HIGH ENERGY OXIDIZERS

CONTRACT Nonr-4019(00)

Project NR 093-035

Richmond Research Center
Richmond, California

No DDC limit

STAUFFER CHEMICAL COMPANY
Richmond Research Center
Richmond, California

"HIGH ENERGY OXIDIZERS"

CONTRACT Nonr-4019(00)

Project NR 093-035

ARPA No. 399-62

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Annual Technical Summary Report

for the Period February 1, 1964 to January 31, 1965

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Foreword

This is the second annual Technical Summary Report of the investigation of complexes based on chlorinefluorides. It covers the period from February 1, 1964 to January 31, 1965. The work was conducted at the Richmond Research Center, Richmond, California, of Stauffer Chemical Company, under the sponsorship of the Advanced Research Projects Agency. The work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer, under ARPA No. 399-62.

Abstract

The structural investigation of the difluorochlorinium cation, ClF_2^+, was completed. Infrared spectra of $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$ proved that the ClF_2^+ cation is bent and not linear. The synthesis of difluorochlorinium complexes containing high-energy anions, such as NO_3^-, N_2OF^-, ClO_4^- or ClO_3^-, was approached from different directions. No indication could be obtained for the existence of the stable compounds, $ClF_2^+NO_3^-$, $ClF_2^+N_2OF^-$, $ClF_2^+ClO_4^-$ or $ClF_2^+ClO_3^-$.

A new oxidizer species based on chlorine fluorides, the difluorochlorate (I) anion, ClF_2^-, has successfully been prepared in the form of its nitrosyl salt. Nitrosyl fluoride reacts with chlorine monofluoride in a 1:1 mole ratio, forming a white solid at -78°, which is completely dissociated in the gas phase at 25°. A pressure-temperature curve gives a heat of reaction, 15.5 kcal $mole^{-1}$, for the dissociation process: complex (s) = NOF (g) + ClF (g). Conductivity and infrared measurements indicate that the complex is ionic in solution and in the solid state, respectively. From these results, the structure, $NO^+ClF_2^-$, is assigned to the solid complex, the ClF_2^- anion (point group $D\infty h$) having a probable trigonal bipyramidal structure (sp^3d-hybrid) with the chlorine atom at the center, the two fluorine atoms at the apexes, and the three free electron-pairs at the remaining corners.

Nitrogen trifluoride, AsF_5, and elementary fluorine under different reaction conditions failed to produce the desired $NF_4^+AsF_6^-$. The only new compound obtained in this reaction was $Ni(AsF_6)_2$ due to interaction of the starting materials with the monel container.

I. Introduction

The preparation, properties and ionic character of the ClF_2^+ complexes were studied during the first year of this contract. This report covers the second year of this contract. The aim for this period was (i) to investigate the structure of the ClF_2^+ cation, (ii) to replace the anions in the known complexes by anions of higher energy content, and, if possible, (iii) to prepare a new ionic species based on chlorine fluorides.

Aims i and iii were successfully achieved. The results of this work are written in the form of two papers, which have been accepted for publication in "Inorganic Chemistry" and "Zeitschrift für anorg. und allg. Chemie". The latter contains the paper, given in the last annual report, plus additional investigation, proving the structure of the ClF_2^+ cation.

A discussion of the results of ii and incomplete work under iii is presented in the appendix.

II. Manuscript of Paper

Ionic Complexes Containing the Difluorochlorinium Cation

(Accepted for publication in Zeitschrift für anorg. und allg. Chemie)

IONIC COMPLEXES CONTAINING THE DIFLUOROCHLORINIUM CATION

By K. O. Christe and A. E. Pavlath

With 1 Figure

SUMMARY

The 1:1 adducts between ClF_3 and the Lewis acids, BF_3, PF_5, AsF_5, and SbF_5 were investigated. The existence of these complexes in the ionic form, in both the solid form and in solvents, such as IF_5 and ClF_3, was proven by IR, conductivity measurements, conductometric titration, and freezing point depression. It could be shown that the difluorochlorinium cation is bent and not linear.

The existence of stable one to one adducts of ClF_3 with PF_5, BF_3, AsF_5, and SbF_5 was first shown by one of us[1]. Later we used these complexes for the electrophilic fluorination of aromatic compounds[2]. Additional work has been done by Seel and Detmer[3,4], who prepared the $ClF_3 \cdot AsF_5$ and $ClF_3 \cdot SbF_5$ complexes. They postulated an ionic structure for these complexes, but this conclusion was supported only by conductivity measurements. An adduct between ClF_3 and PtF_5 has been described also[5], but no comments were made on the possible structure of the compound. Recently, Selig and Shamir[6] investigated the $ClF_3 \cdot BF_3$ complex and suggested the ionic form. The purpose of our investigation was to obtain further evi-

dence for the ionic structure of these complexes and to investigate the structure of the difluorochlorinium cation itself.

Vapor pressure measurements: For $ClF_2^+PF_6^-$ (not yet reported), a heat of dissociation, $\Delta H^\circ_{dissc.} = 16.4$ kcal mole^{-1}, was obtained from the slope of the dissociation pressure curve,

$$\log P_{mm} = 10.53 - 1798\ T^{-1}$$

This value is less than that obtained for $ClF_2^+BF_4^-$, $\Delta H^\circ_{dissc.} = 23.6$ kcal mole^{-1} [6]. Therefore, the stability of the ClF_2^+ complexes, depending on the nature of the anion, increases in the order $PF_6^- < BF_4^- < AsF_6^- < SbF_6^-$.

The conductivity measurements of the complexes in ClF_3 are strong evidence for the presence of ions. A quantitative proof was obtained by conductometric titration of $(ClF_2)^+(AsF_6)^-$ with $K^+(IF_6)^-$ in IF_5 as a solvent:

$$(ClF_2)^+(AsF_6)^- + K^+(IF_6)^- \longrightarrow ClF_3 + IF_5 + K^+(AsF_6)^-.$$

Both the $(ClF_2)^+$ and the $(IF_6)^-$ ions are conductant, but ClF_3 and IF_5 are not, either separately or in mixture. Therefore, the conductance should increase markedly after reaching the equivalence point. The observed titration curve showed a sharp bend at 4.93 ml. Chlorinetrifluoride is not capable of replacing the K^+ with the ClF_2^+, as could be shown by the preparation of $K^+(AsF_6)^-$ from $K^+(AsF_4)^-$ and an excess of ClF_3 (see experimental part), so that a conductivity titration of the ClF_2^+ with K^+ is really meaningful.

Freezing point depression: IF_5 was found to be the most suitable solvent for this investigation. The molal freezing point depression of IF_5 was determined with $K^+(IF_6)^-$ and found to be 7.165°C. mole^{-1}. $K^+(IF_6)^-$ is dissociated in IF_5 solution as could also be shown by its high conductance. In another experiment $(ClF_2)^+(AsF_6)^-$ was dissolved in IF_5 and a freezing point depression of 1.250°C. was observed.

The following freezing point depression and change in the conductance should be expected in the case of:

		ΔT theory	Conductance
A.	Ionic compound, completely dissociated	1.257°C.	conductant
B.	Coordination complex, undissociated	0.628°C.	non-conductant
C.	Decomposition to AsF_5 and ClF_3	1.257°C.	non-conductant

Our experimental results agree with Case A.

The infrared spectra of $(ClF_2)^+(AsF_6)^-$ and $(ClF_2)^+(BF_4)^-$ give strong evidence, that these complexes exist in the ionic form, not only in solvents such as ClF_3 or IF_5, but also in the solid state (see Fig. 1).

Since the known absorptions for the AsF_6^- and BF_4^- were observed and the one to one ratio of the adducts is established, the ClF_3 part of the adduct must be present as ClF_2^+. In addition, two absorptions found in both complexes in the range between 515 and 560 cm^{-1}

must belong to the ClF_2^+ part. Since the highest frequency reported for a deformation vibration of the Cl-F bond is 434 cm^{-1} [7], it is safe to assume that both observed absorptions are stretching modes. Theoretically the ClF_2^+ could either have the symmetry $D_{\infty h}$ (linear sp hybrid + 2 free d-electron pairs) or C_{2v} (bent structure). An XY_2 molecule of symmetry $D_{\infty h}$ would have only one IR active stretching vibration, but XY_2 of symmetry C_{2v} would show 2 IR active stretching vibrations. Therefore, the symmetry C_{2v} has to be favored in our case and it can be assumed that the ClF_2^+ has a bent structure.

EXPERIMENTAL

Preparation of the ClF_3-complexes: All compounds were prepared in a glass vacuum line under anhydrous conditions. The starting materials were commercial products, which were purified by repeated fractionation. Chlorinetrifluoride was always treated for several hours with NaF in order to take out any HF present. All other operations were done in a glove box in a dry nitrogen atmosphere.

The ClF_3-complexes were prepared by condensing the purified starting materials such as ClF_3 and BF_3, PF_5, AsF_5 or SbF_5 together into a trap at -196°C. The more volatile compound was always used in excess. The mixture was warmed up until reaction occurred and the excess of the more volatile compound was pumped off.

The ClF_3-AsF_5 and ClF_3-SbF_5 adducts also were prepared by using

AsF_3 and SbF_3 instead of AsF_5 and SbF_5 as starting materials. In both cases an excess of ClF_3 had to be used in order to oxidize the As^{3+} or Sb^{3+} to the pentavalent state.

Preparation of $K^+(AsF_6)^-$: The preparation of this compound, which was described in the literature[8], was modified in the following way:

$$AsF_3 + KF \longrightarrow K^+(AsF_4)^- \xrightarrow{+ ClF_3} K^+(AsF_6)^-$$

Arsenictrifluoride and ClF_3 were applied in excess, which were pumped off respectively after the completion of each reaction. This clearly shows, that the ClF_3 is not capable of replacing the K^+ with the ClF_2^+. Analysis of $K^+(AsF_6)^-$: Calcd.: F, 50.0, K, 17.1, As 32.9; Found: F, 49.1, K, 17.1, As, 32.7.

Conductivity measurements: The conductivity measurements were carried out in a cell, which was attached to the vacuum line through joints and could be closed by stopcocks. The electrodes consisted of platinized platinum. An excess of ClF_3 was used as a solvent. The concentration of the complex was determined by measuring the volume of the Lewis acid in the vapor phase before condensing it into the conductivity cell, where it formed the complex with a known amount of ClF_3. The SbF_5 is not volatile enough and therefore was weighed in. The resistance was measured by the combination of a Heathkit decade resistance and a Heathkit capacitor checker, Model IT-11. Table 1 gives the results of these measurements.

Table 1

Conductivity measurements

	Temperature (°C.)	Molarity Mole l^{-1}	κ (ohm^{-1}, cm^{-1})	Λ (ohm^{-1}, cm^{-2})
ClF_3 [8]	0	--	$3 \cdot 10^{-9}$	--
SbF_5 [8]	25	--	$1.2 \cdot 10^{-8}$	--
$ClF_2^+BF_4^-$ in ClF_3	-20	2.12	$4.2 \cdot 10^{-3}$	1.99
$ClF_2^+AsF_6^-$ in ClF_3	-15	2.07	$1.1 \cdot 10^{-2}$	5.31
$ClF_2^+SbF_6^-$ in ClF_3	-15	0.67	$2.1 \cdot 10^{-3}$	3.14

Conductometric titration: A solution of $(ClF_2)^+(AsF_6)^-$ in IF_5 was titrated with a solution of $K^+(IF_6)^-$ in IF_5. The conductometric cell was modified in such a way, that it was connected to a burette and that the titration could be carried out in a closed system with the exclusion of moisture. The solution of $K^+(IF_6)^-$ in IF_5 was prepared in the dry box by adding 0.1948 g. of KF to 93.46 g. of IF_5. The density of IF_5 is given by the equation: $d = 4.38-0.004\ T$ [9]. From this the density was calculated to be 3.20 g./cm^3 at 296°K. This gives a concentration of 6.7 mg KF/ml. The $(ClF_2)^+(AsF_6)^-$ (0.1460 g.) was dissolved in 48.1 g. of IF_5. The titer needed for reaching the equivalence point was calculated to be 4.84 ml. The result of the conductometric titration was 4.93 ml. of $K^+(IF_6)^-$ titer solution added.

Freezing point depression: IF_5 was used as a solvent for the freezing point depression measurements. Standard glass equipment provided with a magnetic stirrer and a Beckmann thermometer was used. The molar freezing point depression of IF_5 was determined with $K^+(IF_6)^-$. For this purpose 0.1137 g. of KF were dissolved in 23.55 g. of IF_5. A freezing point depression of 1.213°C. was observed. Since KF forms $K^+(IF_6)^-$ with IF_5, only 23.12 g. of IF_5 can be counted as a solvent. This result gave a molal freezing point depression for IF_5 of 7.615°C. The $(ClF_2)^+(AsF_6)^-$ (0.5748 g.) was dissolved in 24.99 g. of IF_5 and gave a freezing point depression of 1.250°C. The solution showed a strong increase in its conductivity compared with pure IF_5.

Infrared Spectra: A Beckman IR-9 all grating instrument was used for this investigation covering a range from 400 to 4000 cm^{-1}. The spectra in the vapor phase were taken in a 10 cm. gas cell with IR-Tran 2 windows (from 4000-710 cm^{-1}), AgCl and KBr windows (from 710-400 cm^{-1}). The KBr windows were coated with a very thin film of Teflon grease. The spectra of the solid complexes were taken at -196°C. in an IR cell with a cooled center window on which the complexes were sublimed. The spectrum of $K^+(AsF_6)^-$ was taken as a KBr pellet. Table 2 gives the results of this investigation.

X-Ray Studies: The Debye Scherrer powder diagram of $(ClF_2)^+(AsF_6)^-$ was taken in Lindemann glass tubes of 0.5 mm diameter. The samples

Table 2

IR-Investigation

$(ClF_2)^+(BF_4)^-$	$(ClF_2)^+(AsF_6)^-$	$KAsF_6$	$ClF_3(g)$[7]	$ClF_3(s)$	$AsF_5(g)$[10]	$AsF_5(s)$
	405 s (δAsF_6^-)	413 ms (δAsF_6^-)			409 s	404 m
				499 m	488 w	
				508 m		
518 m ($\nu_s ClF_2^+$)	519 m ($\nu_s ClF_2^+$)		518 s			
			535 s			
536 m ($\nu_{as} ClF_2^+$)	558 m ($\nu_{as} ClF_2^+$)			604, 630 vs		
	688	685	694			
	703 vs (νAsF_6^-)	705 vs (νAsF_6^-)	703 vs			
			713			725 vs
	729	725				738 vs
			741 s			
762 m			761 s	765 m		
793 ms				770 w	786 vs	
					811 vs	
					818 m	814 vs
					858 w	
					866 w	
						891 w
			957 m			977 w
1005, 1036 vs (νBF_4^-)			1022 m		1023 w	
						1101 vw
						1127 w
			1223 s			1201 w
	1284 vw		1273 w			
	1298 w					
			1451 s			
			1466 s			
			1488 s			
			1505 s			

were prepared in the dry box. Copper-K_α radiation with Ni filter was used. The data are given in Table 3.

Table 3

Powder diagram of $(ClF_2)^+(AsF_6)^-$

Intensity	dA°	Intensity	dA°
strong	5.34	weak	2.49
weak	4.84	very weak	2.42
very strong	4.21	very weak	2.097
weak	3.81	weak	2.070
medium	3.72	very weak	2.013
medium	3.21	weak	1.826
weak	3.02	weak	1.786
very weak	2.75	very weak	1.663
very weak	2.67	very weak	1.627

NMR: A Varian HR 60 spectrometer was used for the F^{19} nuclear magnetic resonance. The spectra were run at temperatures between -80°C. and +20°C. The samples were prepared in the vacuum line. Different solvents such as ClF_3, BrF_5, and SO_3 were used, but no fine structure could be obtained, due to rapid intermolecular fluorine exchange. A strong chemical shift 800-4000 cps related to pure ClF_3 was observed in all cases.

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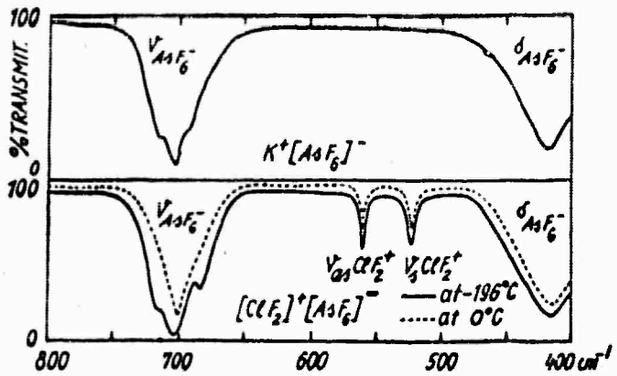

Fig. 1. Infrared spectrum of $K^+[AsF_6]^-$ and $[ClF_2]^+[AsF_6]^-$ at 0 and −196 °C.

II. Manuscript of Paper

The Difluorochlorate (I) Anion, ClF_2^-

(Accepted for Publication in Inorganic Chemistry)

Contribution from the Richmond Research Center,
Stauffer Chemical Company, Richmond, California

The Difluorochlorate(I) Anion, ClF_2^-

By K. O. Christe and J. P. Guertin

ABSTRACT

The difluorochlorate(I) anion, ClF_2^-, a new oxidizer species based on chlorine fluorides, has successfully been prepared in the form of its nitrosyl salt. Nitrosyl fluoride reacts with chlorine monofluoride in a 1:1 mole ratio, forming a white solid at -78°, which is completely dissociated in the gas phase at 25°. A pressure-temperature curve gives a heat of reaction, 15.5 kcal $mole^{-1}$, for the dissociation process: complex (s) = NOF (g) + ClF (g). Conductivity and infrared measurements indicate that the complex is ionic in solution and in the solid state, respectively. From these results, the structure, $NO^+ClF_2^-$, is assigned to the solid complex, the ClF_2^- anion (point group $D_{\infty h}$) having a probable trigonal bipyramidal structure (sp^3d-hybrid) with the chlorine atom at the center, the two fluorine atoms at the apexes, and the three free electron-pairs at the remaining corners.

INTRODUCTION

Self ionization has been postulated for certain halogen fluorides, such as BrF_3[11], in addition to their ability to behave as strong ionizing solvents. However, in the case of chlorine trifluoride, the self ionization of the pure compound must be considered to be very small, as shown by its low conductivity[11]. Association through fluorine bridging seems to be preferred over self ionization[12]. In addition, there is n.m.r. evidence[13], that the fluorine exchange in ClF_3 might be caused by trace quantities of HF present as impurity. Yet, ClF_3 can act as an ionizing solvent towards strong Lewis acids, such as AsF_5, SbF_5[14-16], BF_3[17], PF_5[16], and PtF_5[18], forming the ClF_2^+ cation, or towards Lewis bases, such as NOF[19], KF, RbF, and CsF[20-22], forming the ClF_4^- anion, as shown by the following equations,

$$ClF_3 + A = ClF_2^+ + AF^-$$

$$ClF_3 + ZF = Z^+ + ClF_4^-$$

where A and ZF are a Lewis acid and a Lewis base, respectively.

In the case of chlorine monofluoride, the existence of the corresponding Lewis acid, Cl^+ [23], is known; however, the existence of the Lewis base, ClF_2^-, has not been reported. With the object of similarly establishing ClF as an ionizing solvent represented by the equations,

$$ClF + A = Cl^+ + AF^-$$

$$ClF + ZF = Z^+ + ClF_2^-$$

we have investigated the interaction of ClF with NOF. This research is part of a general investigation of complexes based on chlorine fluorides.

EXPERIMENTAL

Materials. - The materials used in this work were manipulated in a standard pyrex-glass high-vacuum system which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Chlorine monofluoride and NOF (both from Ozark-Mahoning Company) were purified by several low-temperature vacuum distillations. Little etching could be observed in the vacuum line. The purity of the volatile compounds was determined by measurements of their vapor pressures, molecular weights (M), and infrared spectra.

Infrared Spectra. - All infrared spectra were recorded on a Beckman Model IR-9 grating spectrophotometer in the range 4000-420 cm^{-1}. Pyrex glass cells equipped with AgCl windows were used for all spectra. The infrared spectrum of solid $NO^+ClF_2^-$ was taken by condensing the complex onto the internal AgCl plate (cooled with liquid nitrogen) of a low-temperature infrared cell.

Preparation of $NO^+ClF_2^-$. - In a typical experiment, ClF (11.25 mmole) was combined in a vacuum with NOF (7.33 mmole) at -196°. The

mixture was slowly warmed to 0°, kept at that temperature for 15 minutes, and finally cooled slowly to -120°. Unreacted ClF (3.99 mmole) was recovered by distillation at -120°. Therefore, NOF (7.33 mmole) had reacted with ClF (7.26 mmole) in a mole ratio of 1.01:1, producing the complex, $NO^{+}ClF_2^{-}$.

Infrared and molecular weight measurements showed that the gas phase in equilibrium with the solid complex at -45° consisted of ClF and NOF in a 1:1 mole ratio. (Found: intensity of NOF peak corresponds to exactly half the total sample pressure. Found: M, 51.5. Calcd. for ClF: 54.5; for NOF: 49.0; for an average assuming 1:1 mole ratio: 51.7; for $NOClF_2$: 103.5.)

A sample of the complex (~1 g.) was condensed into a weighed pyrex tube equipped with a capillary arm. The tube was sealed off, quickly weighed and cooled again to -196°. The capillary was broken, the tube was warmed to 25°, and the complex slowly hydrolyzed in 5% NaOH.

Anal. Calcd. for $NOClF_2$: N, 13.5; Cl, 34.3; F, 36.7

Found: N, 12.9; Cl, 32.3; F, 36.0

Dissociation Pressure Measurements. - The complex was prepared directly in a LeRoy still[24], the temperature of which could be controlled and measured to ± 0.2°. Pressures were measured (to an accuracy of ± 0.1 mm) in the absence of mercury with a delicate soft glass spoon gauge used as a null indicator. To be certain

that an equilibrium existed at each temperature reading, a sample of the gas above the solid complex was pumped off and a constant pressure was re-established. True equilibrium existed at a given temperature if the pressure before and after the pumping off procedure were identical. Pressure-temperature measurements were made until the complex decomposed irreversibly, as evident by the failure to observe identical pressures before and after the pumping off operation and by the formation of a brown colored gas at pressures greater than 100 mm (probably due to interaction with the glass). Equilibrium pressures were approached from above as well as below a given temperature. A plot was made of log ($pressure_{mm}$) vs. reciprocal temperature and the "heat of dissociation", $\Delta H^{\circ}_{dissc.}$[25] (estimated accuracy, $\pm$ 0.3 kcal $mole^{-1}$) of $NO^{+}ClF_2^{-}$ was found from its slope.

Conductivity Measurements. - The conductivity measurements were taken using a Heathkit decade resistance (Model IN-11), a Heathkit capacitor checker (Model IT-11), and a pyrex cell having a cell constant of 12.4. The apparatus had a conductivity range of 3×10^{-9} to 8×10^{-2} ohm^{-1} cm^{-1}. The cell contained two platinized platinum electrodes and was connected to the vacuum system. Pure ClF and NOF were condensed into the cell in a mole ratio of 1:370 (measured volumetrically) and the obtained molality was converted into molarity using the equation, reported in the literature[26], for the density of liquid NOF.

RESULTS

Synthesis. - Nitrosyl fluoride and ClF (either one in excess) when mixed together in a vacuum at -78° produced the 1:1 complex, $NO^+ClF_2^-$, a white solid, the light blue color of liquid NOF and the faint yellow color of liquid ClF disappearing. Quantitative vacuum synthesis and elemental analysis of the solid complex, molecular weight and infrared measurements of the gas phase above the solid complex, clearly indicate a 1:1 combining ratio, the latter measurements showing that the complex is completely dissociated in the gas phase at 25°.

Thermochemical Properties. - Based on the following observed data: (Temperature [°C], Pressure [mm]): (-103.7, 0.5), (-96.5, 1.1), (-90.4, 2.3), (-83.8, 4.6), (-76.5, 10.5), (-68.7, 20.8), (-63.0, 36.8), (-55.9, 68.0), (-51.2, 100.0), a plot of log P_{mm} vs. T^{-1} for the heterogeneous equilibrium,

$$NO^+ClF_2^- \text{ (s)} = NOF \text{ (g)} + ClF \text{ (g)}$$

is a straight line. The equation,

$$\log K_{P(atm)} = \log \left(\frac{P^2_{atm}}{4}\right) = -\frac{15.5 \times 10^3}{2.3\ RT} + \frac{59.3}{2.3\ R}$$

represents this dissociation data in the temperature range -105 to -50°. At temperatures less than -50°, dissociation pressures were reproducible whether the temperature was increasing or decreasing. At temperatures greater than -50°, the dissociation pressure of the

complex is apparently sufficiently large to cause appreciable interaction of NOF with the glass apparatus, irreversibly forming some NO_2. This was evident from the red-brown colored gas formed inside the apparatus and from the inability to reproduce the dissociation pressure readings previously taken at temperatures less than -50°.

By extrapolation, a dissociation pressure of 760 mm was obtained at -22°. A $\Delta H^\circ_{dissc.}$ = 15.5 kcal mole^{-1} was found from the slope of the log P_{mm} vs. T^{-1} curve. From $\Delta F^\circ_T = -RT \ln K_{p(atm)}$, a free energy change, ΔF°_{298} = -2.1 kcal mole^{-1}, and from $\Delta S^\circ_T = (\Delta H^\circ - \Delta F^\circ_T)T^{-1}$, an entropy change, ΔS°_{298} = 59.3 cal deg^{-1} mole^{-1}, were found for the dissociation process at 25°. A heat of formation, $\Delta H^\circ_{f\ 298,\ NO^+ClF_2^-\ (s)}$ = -44.7 kcal mole^{-1}, was calculated.

Conductivity. - Since $NO^+ClF_2^-$ had a very low solubility in liquid ClF at -120°, conductivity measurements were made on the complex in liquid NOF at -79°. Table I shows the results of these measurements.

TABLE I

Conductivity of $NO^+ClF_2^-$ in Liquid NOF

Compound	Temp., °C	Specific Conductance, σ ohm^{-1} cm^{-1}
ClF	-128	1.9 X 10^{-7}
NOF	-79	5.4 X 10^{-5}
$NO^+ClF_2^-$ in liquid NOF	-79	3.4 X 10^{-4}

The solution containing $NO^+ClF_2^-$ had a molarity of 0.076 mole l^{-1} from which an equivalent conductance, $\Lambda = 4.48$ ohm^{-1} cm^2, was calculated.

$NO^+ClF_2^-$ Infrared Spectrum. - Fig. 1 shows the low-temperature infrared spectrum of solid $NO^+ClF_2^-$. Comparison of the absorption frequencies of NOF, ClF, and the complex is given in Table II.

Some difficulty was encountered if the complex had been prepared from excess NOF. A third absorption band, broad and of medium intensity, would occur at about 2000 cm^{-1}. This was deemed due to an impurity (probably solid NOF) since its intensity ratio varied each time a different sample was used. However, by preparing the complex using excess ClF and subsequently removing this excess, this impurity peak could be eliminated.

DISCUSSION

Stability and Properties of $NO^+ClF_2^-$. - The 16-fold increase in specific conductivity when the complex is dissolved in liquid NOF indicates ions in solution. Also, the equivalent conductance, 4.48 ohm^{-1} cm^2, is of the same order of magnitude as that obtained for ionic ClF_2^+ complexes in liquid ClF_3 for similarly high concentrations[16]. The infrared evidence discussed in the next section strongly supports an ionic structure for the solid complex. Therefore, the conductivity results are consistent with an ionic complex in liquid NOF.

TABLE II

Comparison of Infrared Absorption Frequencies (cm^{-1})

$NO^+ClF_2^-$	ClF		NOF	
	[illegible][27]	[illegible]	[illegible][28]	solid
			3652m	
			2612m	
			2365m	2358m
2279m, $\nu(N\equiv O^+)$			1844vs, $\nu(N=O)$	1967vs, $\nu(N=O)$
				1883m
	1535vs			
			1290m	1320m
			766vs, $\nu(NF)$	639vs, $\nu(NF)$
635s, $\nu_{asym}(ClF_2^-)$	786s(R) 758s(P)	$\nu(ClF)$ 747, $\nu(ClF)$		
			521vs, $\delta(N=O)$	440-420vs, $\delta(N=O)$

The white solid $NO^+ClF_2^-$ complex is stable at temperatures below -110°, since it has no measurable vapor pressure or dissociation pressure at lower temperatures. It does not appear to have any stable liquid state and is completely dissociated in the gas phase at 25°. A violent reaction occurs when $NO^+ClF_2^-$ is placed into water. It behaves as a powerful oxidizer towards most organic compounds.

Table III shows the heats of dissociation[25] and heats of formation of some similar chlorine fluoride ionic complexes.

Nitrosyl difluorochlorate(I) shows a slightly lower thermal stability than nitrosyl tetrafluorochlorate(III), $NO^+ClF_4^-$. While both complexes possess nearly identical "heats of dissociation", $NO^+ClF_2^-$ and $NO^+ClF_4^-$ have dissociation pressures of 760 mm at -22 and -5°[19], respectively. This small decrease in stability could be due to the decreasing coordination number of the chlorine atom towards the fluorine atoms, assuming factors such as lattice energies, etc., may be neglected. Their "heats of dissociation" are of the same order of magnitude as that of some weaker ionic ClF_2^+ complexes. However, the heats of formation are very dependent on the number of fluorine atoms in the complexes and are not a basis for comparing their stabilities.

<u>$NO^+ClF_2^-$ Infrared Spectrum and Structure</u>. - Three reasonable possible structures for the complex are: coordination complex,

TABLE III

"Heats of Dissociation" and Heats of Formation

of Some Ionic Chlorine Fluoride Complexes

Complex	"Heat of Dissociation", $\Delta H^\circ_{dissc.}$ kcal mole^{-1}	Heat of Formation (Calcd.[a]), $\Delta H^\circ_{f\ 298,\ complex\ (s)}$ kcal mole^{-1}	Temp., °C (at $P_{dissc.}$ = 760 mm)
$NO^+ClF_2^-$	15.5	-44.7	-22
$NO^+ClF_4^-$ [19]	15.8	-70.4	-5
$ClF_2^+PF_6^-$ [16]	16.4	-436.7	-38
$ClF_2^+BF_4^-$ [17]	23.6	-333.3	+9

[a]Data used to calculate $\Delta H^\circ_{f\ 298,\ complex\ (s)}$, kcal mole^{-1}:

$\Delta H^\circ_{f\ 298,\ PF_5\ (g)} = -381.4$[29]; $\Delta H^\circ_{f\ 298,\ BF_3\ (g)} = -270.8$[29];

$\Delta H^\circ_{f\ 298,\ ClF_3\ (g)} = -38.9$[30]; $\Delta H^\circ_{f\ 298,\ ClF\ (g)} = -13.5$[30];

$\Delta H^\circ_{f\ 298,\ NOF\ (g)} = -15.7$[30]

$ClF \cdot NOF$ (I); $Cl^+NOF_2^-$ (II); $NO^+ClF_2^-$ (III). Structure I would require an infrared spectrum similar to that of ClF superimposed on NOF with perhaps some shifting of absorption bands. The NO bond in structures I and II has double bond character and should absorb in the 1900-1800 cm^{-1} region[28]. In structure III the NO bond has triple bond character and should absorb in the 2350-2100 cm^{-1} region[31]. In addition, considering only symmetry, structure II would require six infrared active vibrations (probably only four would be observed under the actual experimental conditions), while structure III would result in either two (for a linear ClF_2^- anion) or three (for a bent ClF_2^- anion) infrared active fundamentals in the range, 4000-420 cm^{-1}.

The infrared spectrum of the solid complex shows only two absorptions, 2279 and 635 cm^{-1}. Also, the band at 2279 cm^{-1} occurs at too high a frequency for an N=O bond and is therefore assigned to the NO^+ cation (triple bond character). For these reasons structures I and II are not valid and structure III is considered correct. The 635 cm^{-1} band is assigned to the asymmetric stretching vibration of the ClF_2^- anion.

The ClF_2^- anion is either linear or bent. If it were linear, it would belong to the point group $D\infty h$, and would show only one infrared active stretching vibration. However, if it belongs to the point group C_{2v} (bent molecule), an asymmetric and symmetric infrared active stretching vibration is expected. Since only one

infrared active stretching vibration was observed, ClF_2^- is most probably linear as are other similar triatomic poly and interhalogen anions, such as I_3^- [32-34,39], ICl_2^- [34-37,39], IBr_2^- [32,39], $ClIBr^-$ [34,38,39], Br_3^-, $ClBr_2^-$, $BrCl_2^-$, and $FIBr^-$ [39].

The difluorochlorate(I) anion contains three free electron-pairs, i.e., the chlorine atom has three filled non-bonded orbitals. Three possible models for a linear ClF_2^- anion are:

(i) sp^3d-hybridization of the orbitals of the chlorine atom resulting in a trigonal bipyramid with the two fluorine atoms at the apexes,

(ii) partial hybridization of the orbitals of the chlorine atom resulting in two bonded sp-hybridized orbitals and three non-bonded non-hybridized orbitals (two p and one d),

(iii) little hybridization of the orbitals of the chlorine atom resulting in two semi-ionic F-Cl bonds[34,37] (greater than 50% ionic) using the same p orbital of the chlorine atom for binding both fluorine atoms. This can be regarded as a resonance hybrid of the structures,

F^- Cl-F and F-Cl F^-.

Model ii is energetically less probable than model i. From nuclear electric quadrupole resonance measurements[37], semi-ionic bonds have been proposed for ICl_2^- provided the bonds are more than 50% ionic. Based on the 21% ionic character reported for ClF[40] and assuming a larger ionic character for ClF_2^- (paralleling ICl and ICl_2^-) model

iii cannot be ruled out. While both model i and model iii result in a linear configuration for the atoms of the ClF_2^- anion, the concepts of model i have been generally more accepted than those of model iii. Thus, Fig. 2 shows the proposed structure of the linear ClF_2^- anion (model i) and its comparison with the known structure of the bent ClF_2^+ cation[16].

The observed absorption of the ClF_2^- at 635 cm^{-1} corresponds to the asymmetric stretching vibration of the apex fluorine atoms in ClF_3 gas at 703 cm^{-1} [41]. It is well known that gaseous ClF_3 is also a trigonal bipyramid[41] although somewhat distorted. The difference of 68 cm^{-1} may be due to this distortion. Replacement of a fluorine atom in ClF_3 by a free electron-pair and the phase difference (solid $NO^+ClF_2^-$, gaseous ClF_3) probably contribute to this shift as well. Therefore, the assignment of 635 cm^{-1} to the asymmetric stretching vibration of the ClF_2^- anion is not unreasonable.

The infrared spectrum of solid NOF shows considerable shifting of fundamentals when compared with the infrared spectrum of gaseous NOF. In the infrared spectrum of solid NOF the N=O bond stretching vibration is shifted 123 cm^{-1} to higher frequency and the N-F bond stretching vibration is shifted 126 cm^{-1} to lower frequency. This indicates a strengthening of the N=O bond and a weakening of the N-F bond. It does not correspond to a complete ionization such as $NO^+NOF_2^-$, but shows that the ionic contributions to the bonds are

becoming more important in the solid state.

Conclusion. - The experimental data reveal that the complex in the solid state has the composition represented by $NO^+ClF_2^-$ and that the ClF_2^- anion is most probably linear.

Acknowledgment. - We thank Dr. A. E. Pavlath for many helpful discussions. This work has been supported by the Advanced Research Project Agency and the Office of Naval Research.

Diagram Captions

Fig. 1. - The low-temperature infrared spectrum of solid $NO^+ClF_2^-$.

Fig. 2. - Structure of ClF_2^- and ClF_2^+.

For ClF_2^-: point group $D_{\infty h}$, sp^3d-hybrid; ν_{asym} = 635 cm^{-1}.

For ClF_2^+: point group C_{2v}, sp^3-hybrid; ν_{asym} = 558 cm^{-1}, ν_{sym} = 519 cm^{-1}.

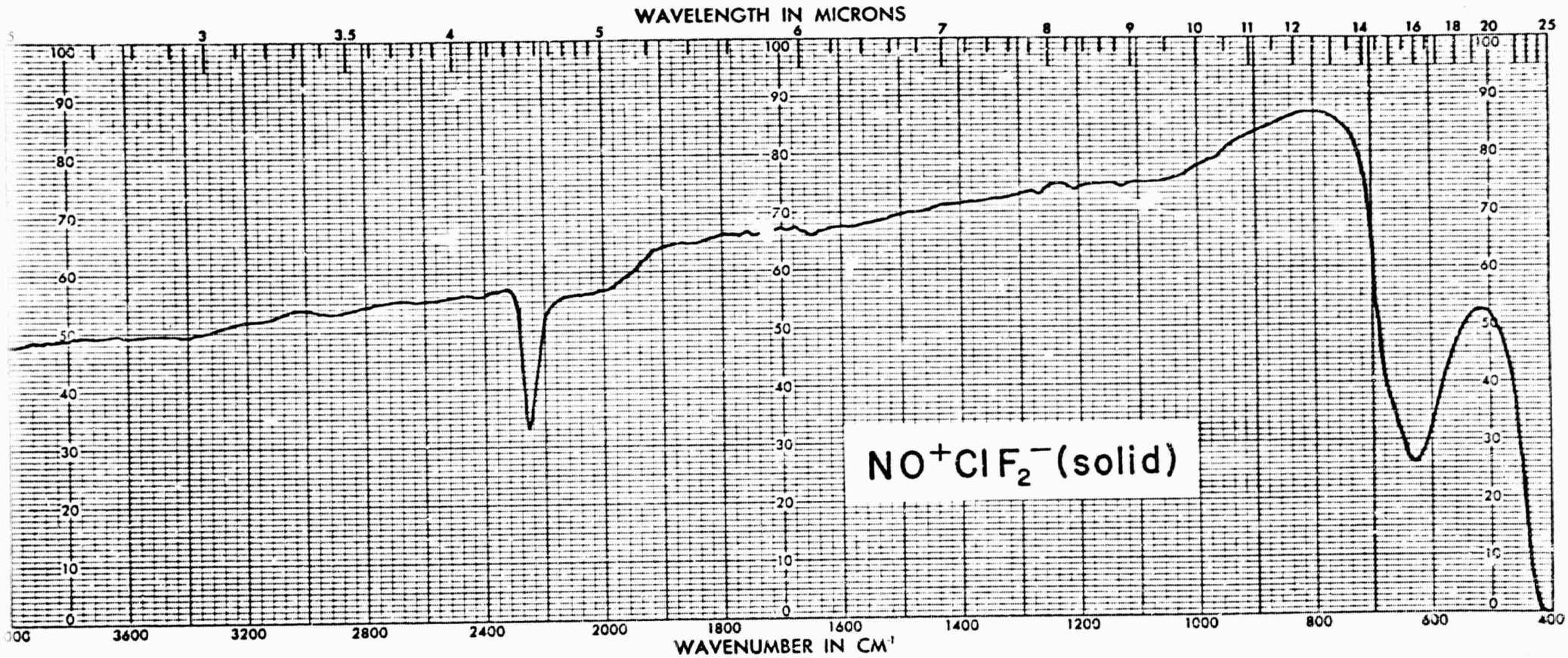
WAVELENGTH IN MICRONS
3
3.5
4
5
6
7
8
9
10
11
12
14
16
18
20
25
100
90
80
70
60
50
40
30
20
10
0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER IN CM⁻¹
NO⁺ClF₂⁻(solid)

FIGURE 1

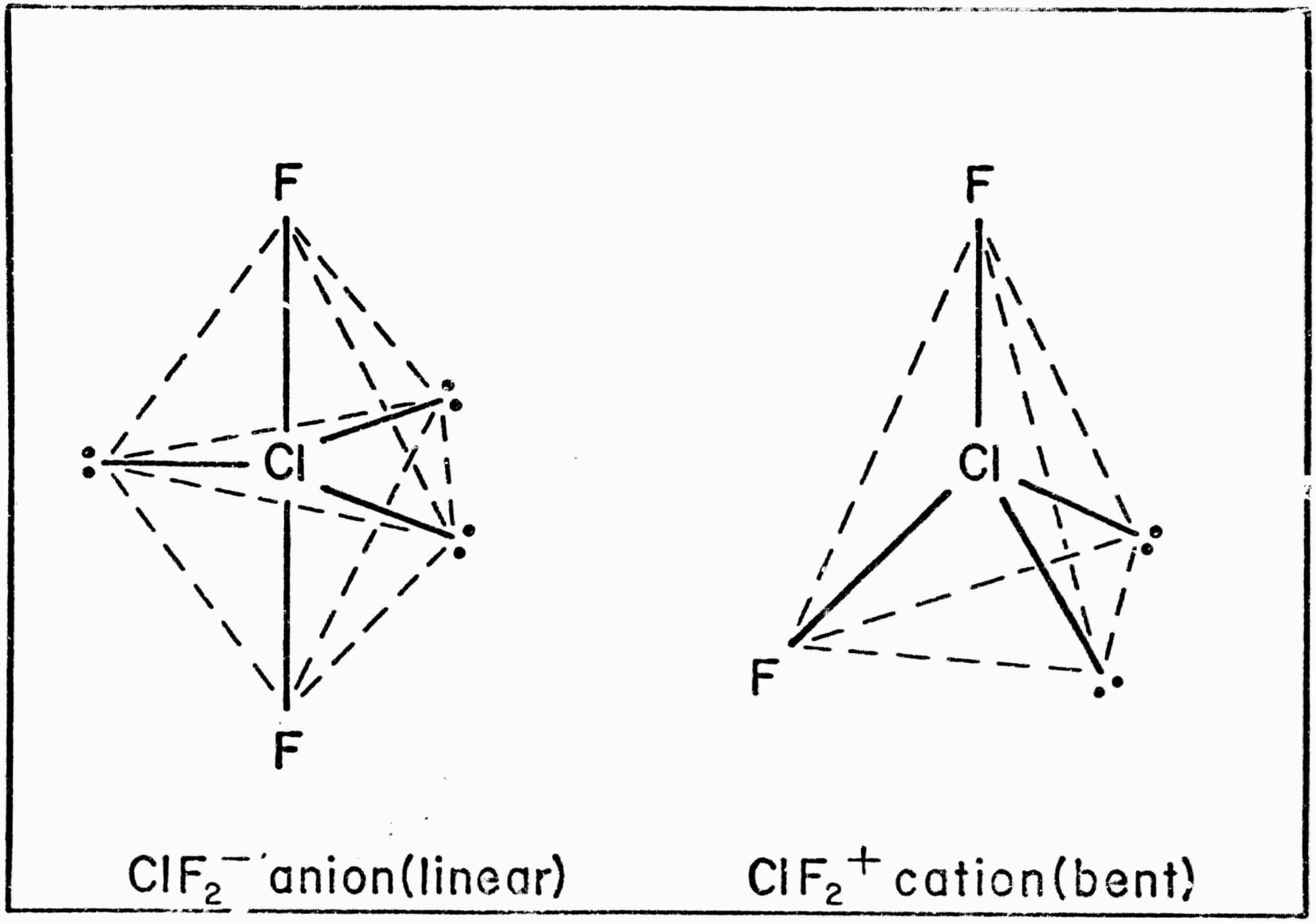

FIGURE 2

IV. Appendix

A. Results and Discussion

1. Attempted Combination of the ClF_2^+ Cation with an Anion of High Energy Content

a. Reaction between ClF_3 and $AgNO_3$

This reaction was carried out in an attempt to prepare $ClF_2^+NO_3^-$ according to the following equation:

$$AgNO_3 + ClF_3 \longrightarrow ClF_2^+NO_3^- + AgF$$

The reaction, however, did not result in $ClF_2^+NO_3^-$, or if it formed it must have been unstable under these conditions and decomposed. Silverdifluoride and NO_2F were identified as the reaction products. Based on this observation, the following equation is suggested tc describe this reaction:

$$2\ AgNO_3 + 3\ ClF_3 \longrightarrow 2\ AgF_2 + 2\ NO_2F + 3\ ClF + O_2$$

b. Reaction between ClF_3 and N_2O_5

The following reaction was desired:

$$NO_2^+NO_3^- + ClF_3 \longrightarrow NO_2F + ClF_2^+NO_3^-$$

The reactants were condensed together at -196°. Upon warming, a vigorous reaction took place as soon as the ClF_3 melted. The volatile products, an yzed by infrared spectroscopy, consisted of NO_2F and excess ClF_3, but no ClF was detected.

A small amount of solid residue was obtained, which was stable at room temperature, although it slowly liberated nitrous vapors. The analysis showed high fluorine and nitrogen, but no chlorine content. The absence of the difluorochlorinium cation was also indicated by its mild reaction with water in which it was clearly soluble. Analysis excludes the possibility of hexafluorosilicate salt. It could be a complex between HF and nitrogenoxides or nitrogenoxyfluorides.

c. Reaction between ClF_3 and HNO_3

The fluorination of nitric acid with elementary fluorine gives fluorinenitrate according to the following equation[42]:

$$HNO_3 + F_2 \longrightarrow NO_3F + HF$$

If the fluorination of HNO_3 is carried out with chlorinetrifluoride, the formation of $ClF_2^+NO_3^-$ might be expected:

$$HNO_3 + ClF_3 \longrightarrow ClF_2^+NO_3^- + HF$$

The reactants were brought together gradually at -78° and a vigorous reaction took place. The volatile part of the reaction mixture contained SiF_4, ClO_2F, ClF_3, HNO_3, N_2O_4, and NO_2. A white solid material melting at ~-10° remained after the evaporization of the volatile part.

In molten state it reacted rapidly with the quartz container with the formation of SiF_4. The liquid residue consisted of nitric acid and nitrogen oxides.

In the reaction of chlorinetrifluoride with $AgNO_3$, HNO_3 and N_2O_5, nitrylfluoride was obtained as main product. This might be explained by the following two equations:

$$ClF_2^+NO_3^- \rightleftharpoons ClF + NO_3F$$

$$NO_3F \longrightarrow NO_2F + 1/2\ O_2$$

The second reaction was investigated by Cady and found to be catalyzed by fluorine and nitrogen oxides[43]. By the continuous decomposition of NO_3F the first equilibrium could be shifted completely to the right.

d. Reaction between ClF_3 and N_2O

This reaction was described in a U. S. Patent as a way to prepare NF_3[44]. The reaction conditions, however, are too drastic (300° and high pressure). It was hoped that under milder conditions the following reaction could take place:

$$N_2O + ClF_3 \longrightarrow ClF_2^+N_2OF^-$$

The N_2OF^- anion would be isoelectronic with N_2F_2 and therefore its existence might be possible. The reaction was investigated at different temperatures between

-196 and 0°, but the infrared spectrum showed in each case only unreacted starting materials.

e. Reaction between ClF_3 and $KClO_4$

The reaction was expected to proceed in the following way:

$$KClO_4 + ClF_3 \longrightarrow KF + ClF_2^+ClO_4^-$$

X-ray analysis of the solid residue showed only unreacted $KClO_4$ and no KF.

f. Reaction between ClO_3F and ClF

Difluorochlorinium cation containing compounds were previously prepared from ClF_3 by the abstraction of a fluoride anion. Theoretically they could be prepared from ClF according to the following scheme:

$$ClF + FX \longrightarrow ClF_2^+X^-$$

The actual reaction mechanism may involve the formation of an intermediate complex, since the formation of an intermediate fluorine cation would require too high an activation energy.

For this purpose ClO_3F was reacted with ClF in freon 11 (used as a solvent) at temperatures between -78 and 20°. No complex formation between the two compounds was observed.

2. Attempted Preparation of the NF_4^+ Cation

Since NF_5 is unknown and unlikely to exist, the preparation of an NF_4^+ cation should be attempted from NF_3 and a fluorine cation. However, the existence of a fluorine cation is also unknown, and a very high energy would be required for its formation. Therefore, a different approach to this problem was chosen. If NF_3, together with a strong Lewis acid, such as AsF_5 or SbF_5, interacts with elementary fluorine, the following reaction might occur:

$$NF_3 + F\text{-}F + AsF_5 \longrightarrow NF_4^+AsF_6^-$$

In this way the full energy for a heterolytic splitting of the fluorine molecule might not be required, since the reaction could proceed through an intermediate activated complex. In addition, the formation of the AsF_6^- anion will contribute strongly to a more favorable energy balance. Once the NF_4^+ cation can be prepared in a stable form, the exchange of the anion with anions of higher energy content would be attempted.

Nitrogen trifluoride was mixed with AsF_5 in the absence of elementary fluorine at temperatures in the range, 25 to 405°, and at pressures in the range, 105 to 1060 p.s.i., to check whether the compounds will interact with each other in the absence of F_2. No reaction between the two compounds was observed in this range. In addition, a reaction between

liquid AsF_5 and gaseous NF_3 was attempted in the vacuum line at -78°, but again no reaction could be observed.

When NF_3 and AsF_5 were mixed with elementary fluorine at temperatures as high as 485° and at pressures as high as 2400 p.s.i., no reaction between the starting materials was observed. A small amount of solid crystalline product was obtained and its structure was investigated by elemental, infrared, and X-ray analysis. It proved to be $Ni(AsF_6)_2$, which has not yet been reported in the literature. It must have been formed by the interaction of monel with AsF_5 and F_2.

B. Experimental

1. Attempted Combination of the ClF_2^+ Cation with an Anion of High Energy Content

a. Reaction between ClF_3 and $AgNO_3$

Chlorinetrifluoride was condensed on powdered $AgNO_3$ at -196°. The mixture was warmed slowly to room temperature. The gases were analyzed by infrared spectroscopy and the presence of NO_2F was established as well as unreacted ClF_3. The dark solid residue was analyzed: Ag = 72.5%, F = 24.9%. This represents an atomic ratio of 1:1.95 between silver and fluorine. The X-ray powder diagram of the compound was also taken.

b. Reaction between ClF_3 and N_2O_5

N_2O_5 was prepared according to Brauer, "Präparative Anorganische Chemie, p. 372 (first edition).

N_2O_5 (5 g.) and excess ClF_3 (15 ml.) were condensed into a trap at -196°. The temperature of the trap was slowly increased and upon melting of the ClF_3 a vigorous reaction took place. A homogeneous dark brown solution formed. The reaction products were fractionated. The fractions were identified by their infrared gas spectra using a 10 cm Pyrex cell with AgCl windows. Nitryl-fluoride was found to be the main product besides ClF_3. When the reaction was done with less pure nitrogen pentoxide, the main product was again NO_2F, but in this case small quantities of ClO_2F, NO_2, N_2O_4, HNO_3, and an unidentified compound (absorptions at 1745 and 1732 cm^{-1}) were also detected. After the evaporation of the volatile part, a solid white material was obtained (150 mg) which was stable at room temperature. Quantitative analysis gave the following results: F = 34.6, 35.1%; Acidity, 28.85 meq/g; N = 13.3%.

c. Reaction between ClF_3 and HNO_3

Red fuming nitric acid (2 ml.) was added dropwise to ClF_3 (10 ml.) in a quartz trap at -78°. A vigorous reac-

tion took place and the resulting mixture was fractionated in the vacuum line. The volatile part consisted of SiF_4, ClF_3, ClO_2F, NO_2, HNO_3 as identified by their IR spectra. A white solid residue was obtained. It melted at around -10° and reacted rapidly with the quartz container liberating SiF_4. After this reaction, a liquid remained which was found to contain mostly HNO_3 with some dissolved nitrogen oxides.

d. Reaction between ClF_3 and N_2O

The two components were condensed on the cold AgCl window of the low-temperature infrared cell. The infrared spectrum, at temperatures between -196 and 0°, showed only the absorptions of the starting materials. In another attempt the two components were condensed together in the vacuum line at -196° and were allowed to warm up to 0°. No sign of any reaction was observed. When the liquid was warmed to room temperature everything evaporated, leaving no residue and the vapor phase again showed only ClF_3 and N_2O.

e. Reaction between ClF_3 and $KClO_4$

This reaction was done analogous to the reaction of ClF_3 with $AgNO_3$. The vapor phase consisted only of ClF_3 according to the infrared analysis. The white solid

residue was identified by X-ray analysis as unreacted starting material.

f. Reaction between ClO_3F and ClF

Trichlorofluoromethane, CCl_3F (50 ml.), was placed in a two-necked flask and was saturated with ClF (b.p., -101°) at -78°. Then ClO_3F was passed into the solution at the same temperature. No solid formation was observed in the temperature range -78 to 20°.

2. Attempted Preparation of the NF_4^+ Cation

a. Reaction between NF_3 and AsF_5 at -78°

NF_3 and AsF_5 were purified by fractionation in the vacuum line. Then, NF_3 was allowed to stand above liquid AsF_5 at -78° at a pressure of 740 mm. The NF_3 showed only a low solubility in the AsF_5 and no interaction between the two compounds could be observed.

b. Reaction between NF_3 and AsF_5 at 20 to 405°

NF_3 and AsF_5 were purified by fractionation in the vacuum line. NF_3 (0.1 mole) and AsF_5 (0.1 mole) were condensed into a 100 ml. monel cylinder, equipped with a Helicoid pressure gauge and a monel Whitey valve. The cylinder was placed into an electrically heated vertical tube furnace and slowly heated up to a temperature of 405°. The pressure increased from an initial pressure of 420 p.s.i. at 20° to 1060 p.s.i. at 405°. The cylinder

was kept for 12 hours at 405°. After cooling to 20° the initial pressure of 420 p.s.i. was obtained again, indicating that no reaction had occurred between NF_3 and AsF_5.

c. Reaction between NF_3, AsF_5, and elementary fluorine

Nitrogentrifluoride (0.1 mole) and AsF_5 (0.1 mole) were condensed into a 100 ml. monel cylinder as described above. Then, excess elementary fluorine was condensed into the cylinder at -196°. The cylinder was warmed to room temperature and heated to 485°, a pressure of 2400 p.s.i. resulting. After cooling to room temperature no pressure change was observed. The cylinder was cooled to -196° followed by slow warming to room temperature. The volatile gases were bled off, as soon as slight pressure developed in the cylinder. After pumping on the cylinder at room temperature for about 10 minutes, the cylinder was weighed, but no appreciable weight increase could be noticed. After three different runs at various temperatures and pressures, the cylinder was disassembled and a small amount of a pale yellow solid (~2 g.) was found in the upper part of the reactor. This was shown to be $Ni(AsF_6)_2$.

Anal. Calcd. for $Ni(AsF_6)_2$: Ni, 13.45%; As, 34.33%; F, 52.22%

Found: Ni, 13.9%; As, 32.5%; F, 53.7%

Infrared: In the range between 450 to 4000 cm^{-1}, there was only one strong absorption at 725 cm^{-1}, which is characteristic of the AsF_6^- anion.

The X-ray powder diagram was taken, but it could not be successfully indexed.

ls

March 4, 1965

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