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RESEARCH ON LIGHT METAL FUELS AND OXIDIZER CHEMISTRY (U)
QUARTERLY PROGRESS REPORT NO. 4

PART 2 - OXIDIZER CHEMISTRY
MAY - JULY 1964

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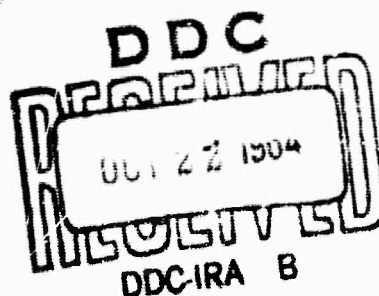
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PART II

OXIDIZER CHEMISTRY

Quarterly Progress Report No. 4
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Sponsored by: Advanced Research Projects Agency, Propellant Chemistry
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California

Work Conducted by

W. E. Becker
D. H. Campbell

Supervised by:

S. E. Cook

ETHYL CORPORATION
P. O. Box 53091
Baton Rouge, Louisiana
70805

TABLE OF CONTENTS

	Page
INTRODUCTION	1
SUMMARY	1
RESULTS AND DISCUSSION	1
Cryoscopic Studies	1
Isotopic Exchange of Hydrogen Between HNF_2 and H_2O	2
Chlorine Exchange Between HCl and ClNF_2	3
Conductivity of ClNF_2 in Nitrobenzene Solution	4
REFERENCES	6

PART II - OXIDIZER CHEMISTRY

INTRODUCTION

Contract AFO4(611)-9376 includes two parts as follows: Part I - Research on Light Metal Fuels and Part II - Oxidizer Chemistry. Part I is issued separately as a classified report.

Part II - Oxidizer Chemistry has the objective of investigating the ionic behavior of inorganic NF_2 compounds by means of electrochemical and kinetic studies.

SUMMARY

Investigation of the chemistry of inorganic NF_2 compounds is proceeding along the following lines.

1. The cryoscopic behavior of HNF_2 in concentrated sulfuric acid solutions has been measured. The average of the values for the molecular weight of HNF_2 was 52.7 compared to the calculated formula weight of 53. These data indicate that little or no ionization of HNF_2 occurs in H_2SO_4 at room temperature.
2. A kinetic investigation of the reaction of HNF_2 with deuterium oxide is in progress. The results indicate that HNF_2 ionizes slightly in tetrahydrofuran (THF) solutions. The ionization constant is lower than that of water.
3. A similar investigation of the isotopic exchange of ClNF_2 with HCl has been initiated. It has been demonstrated that there is little or no exchange in the gaseous state. This indicates no ionization of ClNF_2 into chloride ions in the gaseous phase. Further experimentation in solution is planned.
4. An investigation of the conductivity of ClNF_2 in nitrobenzene solution is in progress. Although the conductivity of nitrobenzene increases when ClNF_2 is dissolved into the liquid, the increase in conductivity is irreversible and is probably best explained by chemical decomposition reactions rather than ionization of ClNF_2 .

RESULTS AND DISCUSSION

Cryoscopic Studies

The technique was described in a previous report.¹ The objective was to determine the molecular weight of HNF_2 in H_2SO_4 in order to detect ionization. This study has now been completed and the conclusion is that HNF_2 does not ionize in H_2SO_4 to any appreciable extent.

The results are summarized in Table I.

Table I - Molecular Weight Determination of HNF₂ in H₂SO₄

<u>mmoles HNF₂</u>	<u>f.p. Depression</u>	<u>M</u>	<u>mmoles HNF₂ Cumulative</u>	<u>Δt Cumulative</u>	<u>M</u>
1.04	0.036	47.7	1.95 3.25	0.061 0.101	52.7 53.1
0.91	0.025	60.0			
1.30	0.040	53.6			
	Avg.	53.8			
1.75	0.055	50.4	3.90 6.71	0.125 0.205	49.4 51.8
2.15	0.070	48.7			
2.81	0.080	55.7			
	Avg.	51.6			

Each of the two runs shown in Table I consisted of three successive additives of HNF₂. While there is considerable variation among the individual additives, the overall values are quite close to the monomeric molecular weight of HNF₂.

Isotopic Exchange of Hydrogen Between HNF₂ and H₂O

The kinetics of the exchange reaction $\text{HNF}_2 + \text{D}_2\text{O} = \text{DNF}_2 + \text{H}_2\text{O}$ have now been determined. The reaction is 1st order with respect to HNF₂ and zero order with respect to D₂O. The rate-determining step is the dissociation of HNF₂. The most probable mechanism is the ionization of HNF₂ into H⁺ and NF₂⁻ ions.

The results of the exchange runs are summarized in Table II.

Table II - Isotopic Exchange Runs (-20° in THF-d₈)

<u>(D₂O) m/l</u>	<u>(HNF₂) m/l</u>	<u>t ½ (min.)</u>	<u>R (moles) liter-min</u>	<u>R/(H₂F₂)</u>
0.64	1.18	13.4	0.060	0.051
1.27	1.28	9.2	0.064	0.050
1.91	1.16	9.8	0.063	0.054
1.40	0.69	11.3	0.034	0.049
1.38	2.08	10.3	0.080	0.038
1.31	1.87	10.3	0.073	0.039
1.04	0.28	14.1	0.012	0.043
				Avg. 0.046±.005

The techniques used to obtain this data are described in a previous report.¹

We plan to test for acid catalysis and to make several runs at another temperature in order to determine the activation energy.

The fact that the exchange is first order in HNF_2 and zero order in H_2O indicates that HNF_2 is less ionized than H_2O . We plan to investigate the exchange of HNF_2 with several deuterated alcohols having smaller ionization constants than H_2O . If the exchange with an alcohol should be 1st order in alcohol and zero order in HNF_2 , then we would be able to bracket the ionization constant of HNF_2 .

Chlorine Exchange Between HCl and ClNF_2

This study is analogous to the hydrogen exchange reaction discussed above. If ClNF_2 will exchange Cl with some ionic chloride and if this exchange is first order in ClNF_2 and zero order in chloride, then the rate-determining step would be the dissociation of ClNF_2 . In this manner it may be possible to determine if ClNF_2 will ionize into Cl^- and NF_2^+ ions. Lack of exchange will prove the absence of Cl^- ions. Chlorine exchange can be followed by using tagged chlorine. The common isotope used for this purpose is Cl^{36} which has a half-life of 4.4×10^5 years. It decays by beta emission with an energy of 0.7 MEV.

Labelled HCl has been obtained and diluted to a useful level of activity. We are counting this as AgCl using a proportional counter. The AgCl samples are prepared by the method of Hahn et.al.² The self absorption curve for AgCl has been determined as well as the specific activity of the HCl^{36} .

The first exchange reaction tried was HCl with ClNF_2 in the gas phase. After 10 days at 25° less than 1% exchange was observed. Separation was accomplished by passing the mixture through an Ascarite column. The ClNF_2 was then condensed into a tube containing AgNO_3 and HNO_3 . The resulting AgCl was counted.

We would like to study this exchange in a solvent and are actively searching for a suitable solvent. Some solubilities which we have recently measured are shown in Table III.

Table III - Solubility of ClNF_2 in 100 g. Solvent at 25°

<u>Solvent</u>	<u>Sol. g/100 g.</u>	<u>Pressure (cm)</u>
ONO_2	0.12	10
dioxane	0.07	20
0.1N NaOH	0.07	20
H_2O	decomposed to N_2	
Et_2O	>1 g could not recovery by vacuum distillation	

Of these solvents ether appears promising provided the system is stable. Carbon tetrachloride is another solvent that may prove useful. By running the exchange in a solvent in which chloride ions are known to exist, we should be able to determine whether ClNF_2 will ionize into Cl^- and NF_2^+ ions.

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It is unfortunate that fluorine has no convenient isotope for studying fluorine exchange. The only stable isotope is F^{19} and the longest-lived radio isotope is the 112 minute F^{18} . Thus, there is no convenient way to follow the potentially interesting exchange of F between $ClNF_2$ and an ionic fluoride.

Conductivity of $ClNF_2$ in Nitrobenzene Solution

Results of previously reported experiments have indicated that $ClNF_2$ reacts slowly with protonic solvents, producing hydrogen chloride. This gradual formation of hydrogen chloride readily explains the observed increase in electrical conductivity of these solutions over periods of several hours, but it also obscures the effects of any ionization of $ClNF_2$ in the solvent. In order to observe a conductivity change resulting from ionization of $ClNF_2$, one should use an aprotic solvent with low electrical conductivity and a fairly high dielectric constant. Nitrobenzene fits these requirements and has been used in a series of conductivity experiments.

In the first experiments with nitrobenzene as solvent, conductivities of the purified solvent were measured at about $3 \times 10^{-7} \text{ohm}^{-1}\text{cm}^{-1}$, compared to $1 \times 10^{-10} \text{ohm}^{-1}\text{cm}^{-1}$ reported by Kraus and co-workers. The electrical conductivity of a solution of $ClNF_2$ in this solvent was observed to increase gradually, similar to solutions in protonic solvents. However, the observed behavior may have been due to the presence of the traces of impurities which were responsible for the high conductivity of the solvent rather than to any interaction between $ClNF_2$ and nitrobenzene.

By the use of the purification method given by Witschonke and Kraus [J. Am. Chem. Soc., 69, 2472-81 (1947)], samples of nitrobenzene have been prepared with specific conductances as low as $5 \times 10^{-10} \text{ohm}^{-1}\text{cm}^{-1}$. It was observed, however, that a conductivity cell which was satisfactory for use at atmospheric pressure might leak sufficiently under vacuum to cause an increase of two or three orders of magnitude in the specific conductance of nitrobenzene. The leaks always occurred in the platinum-to-Pyrex seals used for conducting the electrical leads into the cell. These could be sealed with a pool of mercury for most purposes, but not for this work because of the rapid reaction that occurs between mercury and $ClNF_2$.

A vacuum tight metal-to-glass seal was made by welding a nickel bead to a 20 gauge tungsten wire, welding a short piece of platinum wire to the nickel bead, and then making a standard tungsten-to-Pyrex seal and extending the glass bead down past the nickel bead and along the platinum wire for about 5 mm.

When $ClNF_2$ at a pressure of 255 mm Hg was admitted to the cell containing 4.64 g nitrobenzene the specific conductance increased from $6.22 \times 10^{-10} \text{ohm}^{-1}\text{cm}^{-1}$ to $1.58 \times 10^{-8} \text{ohm}^{-1}\text{cm}^{-1}$ during the first three minutes and to $2.11 \times 10^{-7} \text{ohm}^{-1}\text{cm}^{-1}$ during the next seven minutes. The pressure drop during that period indicated that about 3% (0.03 millimole) of the $ClNF_2$ sample had passed into solution. At that point in the experiment the gaseous $ClNF_2$ was condensed in a trap at -196°C in an

effort to reverse the conductivity trend by removing ClNF_2 from solution. Measurement of the gas collected over a period of one hour showed that 98% of the original sample had been recovered. However, no decrease in electrical conductivity was observed; instead, the conductivity slowly increased to $1.2 \times 10^{-6} \text{ohm}^{-1} \text{cm}^{-1}$ after 90 minutes and to $1 \times 10^{-5} \text{ohm}^{-1} \text{cm}^{-1}$ after seven days. The infrared spectrum of the recovered ClNF_2 was identical to that of the starting material.

1.

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Results of experiments on ClNF_2 in nitrobenzene are inconclusive. An increase in conductivity resulting from ionization of ClNF_2 should occur immediately upon dissolution and should be reversed by withdrawal of the ClNF_2 from solution. However, if the rates of dissolution and removal of ClNF_2 are slow, the changes in conductivity caused by changes in the concentration of conducting species resulting from the ionization of ClNF_2 could be obscured by changes resulting from chemical reaction of ClNF_2 with the solvent or traces of impurities in the system. The fact that the solution remains very weakly conducting after several days suggests that traces of impurities, such as adsorbed water, may be responsible for the observed change in conductivity.

A cell is now being constructed which will allow better stirring of the solution during the conductivity experiment. More rigorous cleaning and drying of the cell will be attempted in order to eliminate traces of impurities.

REFERENCES

1. Ethyl Corporation, Annual Technical Summary Report No. 1, Contract No. AF04(611)9376, June 1964.
2. M. Kahn, A. J. Freeman, R. D. Feltham, and M. L. Lark, Nucleonics 13, No. 5, 58 (1955).