in which (N) is the total concentration of ammonia plus ammonium ion and the term in parentheses is to take account of the ammonium ion equilibrium, K_a being the acid dissociation constant of NH_4^+, equal to 5.5×10^{-10} at 25°.

Evaluation of the ratio, R_n/R_o, for equal concentrations of bromide and ammonia nitrogen gives values of 750 at pH 9, 110 at pH 8, 11 at pH 7, and 1.1 at pH 6.

In qualitative agreement with these calculations we have found that when hypochlorite and ammonium bromide are mixed at concentrations of 2.3×10^{-4} and 4.6×10^{-4} *M*, respectively, only NH_2Cl is formed when the reaction occurs at pH 8 or greater, some bromamides are formed when the reaction occurs at pH 7, NBr_3 being the one chiefly detected, and predominant formation of bromamides accompanied by very rapid loss of oxidizing halogen (90% within 7 min.) takes place at pH 6.

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

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The difluorochlorate(I) anion, ClF_2^-, a new oxidizing 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,[1] 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.[1] Association through fluorine bridging seems to be preferred over self-ionization.[2] In addition, there is n.m.r. evidence[3] 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 toward strong Lewis acids, such as AsF_5, SbF_5,[4-6] BF_3,[7] PF_5,[6] and PtF_5,[8] forming the ClF_2^+ cation, or toward Lewis bases, such as NOF,[9] KF, RbF, and CsF,[10-12] forming the ClF_4^- anion, as shown by the 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^+,[13] 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 Co.) 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, 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^+-

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[1] A. A. Banks, H. J. Emeléus, and A. A. Woolf, *J. Chem. Soc.*, 2861 (1949).

[2] H. C. Clark, *Chem. Rev.*, **58**, 869 (1958).

[3] A. N. Hamer, J. Leece, and P. G. Bentley, United Kingdom Atomic Energy Authority Industrial Group Headquarters, Risley, Warrington, Lancashire, IGR-TN/CA-1048 (1959).

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[6] K. O. Christe and A. E. Pavlath, *ibid.*, **335**, 210 (1965).

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[9] E. D. Whitney, R. O. MacLaren, T. J. Hurley, and C. E. Fogle, *J. Am. Chem. Soc.*, **86**, 4340 (1964).

[10] L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *ibid.*, **83**, 2955 (1961).

[11] D. H. Kelly, B. Post, and R. W. Mason, *ibid.*, **85**, 307 (1963).

[12] E. D. Whitney, R. O. MacLaren, C. E. Fogle, and T. J. Hurley, *ibid.*, **86**, 2583 (1964).

[13] Summary Report on the Inorganic Fluorine Chemistry Meeting, Argonne, Ill., 1963; *Science*, **143**, 1058 (1964).

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 mmoles) was combined under vacuum with NOF (7.33 mmoles) at −196°. The mixture was slowly warmed to 0°, kept at that temperature for 15 min., and finally cooled slowly to −120°. Unreacted ClF (3.99 mmoles) was recovered by distillation at −120°. Therefore, NOF (7.33 mmoles) had reacted with ClF (7.26 mmoles) 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. (Intensity of NOF peak corresponds to exactly half the total sample pressure. Mol. wt. found, 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,[14] 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 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," $\Delta H°_{\text{dis}}$[15] (estimated accuracy, ±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 1T-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,[16] for the density of liquid NOF.

Results

Synthesis.—Nitrosyl fluoride and ClF (either one in excess) when mixed together under 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 and 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

$$NO^+ClF_2^-(s) = NOF(g) + ClF(g)$$

is a straight line. The equation

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

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 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 $\Delta H°_{\text{dis}} = 15.5$ kcal. mole^{-1} was found from the slope of the log P_{mm} *vs.* T^{-1} curve. From $\Delta F°_T = -RT \ln K_{P\,(\text{atm})}$, a free energy change, $\Delta F°_{298} = -2.1$ kcal. mole^{-1}, and from $\Delta S°_T = (\Delta H° - \Delta F°_T)T^{-1}$, an entropy change, $\Delta S°_{298} = 59.3$ cal. deg.^{-1} mole^{-1}, were found for the dissociation process at 25°. A heat of formation of $NO^+ClF_2^-(s)$, $\Delta H_f°_{298} = -44.7$ 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	1.9×10^{-7}
NOF	−79	5.4×10^{-5}
$NO^+ClF_2^-$ in liquid NOF	−79	3.4×10^{-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.—Figure 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

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[14] D. J. LeRoy, *Can. J. Res.*, **288**, 492 (1950).

[15] It is not strictly correct to infer that the measured heat of reaction for the dissociation process equals the thermodynamic heat of dissociation. This would only be appropriate if the complex was in the gas phase or if the heat of sublimation of the complex was zero. But, for convenience, $\Delta H°_{\text{dis}}$ will be used throughout the text to mean the heat of reaction of a complete dissociation process of the type complex(s) = gas + gas.

[16] J. H. Simons, "Fluorine Chemistry," Vol. 1, Academic Press Inc., New York, N. Y., 1950, p. 89.

TABLE II

COMPARISON OF INFRARED ABSORPTION FREQUENCIES (CM.$^{-1}$)

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

[a] A. H. Nielsen and E. A. Jones, *J. Chem. Phys.*, **19**, 1117 (1951). [b] P. J. H. Woltz, E. A. Jones, and A. H. Nielsen, *ibid.*, **20**, 378 (1952). The band at 1037 cm.$^{-1}$ reported by the above authors for NOF(g) is probably due to SiF_4 impurity and was not present in our spectrum.

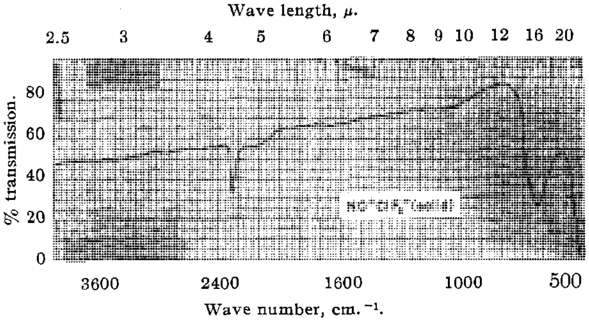

Figure 1.—The low-temperature infrared spectrum of solid $NO^+ClF_2^-$.

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.[6] 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.

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 toward most organic compounds.

Table III shows the heats of dissociation[15] and heats of formation of some similar ionic chlorine fluoride complexes.

TABLE III

"HEATS OF DISSOCIATION" AND HEATS OF FORMATION OF SOME IONIC CHLORINE FLUORIDE COMPLEXES

Complex	$\Delta H°_{dis}$, kcal. mole^{-1}	$\Delta H_f°_{298}$, complex(s) (calcd.),[a] kcal. mole^{-1}	Temp., °C. (at P_{dis} = 760 mm.)
$NO^+ClF_2^-$	15.5	−44.7	−22
$NO^+ClF_4^-$ [9]	15.8	−70.4	−5
$ClF_2^+PF_6^-$ [6]	16.4	−436.7	−38
$ClF_2^+BF_4^-$ [7]	23.6	−333.3	+9

[a] Data used to calculate $\Delta H_f°_{298}$, complex(s), kcal. mole^{-1}: $\Delta H_f°_{298}$, $PF_5(g) = -381.4$[b]; $\Delta H_f°_{298}$, $BF_3(g) = 270.8$[b]; $\Delta H_f°_{298}$, $ClF_3(g) = -38.9$[c]; $\Delta H_f°_{298}$, $ClF(g) = -13.5$[c]; $\Delta H_f°_{298}$, NOF(g) = −15.7.[c] [b] P. Gross, C. Hayman, D. L. Levi, and M. C. Stuart, U. S. Department of Commerce, Office of Technical Services, P.B. Rept. 153,445, 1960, p. 32. [c] Janaf Interim Thermochemical Tables, Vol. II, The Dow Chemical Company, Midland, Mich., 1961.

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°,[9] respectively. This small decrease in stability could be due to the decreasing coordination number of the chlorine atom toward 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.

$NO^+ClF_2^-$ Infrared Spectrum and Structure.—Three reasonable possible structures for the complex are: coordination complex, ClF·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.[17] In structure III the NO bond has triple bond character and should absorb in the 2350–

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(17) See Table II, footnote *b*.

2100 cm.$^{-1}$ region.[18] 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^-,[19–22] ICl_2^-,[21–25] IBr_2^-,[19,22] $ClIBr^-$,[21,22,26] Br_3^-, $ClBr_2^-$, $BrCl_2^-$, and $FIBr^-$.[22]

The difluorochlorate(I) anion contains three free electron pairs, *i.e.*, the chlorine atom has three filled nonbonded 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 nonbonded nonhybridized orbitals (two p and one d), (iii) little hybridization of the orbitals of the chlorine atom resulting in two semi-ionic F–Cl bonds[21,25] (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,[25] 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[27] 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, Figure 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.[6]

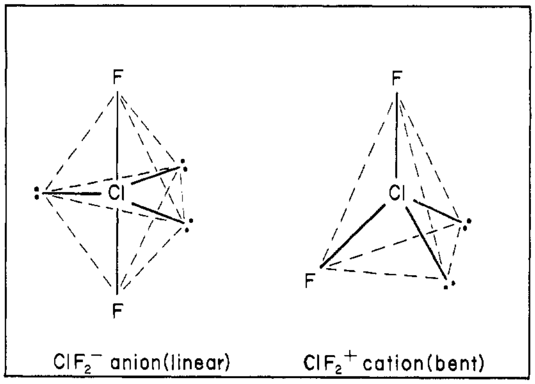

Figure 2.—Structure of ClF_2^- and ClF_2^+. For ClF_2^-: point group $D_{\infty h}$, sp^3d-hybrid; $\nu_{asym} = 635$ cm.$^{-1}$. For ClF_2^+: point group C_{2v}, sp^3-hybrid; $\nu_{asym} = 558$ cm.$^{-1}$, $\nu_{sym} = 519$ cm.$^{-1}$.

The observed absorption of ClF_2^- at 635 cm.$^{-1}$ corresponds to the asymmetric stretching vibration of the apex fluorine atoms in ClF_3 gas at 703 cm.$^{-1}$.[28] It is well known that gaseous ClF_3 is also a trigonal bipyramid,[28] 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.

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