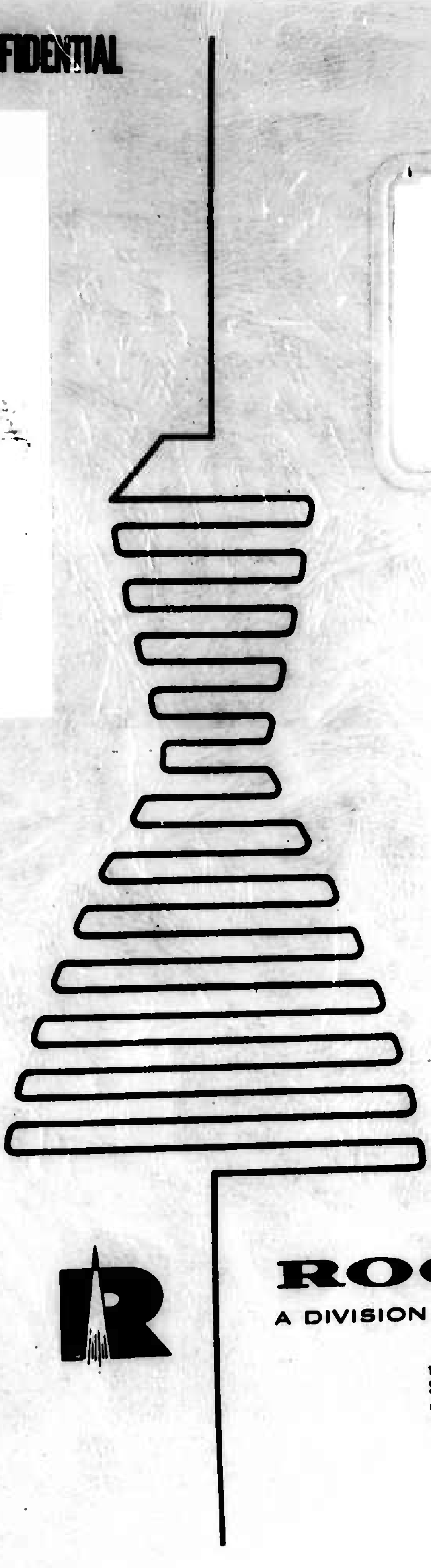
AD 318195

CONFIDENTIAL

(10)

348 193



ASTIA
RECEIVED
AUG 8 1960
TIPDR A

ROCKETDYNE

A DIVISION OF NORTH AMERICAN AVIATION, INC.

CANOGA PARK, CALIFORNIA

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18 U.S.C., Sections 793 and 794. Its Transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

CONFIDENTIAL

R-334-12

43

(Unclassified Title)

RESEARCH ON FLUORINE PROPELLANTS QUARTERLY PROGRESS REPORT FOR PERIOD ENDING 15 JUNE 1960

ROCKETDYNE
A DIVISION OF NORTH AMERICAN AVIATION, INC.
6633 CANOGA AVENUE
CANOGA PARK, CALIFORNIA

Contract Nonr 1818(00)
GO 9243

PREPARED BY

Experimental Chemistry Group

APPROVED BY

R. J. Thompson Jr.

R. J. Thompson, Jr.
Director
Research

NO. OF PAGES 28 & iv

REVISIONS

DATE 25 July 1960

DATE	REV. BY	PAGES AFFECTED	REMARKS

FORM R 18-G-1

FOREWORD

This report was prepared by the Experimental Chemistry Group of the Research Department of Rocketdyne. Support for this research effort was obtained from the Office of Naval Research under Contract Nonr-1818(00). Supplementary funds were provided by the Advanced Projects Research Agency under ARPA Order No. 23-60, Amend. 6. This report covers the period 16 March 1960 through 15 June 1960.

The responsible scientist for this work is Dr. Emil A. Lawton. Dr. Walter Maya, John Q. Weber, David F. Sheehan and Michael Warner wer full time associates on this project and Richard Wilson half time. The analytical support and infrared interpretations were furnished by E. F. C. Cain.

ABSTRACT

The solid oxidizer reported previously has been identified as unsymmetrical difluorourea, F_2NCONH_2, mp 41.0 to 41.5 C. The evidence for the structure of the compound and some of its properties are described. The results of more fluorinations are described and additional reactions of difluoramine are reported. The heat of dissociation of the $RbF \cdot HNF_2$ complex has been determined and evidence is presented that CsF forms more than one complex.

Difluoradiazine and dioxygen difluoride, O_2F_2, were found not to react with one another but it was observed that electrical excitation of nitrogen-fluorine gas mixtures at 196 C yielded NF_3 and an unstable species which has not yet been identified.

(CONFIDENTIAL ABSTRACT)

CONTENTS

TABLES

ILLUSTRATIONS

Figure:

INTRODUCTION

The synthesis of high-performance oxidizers is an ultimate goal of the research in this program. The approach utilized has been the study of the chemistry of compounds containing NF and OF bonds since large gains in impulse over that achieved with conventional oxidizers could be obtained with oxidizers containing these goups.

In the previous report (Ref. 1), we reported the isolation of crude solid products from the urea fluoridate residues containing up to 22 percent active fluorine. We have isolated the principal constituent as a pure compound and identified it as difluoruorea. In addition, the acid properties of difluoramine were studied further through its reactions with mild bases, such as the alkali metal fluorides. Additional fluorinations are reported as well as some of the results obtained with dioxygen difluoride, O_2F_2. Reactions initiated by electrical discharge are also discussed.

DISCUSSION

DIFLUOROUREA

The separation of crude solid products from the residues obtained on the distillation of fluorinated urea liquids has already been reported (Ref. 1, 2). The most interesting facet was the isolation of small quantities of fine needles melting from 40.7 to 41.1 C. The solid was found to react slowly with glass and mercury, and to be rather hygroscopic. Larger quantities were obtained by extraction of the solid residues with dichloromethane, evaporation of the solvents at low temperatures and low pressures in polyethylene apparatus and then subliming the crude residue at somewhat reduced pressures. The highest melting range observed for the solid was 41.0-41.5 C. From elemental analyses and infrared spectra, the compound has been identified as uns-difluorourea, NF_2CONH_2.

The infrared spectra of difluorourea were obtained both as a solution in dichloromethane (Fig. 1) and as a mineral oil mull (Fig. 2). The details of the spectra are described in Table 1.

Both spectra were obtained on a Beckman IR-7 spectrophotometer; the solution spectrum was run with a solvent reference. The evidence is as follows:

1. NH Stretching Modes
   Medium intensity absorptions in dilute solution at 3520 and 3420 cm-1 correspond to the free NH stretch frequency of a primary amide,  $-N\begin{smallmatrix}H\\H\end{smallmatrix}$.

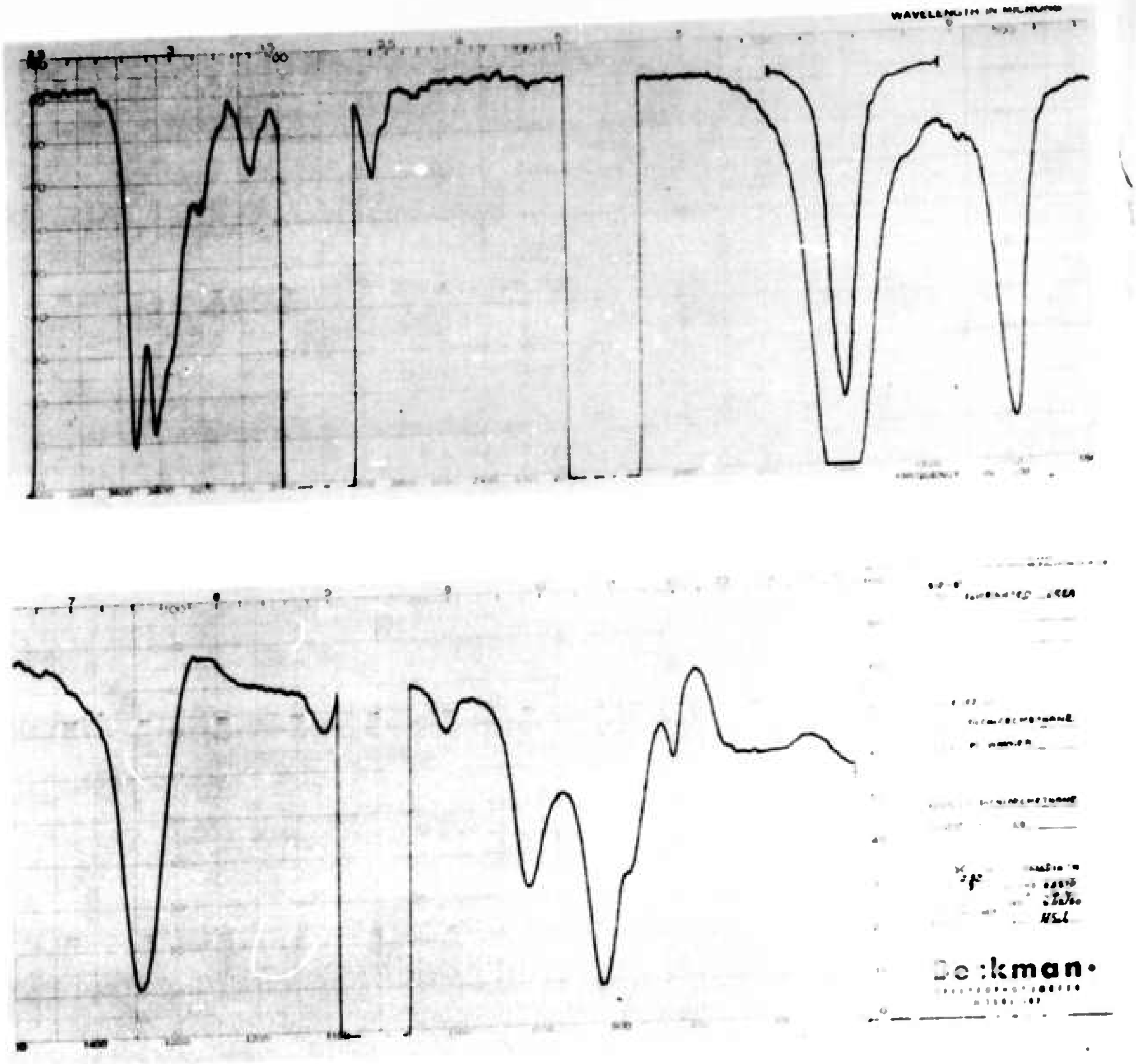


Figure 1. Infrared Spectrum of Difluorourea in Solution

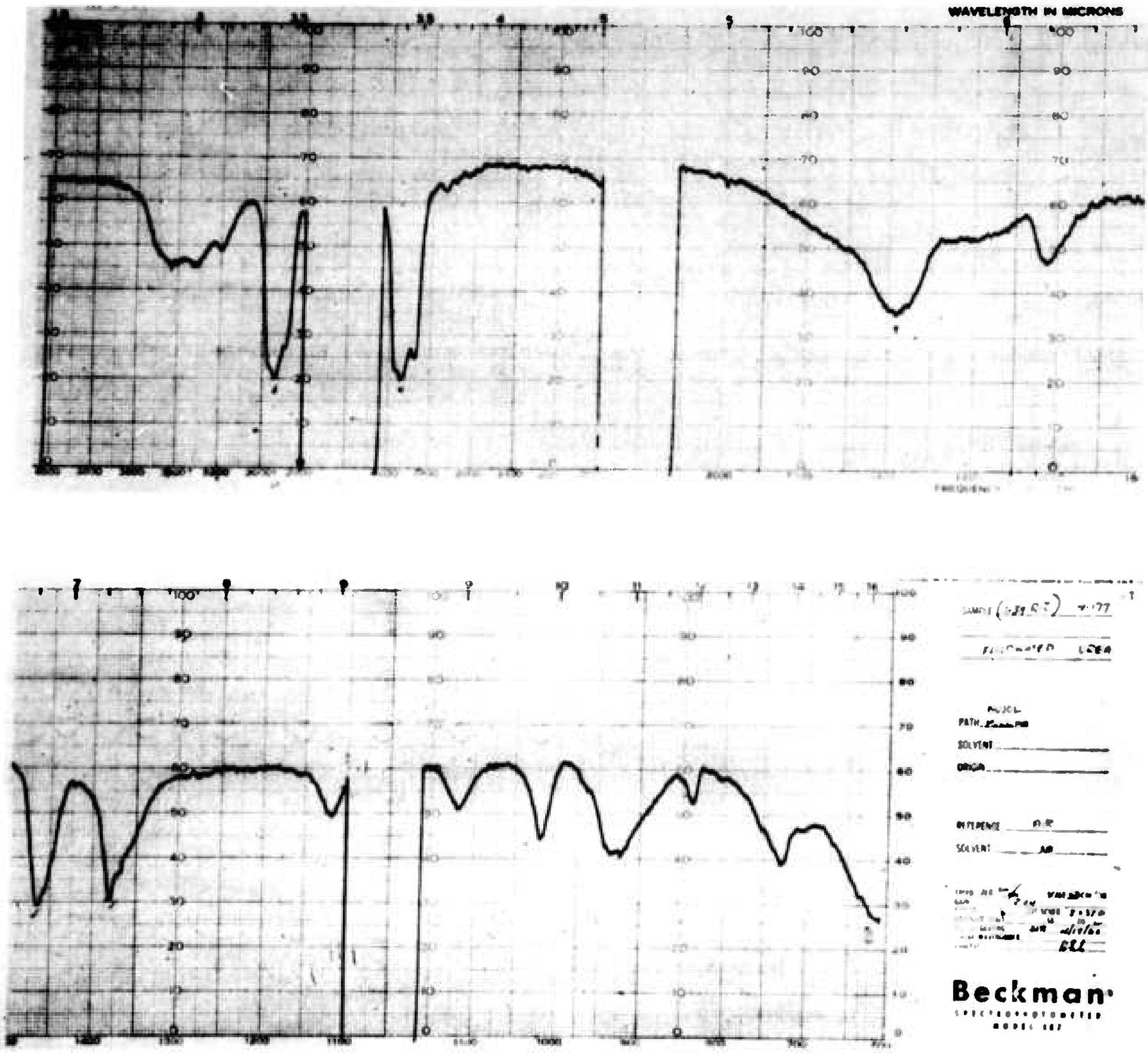


Figure 2. Infrared Spectrum of Difluorourea in a Mineral Oil Mull

TABLE 1

INFRARED SPECTRUM OF UNSYMMETRICAL DIFLUOROUREA

Dilute Sol'n	Solid State	Intensity	Assignment
CM^{-1}	CM^{-1} (Nujol Mull)		
3520		m	N-H stretch (free)
	3425	m	N-H stretch (bonded)
3420		m	N-H stretch (free)
	3320	m	N-H stretch (bonded)
3200	3200	w	――
2940	――	w	――
1803	1790	s	Amide I
1592	1613	m	Amide II
1345	1343	m	――
1115	1118	w	――
1018	1020	m	――
925	925	m	N-F (tentative)
892	――	w	――
836	836	w	――

In the solid state these absorptions are shifted to lower frequencies, 3425 and 3320 cm-1 respectively, which would be expected due to the association of a primary amide.

2. CO Absorption (Amide I) Band

   In dilute solution, a strong band at 1803 cm^{-1} corresponding to a carbonyl absorption with a strong electronegative group in the α position. (The carbonyl stretch of $CH_3C\overset{=O}{—}NF_2$ has been reported at ca. 1803 cm^{-1}.) (Ref. 3) In the solid state, this absorption shifts to a lower frequency, 1790 cm^{-1}. The direction of the shift is as expected.

3. NH_2 Deformation (Amide II) Band

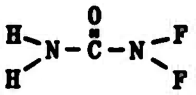
   In dilute solution, a strong band at 1592 cm^{-1} corresponding to the Amide II absorption of a primary amide. In the solid state, this absorption is shifted to a higher frequency, 1613 cm^{-1}. The direction of the shift is as expected.

4. The absorptions at 1803 cm^{-1} and 1592 cm^{-1} in the dilute solution of the material are shifted in the spectrum of the solid. These shifts confirm the assignment of the Amide I and Amide II Bands of a primary amide to these absorptions. (Ref. 4)

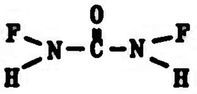
5. NF_2 Grouping

   The large frequency shift of the Amide I Band from a nominal 1690 cm^{-1} in dilute solution to 1803 cm^{-1} indicates the presence of a strong electronegative group attached to the carbonyl carbon atom. A strong absorption at 925 cm^{-1} has been assigned to the N-F stretch frequency and is compatible with the remainder of the spectrum.

6. On the basis of the infrared spectrum, the solid material may be represented by Structure I. Structure II is not compatible with the infrared spectrum.



I
Primary Amide



II
Secondary Amide

The infrared structure was confirmed by wet chemical techniques. Analyses were carried out to determine active fluorine and total fluorine. By modification of the Kjeldahl nitrogen technique it was possible to differentiate between the N-H_2 structure and the N-F_2 structure. The results of these analyses are shown in Table 2.

TABLE 2

SUMMARY OF WET CHEMICAL ANALYSES

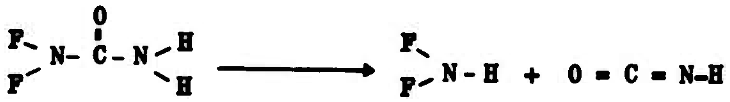
Sought	Calc.	Found
Active Fluorine	39.6	38.
Total Fluorine	39.6	38.6
Total Nitrogen	29.2	29.3
Amino Nitrogen (NH_2)	14.6	14.6

The mass spectrum of a sample of moderate purity gave principally peaks for HNF_2, HNCO and some difluorodiazine. The compound is very soluble in water, and soluble in dichloromethane and tetrahydrofuran. Cautic in handling is required since it is a vesicant and laohrymator. Difluorourea is stable to at least 50 C but it can be detonated by heat.

FLUORINATION OF NITROGEN COMPOUNDS

Work has continued on the fluorination of urea with two objectives in mind: first, to supply difluoramine and difluroourea for other chemical syntheses, and second, to obtain a better understanding of the fluorination itself. In view of the relatively drastic conditions of direct fluorination it is not surprising that the percent of both active fluorine and total fluorine content vary considerably from one fluorination to another. Examination of the data compiled from all previous fluorinations and distillations indicated that mechanical difficulties such as plugging, channeling of the fluorine-nitrogen mixture through the solid, and caking up of the partially fluorinated product, caused some of the variability observed. These difficulties might cause incomplete fluorination or bring about local hot spots which alter the products obtained even though equivalent or slightly excess amounts of fluorine are used in all fluorinations.

The variability in the amount of difluoramine obtained by vacuum distillation, even from quite similar liquids, tends to suggest that either these samples are in different stages of fluorination, or that there is an intermediate compound which subsequently decomposes to different degrees depending on the conditions of the reaction and subsequent handling of the liquid product. An argument for the latter is supported by the fact that since, in addition to difluoramine, difluorourea has been isolated from the fluorinated liquid, other forms such as the monofluoro and trifluoro urea may well exist in the liquid, but have not yet been identified. It is reasonable to postulate the reaction of difluoroourea going to difluoroamine and isocyanic acid.



A similar reaction when applied to mono- or trifluoroourea might yield as yet unobserved products such as H_2NF. While it has not been established quantitatively, there has been indication that the fluorinated liquid which gives the greatest yield of difluoramine yields the least difluoroourea and vice versa. It may well be possible to maximize either yield, or to optimize the yield of both by suitable modifications of conditions and apparatus.

Two exploratory direct fluorinations of cyanoguanidine were made with the view that perhaps cyanodifluoramine would be one of the products as well as difluoramine itself. The products were solids with no oxidizing power, and a mixture of gases. This mixture was shown by infrared analysis to be mainly CF_4, CF_3NF_2, HNF_2, FCN (Ref. 5, 6), and smaller amounts of $(CF_3)_2NF$, $(CF_3)_3N$, N_2F_2, N_2F_4, and SiF_4. There were some unidentified peaks but these were not in the N-F band region. These results agree well with those of Minnesota Mining and Manufacturing Co. (Ref. 7)

CHEMISTRY OF DIFLUORAMINE

The acid character of difluoramine has been previously reported by Rocketdyne and others. The reactions of difluoramine with potassium fluoride and with trimethylamine have been reported recently (Ref. 1).

The formation of a weak compound of KF with difluoramine was demonstrated, and we are reporting our results with other metal fluorides as well as other bases.

Difluoramine-Alkali Metal Fluorides*

The low temperature reaction of KF with HNF_2 results in the formation of an adduct with a heat of dissociation of 6.7 Kcal/mole. Rubidium fluoride is a stronger base and, as expected, forms a more stable compound. From the plot of the dissociation pressure versus the reciprocal of temperature, the following expression was obtained for the adduct with RbF.

$$\log_{10} Kp_{mm.} = \frac{-2166}{T} + 10.338$$

From the slope of the straight line represented by the above equation, the heat of dissociation for the reaction was calculated to be 9.9 Kcal/mole

$$RbF\cdot HNF_2\ (s) = RbF\ (s) + HNF_2\ (g)$$

A similar study of difluoramine over CsF was conducted. A complex was formed; however, its behavior was different from the other complexes discussed above. The vapor pressure of the complex was measured as 1.2 mm at -64.8 C. This pressure is higher by 0.8 mm for that of RbF complex at the same temperature. This was surprising since CsF is a stronger base than RbF and it would be expected that difluoramine would be more tightly bound to CsF than to RbF. However, it was found that

---

*Work on difluoramine-alkali fluorides was supported in part by the Air Force under Contract AF 33(616)-6768.

approximately 50 percent of the HNF_2 introduced over the CsF could be pumped off at -65 C, after which the pressure exhibited by the solid complex was essentially zero. A tentative explanation for the anomalous behavior involves a complex equilibrium:

1. $CsF \cdot 2HNF_2(s) = CsF \cdot HNF_2(s) + HNF_2(g)$
2. $CsF(s) + HNF_2(g) = CsF \cdot HNF_2(s)$

The formation of a higher complex such as the 2:1 complex in 1. might account for the higher dissociation pressure initially observed. However, the reaction shown in 2. once equilibrium in 1. has been established, might be slow due to the limited surface area of the CsF. After the loosely bound HNF_2 was pumped off, (Eq. 1,) the remaining complex is tightly bound at -65 C.

No dissociation pressures were measured for $CsF \cdot HNF_2$ because of the explosive nature of the complex. In every experiment, a sharp detonation occurred upon warming the complex to about 0 C.

Fluorides other than those of the alkali metals were used in an attempt to convert HNF_2 to N_2F_2. No effect was noted when HNF_2 was contacted with CaF_2 and NiF_2 at ambient temperature.

Reaction of Difluoramine with Tetramethylammonium Hydroxide

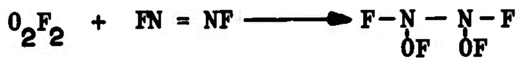
The possible interaction of a strong amine base, trimethylamine with HNF_2 to form the NF_2^- ion was examined. The results were not reproducible. A strong base with a large cation, tetramethylammonium hydroxide, was tried next.

The tetramethylammonium hydroxide was obtained as a 10 percent aqueous solution, and vacuum evaporation at room temperature yielded white hydrated crystals having from 4 to 5 moles of water of hydration. Warming to 65 C with pumping gave the anhydrous base. Neither the hydrated nor anhydrous base was found to be soluble in dimethyl ether, or tetrahydrofuran; however both were quite soluble in methanol.

Although residues ranging from white solids to yellow liquids were obtained, only a few showed any oxidizing power and these were not reproducible. Three reactions resulted in sharp detonations, each occurring just after condensing the difluoramine into the reactor at -142 C and bringing it up to -80 C. A probable cause of these explosions is that the difluoramine did not vaporize before it ran down the walls of the reactor. The liquid, on contacting the base, reacted exothermically, thereby detonating the difluoramine.

O F COMPOUNDS

New compounds containing the OF moiety are of great interest as oxidizers. To this end, the reaction of O_2F_2 with N_2F_2 was investigated in the hope of obtaining a new oxidizer according to the following equation:



$$O_2F_2 + FN = NF \longrightarrow F-\underset{OF}{N}-\underset{OF}{N}-F$$

To test the possibility of O_2F_2 adding to the double bond of N_2F_2, the two compounds were mixed in a cold trap. The contact time and temperature were varied from simple warming from -196 C to room temperature to allowing a contact time of 30 minutes at -95 C. Higher temperatures were not used due to the well-known instability of O_2F_2. No indications were found that any reaction took place between the two compounds.

Other evidence in the literature points to the reluctance of O_2F_2 in yielding OF radicals. The reaction of O_2F_2 with N_2F_4 (Ref. 8) did not yield any OF species, nor did O F compounds result from the reaction with tetrafluoroethylene and 3-chloroperfluoropropene (Ref. 9). On the other hand, N_2F_4 did not add to the double bond of difluorodiazine (Ref. 10), indicating that the double bond is an unreactive one. It thus seems that the reaction is energetically unfavored, and that some source of energy must be provided to induce the desired path. This will be attempted by having the reactants excited by an electric discharge in a cell cooled to an appropriate temperature, where O_2F_2 and N_2F_2 have a vapor pressure of a few millimeters.

ELECTRIC DISCHARGE REACTIONS

Difluorodiazine was exposed to a glow discharge at -156 C to test its stability under these conditions, and also to determine if any condensation product of new binary NF compounds would result. The only products found were unreacted N_2F_2, noncondensable gas, SiF and nitrogen oxides.

During the course of preparing O_2F_2, a mixture of gases was employed that contained oxygen, fluorine and some nitrogen. Nitrogen trifluoride was found among the products. It seemed quite possible that the NF_3 had been produced from nitrogen and fluorine in the discharge at -196 C. Previous findings show that at higher temperatures NF_3 decomposes in an electric discharge back to the elements (Ref. 11) with small amounts of N_2F_4 and N_2F_2 also forming. A report also exists on the formation of NF_3 from the electric discharge reaction of O_2F, N_2 and O_2 mixtures (Ref. 12). There are, however, several reports in the literature that fluorine and nitrogen do not combine under these conditions. The first was by O. Ruff (Ref. 13) and more recent reports in the classified literature had apparently confirmed this. (Ref. 12,14)

In a test experiment, a mixture containing 75 percent fluorine and 25 percent nitrogen was subjected to a glow discharge at -196 C. A 15 percent yield of nitrogen trifluoride was obtained. No effort was made to maximize the yield, so that 15 percent is not necessarily the best obtainable. An unstable species was also formed, and is under investigaton. As always, SiF_4 and nitrogen oxides were formed, resulting from the attack on glass by the mixture during discharge. This is the first time, to our knowledge, that elemental nitrogen and fluorine have been combined.

EXPERIMENTAL SECTION

ISOLATION AND PURIFICATION OF uns-DIFLUOROUREA

After difluoramine had been distilled from the fluorinated urea liquid, about 5 ml of the liquid residue were placed in a polyethylene bottle and extracted three times with 20 ml portions of dichloromethane. The dichloromethane solutions were decanted from the residue, combined, and placed in a wide mouth polyethylene evaporating dish. The solution was then evaporated to dryness under gradually reduced pressure in a vacuum desiccator. The conventional desiccator cover used during evaporation was replaced with a four-hole desiccator cover, housing the sublimation apparatus. To provide a cold surface for the sublimation, a round bottom flask coated with polyethylene was mounted in the center hole of the cover. The flask completely covered the mouth of the evaporating dish and was attached to it securely. Ice water was circulated through the flask. The bottom of the sample dish was warmed by a spiral of copper tubing through which water at about 50 C was circulated. The warm water connections were passed through an air tight seal in the desiccator cover. The two remaining holes in the cover were fitted with stopcocks for circulating dry nitrogen through the desiccator. After about two hours of operation, the apparatus was disassembled in a dry box and the sublimed material transferred to a polyethylene vial for storage. Occasional difficulties were observed in the sublimation due to the presence of water.

Other samples were obtained from the -80 C trap where rings of comparatively pure compound were formed on the warm arm of the trap. These samples were also purified by sublimation.

Analysis of Difluorourea

The Kjehldahl analyses were conducted in two ways. Adding the difluorourea directly to concentrated sulfuric acid resulted in quantitative release of the NF_2 group presumably as difluoramine. Subsequent analyses gave the amino nitrogen quantitatively. Prior addition of hydriodic acid before treatment with concentrated sulfuric acid yielded the total nitrogen.

The analytical methods for active and hydrolyzable fluorine have already been described. (Ref. 15).

Fluorination of Urea

Fluorinations 38 through 42 were carried out during this quarter and are summarized in Table 3. Runs No. 39 and 42 both ran smoothly to completion with all the urea being reacted. Run No. 38 was aborted early due to outside interference, and approximately 15 gm of unreacted urea was recovered from the reactor, which had no appreciable oxidizing power. Run No. 40 burned out due to a corroded needle valve in the fluorine line which allowed too great a $F_2:N_2$ ratio. Run No. 41 proceeded smoothly except that some of the urea sifted through the porous plate to the bottom of the reactor and did not become fluorinated. In Run No. 40 a -156 C cold trap was placed down stream of the reactor and analysis of the gas condensed in this trap during the fluorination showed CO_2 and SiF_4 as the main products with smaller amounts of CF_4 and COF_2.

The distillations of the fluorinated urea liquids (Table 3) to prepare difluoramine were carried out at room temperature and at a pressure of less than 2 mm of Hg. Distillation times shown are total times on each aliquot. The age of the liquid is determined from the date of fluorination to the date of distillation. In all cases, large quantities of CO_2 and SiF_4 were obtained.

CONFIDENTIAL

PREPARAT

FLUORINATION DATA

Run No.	Urea, gm	Liquid gm	Act F %	Tot F %	F_2 gm	F_2-N_2	F mol
35	60	68.7	12.2	27	36.1	1:4	0.
36	30	41.4	14.7	43.1	26.6	1:4.7	0.
37	90	136.1	18.6		NOT KNOWN		
38	30	19.8	16.6	38.1	20.5	1:7	0.1
39*	90	141	17.3	43.4	110.6	1:4	0.5
40	Burned out due to corroded valve						
41	90	70	7.0%		35.9	1:4	0.27
42	60	80.6	12%		38	1:3.5	0.25

* Fluorinated Ureas Liquid No. 39 was divided into two parts and is designated 39-1 and 39-2

TABLE 3

PREPARATIONS OF DIFLUORAMINE

		DISTILLATION DATA						
F_2-N_2	F_2 mole/hr	Dist. Aliquot	Liquid gm	Dist. Time, hr	Liq. Age Days	HNF_2 cc	HNF_2 % on F_2	HNF_2 % on AcT F
1:4	0.19	C	9.8	3.0	218	28	1.8	4.0
1:4.7	0.14	B	5.3	3.0	98	170	12.6	37.1
		C	5.3	4.0	100	197	14.6	42.9
		D	10.1	4.0	104	370	14.4	42.2
		E	9.1	4.0	107	285	12.3	36.2
		F	11.2	4.0	118	323	11.3	33.3
KNOWN		J	15.0	4.0	64	140		8.5
		K	16.6	3.0	65	160		8.8
1:7	0.16	A	16.7	4.0	47	34	0.9	2.1
1:4	0.52	39-2-A	6.1	4.0	10	52	3.3	8.3
		B	12.0	4.0	38	113	3.7	9.2
		C	11.7	3.0	43	107	3.6	9.0
		D	10.7	4.0	44	92	3.4	8.4
		E	10.4	4.0	45	85	3.2	8.0
		39-1-A	9.5	3.0	64	93	3.8	9.6
		B	10.3	3.0	67	82	3.1	7.8
1:4	0.27							
1:3.5	0.25							

into two

FLUORINATION OF OTHER SOLID NITROGEN COMPOUNDS

These fluorinations were run in the same reactor and utilized the same conditions as with urea.

Fluorination of Cyanoguanidine

Test No. 1

Cyanoguanidine = 8.4 g. (.1 mole)

Fluorine = 3.8 g. (.1 mole)

Fluorine flowrate = 0.1 mole/hr

Fluorination time = 1 hr

Fluorine:Nitrogen ratio = 1:10

A -156 C trap was used downstream of the reactor to capture gaseous products passing through the reactor. The cyanoguanidine did not yield a liquid when fluorinated but rather a small amount of red solid which displayed no oxidizing power. The gaseous products from the trap were examined by infrared analyses and found to contain CF_4, HNF_2, CF_3NF_2 and small amounts of SiF_4, N_2F_2, N_2F_4 and NF_3.

Fluorination of Cyanoguanidine

Test No. 2

Cyanoguanidine = 42 g. (.5 moles)

Fluorine = 19 g. (.5 moles)

Fluorine flowrate = 0.1 mole/hr

Fluorination time = 5 hrs

Fluorine:Nitrogen ratio = 1:8

In this run, most of the cyanoguanidine was found as a large brick-red clinker in the reactor but no liquid was formed. The gaseous products were again trapped at -152 C and examined by infrared analyses. The gaseous products identified were FCN, HNF_2, CF_3NF_2, $(CF_3)_2NF$, $(CF_3)_2NH$ and SiF_4. There were a few unidentified bands but these were not in the N-F region.

Dissociation Pressure of Difluoramine Over Rubidium Fluoride

The system and techniques used to perform the measurements on the RbF-HNF_2 system were the same as described in the previous report. The results of the measurements are given in Table 4 . Higher temperatures were not used to prevent the formation of difluorodiazine.

TABLE 4

VAPOR PRESSURE OF HNF_2 OVER RbF

Temp., C	Pressure (obs.) mm	Pressure (calc.) mm
-81.6	0.0	--
-72.0	0.0	--
-65.0	0.8	0.86
-57.8	1.9	1.9
-45.8	6.5	6.5
-31.6	23.5	23.6

Difluoramine and Tetramethylammonium Hydroxide

The general procedure in reacting difluoramine with tetramethylammonium hydroxide follows. The solid base was dissolved in the solvent and then the difluoramine was condensed in the reactor at -142 C. Most runs were allowed to equilibrate at -80 C for one hour before vacuum distillation.

Dissociation Pressure of Difluoramine Over Rubidium Fluoride

The system and techniques used to perform the measurements on the RbF-HNF_2 system were the same as described in the previous report. The results of the measurements are given in Table 4. Higher temperatures were not used to prevent the formation of difluorodiazine.

TABLE 4

VAPOR PRESSURE OF HNF_2 OVER RbF

Temp., C	Pressure (obs.) mm	Pressure (calc.) mm
-81.6	0.0	--
-72.0	0.0	--
-65.0	0.8	0.86
-57.8	1.9	1.9
-45.8	6.5	6.5
-31.6	23.5	23.6

Difluoramine and Tetramethylammonium Hydroxide

The general procedure in reacting difluoramine with tetramethylammonium hydroxide follows. The solid base was dissolved in the solvent and then the difluoramine was condensed in the reactor at -142 C. Most runs were allowed to equilibrate at -80 C for one hour before vacuum distillation.

The usual gaseous products of distillation were difluoramine and traces of the solvent. The residues ranged from white or yellow solids to yellow liquids with little oxidizing power except for Run No. 6. This run was not evaporated before testing for active fluorine. Even so, all the active fluorine was not accounted for; only 70 percent of theory was found by HI addition to the solution at -80 C.

Table 5 shows the amount of difluoramine recovered by distillation and the percent accounted for in both the gaseous and solid products. Little noncondensible gas was found in most cases and in Run No. 18 may have been due to a leak. In Run No. 12, the noncondensible gas may have come from the products of combustion as a flash took place in the reactor on warming from -80 C to room temperature. Runs No. 14, 15 and 16 all exploded on changing baths on the reactors from -142 to -80 C.

Dioxygen Difluoride (O_2F_2) and Difluorodiazine

The apparatus and procedure for the synthesis of O_2F_2 was described in the last report (Ref. 1).

The procedure generally consisted in transferring an excess of O_2F_2 from the reactor onto a trap cooled at -196 C, and condensing N_2F_2 into the same trap. The temperature of the trap and contact time was varied from experiment to experiment. The trap was designed so that it was almost completely immersed in the slush bath, in order to minimize decomposition of the O_2F_2 vapor. This proved successful, and O_2F_2 could be kept this way for over 30 min at -95 C.

TABLE

REACTION OF HNF_2

Run No.	$(CH_3)_4NOH$ gm	Form	Solvent	Amount	HNF_2 in cc STP	HNF_2 out, cc STP	Perc Acco
1	.1975	hyd	$(CH_3)_2O$	86.4 cc	14.5	mix HNF_2, $(CH_3)_2O$	
2	.240	hyd	$(CH_3)_2O$ (mixture from #1)			mix HNF_2, $(CH_3)_2O$	
3	.1250	hyd	aqueous		10.1	9.3	
4	.0233	hyd	CH_3OH	1 ml	10.8	mix HNF_2, CH_3OA	
5	.125	hyd	aqueous		21.6	23.6 HNF_2 trace CH_3OH	
6	.0190	anhyd	CH_3OH	1 ml	10.6	none	7
7	.0056	anhyd	CH_3OH	1 ml	10.2	trace	
8	.0676	hyd	none		8.6	4.8	2
9	.1262	hyd	none		26.4	12.1	
10	.2785	hyd	none		25.1	8.8	
11	.1768	hyd	none		20.8	?	3
12							

TABLE 5

REACTION OF HNF_2 AND $(CH_3)_4$ NOH

$_2$ in STP	HNF_2 out, cc STP	Percent NF_2 Accounted for	N.C.G. cc STP	Remarks
3	mix HNF_2, $(CH_3)_2O$	0	none	$(CH_3)_4$ NOH insoluble in $(CH_3)_2O$, turned yellow
	mix HNF_2, $(CH_3)_2O$	0	2.5	The same as in Run No. 1
1	9.3	0	trace	Crystals form when liquid evap. under vacuum
8	mix HNF_2, CH_3OA	0	none	Residue left on evap. under vacuum
6	23.6 HNF_2 trace CH_3OH	0	none	Vacuum evap. produced residue
5	none	70	30	Not evap., solution tested
2	trace	0	2	Evap. under vacuum left white film
5	4.8	27	1	A liquid formed on warming to room temperature
4	12.1	0	a few	Yellow liquid at room temperature
1	8.8	0	4	Warmed to 50 C, the liquid went to paste
8	?	3.4	15.7	On warming there was a flash in the reactor
				Contaminated with $(CH_3)_2O$, not run

2

TAB
(Cont

Run No.	$(CH_3)_4NOH$ gm	Form	Solvent	Amount	HNF_2 in cc STP	HNF_2 out, cc STP
13	.0657	hyd	none		26.2	14.8
14	.2982	hyd	none		37.8	
15	1.1169	anhyd	none		23.0	
16	.4319	anhyd	THF	2 ml	28.0	
17						
18	.1410	anhyd	CH_3OH	3 ml	30.5 in 1 ml CH_3OH	none
19	.2678	anhyd	CH_3OH	3 ml	31.9 in 1 ml CH_3OH	none

2

TABLE 5
(Continued)

NF$_2$ in c STP	HNF$_2$ out, cc STP	Percent NF$_2$ Accounted for	N.C.G. cc STP	Remarks
6.2	14.8	0		The same liquid as No. 8
7.8				Explosion occured during warming from -142 C to -80 C
3.0				Same
8.0				Same except that the solid was not soluble, turned yellow
				Not run, damaged by explosion of No. 16
0.5 in 1 CH_3OH	none	11	30	Most of the CH_3OH removed before titration
1.9 in 1 CH_3OH	none	16	a few	A white solid observed at -80 C but absent at room temperature, probably CO_2

Reactions were tried where the two compounds were warmed from -196 C to room temperature, reacted at -95 C for 5 min and 30 min, and at -142 C for 15 min. In the latter case, the N_2F_2 was quantitatively recovered. Among the products were found unreacted N_2F_2, noncondensibles from the decomposition of O_2F_2, and SiF_4. Some unidentified fluorocarbons, as well as CF_4 and COF_2 were frequently encountered, due to the action of fluorine on the stopcock grease.

Difluorodiazine Under Electric Discharge

Difluorodiazine (12.5cc) was admitted into the glow discharge cell at -156 C. The vapor pressure of N_2F_2 at this temperature is 8 mm. The pressure in the system quickly rose, once the discharge was initiated. The experiment was interrupted, once the pressure had increased to a point where a discharge could no longer be maintained, and 9.1 cc of impure N_2F_2 was recovered from the noncondensible gases formed. Infrared examination showed the impurities to be N_2O, COF_2, SiF_4 and fluorocarbons.

Synthesis of Nitrogen Trifluoride

A mixture of nitrogen (10.5 cc) and fluorine (34 cc) was submitted to an electric discharge (10-15 ma), 5000 volts, at -196 C. The pressure in the reactor was maintained between 10 to 17 mm by adding gas to the system as it was consumed. After 29 cc of the mixture had been reacted, the discharge cell was allowed to warm up with pumping, the gases passing through a -196 C and -210 C (solid nitrogen) trap.

The -210 C trap afforded NF_3 (3.2 cc), contaminated with a trace of CF_4. The -196 C trap contained 4.9 cc of gas which, however, could not be completely recondensed. After pumping off the noncondensibles, 2.6 cc remained, which were mainly SiF_4, COF_2, N_2O, and some C-F compound.

Further work is contemplated to identify the unstable species, and to determine the best conditions for the formation of NF_3.

Essentially the same experiment was done with a 50 percent fluorine-nitrogen mixture, except that a -210 C trap was not employed. No evidence was found for the presence of N_2F_2 or N_2F_4.

CONCLUSIONS AND FUTURE WORK

The isolation of uns-difluorourea from the fluorination products of urea has provided a new NF intermediate for further research as well as suggested methods for preparing other solid oxidizing species. As a result, work on the fluorination of nitrogen compounds other than urea has been intensified.

The formation of adducts of difluoramine with metallic fluorides is of intrinsic interest in the theory of acids and bases. The reactions of bound difluoramine with other materials may provide additional synthetic routes to NF compounds. The possibility of ionic reactions are not excluded.

The preparation of NF_3 by direct combination of the elements by electrical excitation suggests that an alternate process for the preparation of this key intermediate may be practical. Work on electrical discharge reactions will be continued.

REFERENCES

1. R-2296, Research on Fluorine Propellants, Summary Progress Report for Period 16 March 1959 through 15 March 1960, Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, California, 22 April 1960, CONFIDENTIAL.

2. Lawton, E. A., J. Q. Weber, and D. F. Sheehan: R-334-11, Research on Liquid Propellants, Quarterly Progress Report for Period Ending 15 December 1959, Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, California, 31 December 1959, CONFIDENTIAL.

3. P-59-12, Quarterly Progress Report on Synthetic Chemistry, Part II 1 April 1959 to 30 June 1959, Rohm and Haas Co., Huntsville, Alabama, CONFIDENTIAL.

4. Bellamy, L. G.: The Infrared Spectra of Complex Molecules, Second Edition, John Wiley and Sons, Inc., New York, New York, 1958, pp.203-23.

5. Fawcett, F. S., and R. D. Lipscomb: J. Am. Chem. Soc., 82, 1509 (1960).

6. Aynsley, E. E., R. E. Dodd and R. Little: Proc. Chem. Soc., 1959, 265.

7. Chemical Research as Related to Advanced Solid Propellants, Report No. 3, Annual Report 1 Feb. 1959 - 31 Dec. 1959, Minnesota Mining and Manufacturing Co., 15 Mar. 1960, CONFIDENTIAL.

8. Report No. PR-3, Research on High Energy Oxidizers for Advanced Solid Rocket Propellants, General Chemical Division, Allied Chemical Corp., Morristown, New Jersey, 31 December 1959, CONFIDENTIAL.

REFERENCES - continued

9. Report No. PR-2, Research on High Energy Oxidizers for Advanced Solid Rocket Propellants, General Chemical Division, Allied Chemical Corp., Morristown, New Jersey, 30 September 1959, CONFIDENTIAL.

10. Report No. P-58-23, Quarterly Progress Report on Physical Chemistry, Rohm and Haas Company, Redstone Arsenal Research Division, Huntsville, Alabama, 25 December 1958, CONFIDENTIAL.

11. Frazer, J. W., Preparation of N_2F_4 and N_2F_2 J. Inorg. Nucl. Chem., 11, 166, (1959).

12. Report No. PR-4, Research on High Energy Oxidizers for Advanced Solid Propellants, General Chemical Division, Allied Chemical Corp., Morristown, New Jersey, 31 March 1960, CONFIDENTIAL.

13. Ruff, O.; Zedner, J.: Behaviour of Fluorine Toward Nitrogen, Oxygen, Chlorine in Electric Arc and Induction Sparks, Ber. 42, 1037, 1909.

14. Report No. 2, ARF 3158-8, Preparation of High Energy Storable Propellants, Armour Research Foundation, Chicago 16, Illinois, 3 February 1960, CONFIDENTIAL.

15. Lawton, E. A., and J. Q. Weber: R-1025, Fluorine Propellant Study, Final Progress Report for Period 1 June 1957 through 31 May 1958, Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, California, 31 July 1958, CONFIDENTIAL.