indicating formation of an essentially 1:2 complex ($1.00F_3NO \cdot 2.02BF_3$). However, continuous high-vacuum pumping for 3 hr from this complex at −120° led to the recovery of an additional 0.95 mmol of $BF_3$, leaving an adduct of 1:1 composition ($1.00F_3NO \cdot 1.07BF_3$). Further pumping for 3 hr at −120° produced no additional $BF_3$, indicating that the 1:1 composition was quite stable at this low temperature. The 1:1 complex also appeared to be stable at −78° (no detectable vapor pressure), but on warming to room temperature the material slowly dissociated completely to gaseous $F_3NO$ and $BF_3$, leaving no residue.

**Reaction of $F_3NO$ with $BCl_3$.**—Equimolar quantities of $F_3NO$ and $BCl_3$ (*ca.* 1 mmol each) were condensed into a glass ampoule at −196° and warmed to −78°. At −78° (considerably above the melting points of the reactants) only a white solid was observed initially, but this became yellow and partially liquefied over a period of 5 min. Upon warming to room temperature, the entire mass vaporized to 1.5 mmol of a mixture comprised (mass spectral and infrared analysis) of approximately equal amounts of NOCl, $Cl_2$, and $BF_3$; no $BCl_3$ remained and only a trace of $F_3NO$ was detectable. These results suggest that the reaction proceeded according to the equation $F_3NO + BCl_3 \rightarrow [F_3NO \cdot BCl_3] \rightarrow Cl_2 + NOCl + BF_3$.

**Reaction of $F_3NO$ with HCl.**—Millimolar quantities of $F_3NO$ and HCl were essentially unchanged after several days at 25° in a Pyrex ampoule. However, the addition of $BF_3$ to one reaction mixture (mole ratio $F_3NO:HCl:BF_3 = 1:1:2$) resulted in rapid and extensive reaction within minutes, producing large amounts of $SiF_4$ (from attack on the glass vessel), $Cl_2$, and a white solid identified by X-ray diffraction as $NOBF_4$. No $F_3NO$ remained, indicating that the major reactions were

$$F_3NO + 2HCl \longrightarrow NOF + Cl_2 + 2HF$$

$$NOF + BF_3 \longrightarrow NOBF_4$$

**Other Reactions.**—In a number of additional studies, either no reaction occurred between $F_3NO$ and the inorganic substrate or the reactions were sufficiently complex that complete product characterization and material balances were unobtainable and no reasonable stoichiometry could be inferred from the data. In the first category, $F_3NO$ under ambient conditions did not react with HF, $FClO_3$, ClF, $ClF_3$, $ClF_5$, $BrF_3$, $BrF_5$, $IF_5$, $PF_3$, $PF_5$, $AsF_3$, CO, $CO_2$, $CF_3OF$, $SO_2$, $SO_2F_2$, or $FSO_2OOSO_2F$. Trifluoramine oxide was found by nmr measurement to be soluble in the liquid phases of some of these materials without visible effect on the nmr spectrum of either the $F_3NO$ or solvent. The solvent, temperature, and mole per cent of $F_3NO$ in solution follow: $ClF_5$, 0°, 20%; $SO_2$, −30°, >20%; $SO_2F_2$, −78°, >20%; $ClF_3$, −78°, 10%; HF, −78°, 2%; $IF_5$, 25°, slightly soluble. The complex $F_3NO$ reactions which were observed in this study are summarized in Table I. The products listed were only those present to the extent of more than 5–10% of the reaction mass, as determined by a combination of infrared spectroscopy, mass spectrometry, and wet-chemical analyses.

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# The Chemistry of Trifluoramine Oxide. III. Lewis Acid Complexes of $F_3NO$. Structure and Reactions of the $F_2NO^+$ Ion

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Complexes of $F_3NO$ with the Lewis acids $BF_3$, $AsF_5$, and $SbF_5$ were found to exist in the ionic form $F_2NO^+A^-$, where $A^- = BF_4^-$, $AsF_6^-$, or $SbF_6^-$. Infrared spectra of the solid complexes as well as infrared, nmr, and conductivity studies of the complexes dissolved in polar fluorinated solvents confirm their ionic constitution and indicate that the $F_2NO^+$ cation exhibits the same planar geometry as the isoelectronic $COF_2$ molecule.

## Introduction

Previous papers in this series have described the synthesis and characterization of the compound trifluoramine oxide, $F_3NO$,[1] and cited its reactions with a variety of inorganic substrates.[2] The complexes of $F_3NO$ with the Lewis acids $BF_3$, $AsF_5$, and $SbF_5$ described in the latter of these papers were investigated further in a study of their structures and potential use in the metathetical synthesis of ionic derivatives of $F_3NO$. Examination of the $F_3NO$–Lewis acid complexes by nmr and infrared spectroscopy reveals a common structural feature attributable to the previously unknown cation $F_2NO^+$.

## Experimental Section

The manipulation of $F_3NO$ and other compounds in the course of this study was carried out in Monel Metal vacuum systems provided with suitable valves and fittings for connection of gas cylinders, reaction vessels, gas infrared cells, and Plaskon nmr sample tubes.[3] Pressures were measured through a sensitive all-nickel pressure transmitter connected to a mercury manometer and pressure-balancing system.[4] The all-plastic apparatus used in manipulating corrosive fluorinated solvent systems (HF, $SbF_5$, etc.) were developed as a part of this investigation and have been described elsewhere.[3]

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(1) W. B. Fox, J. S. MacKenzie, E. R. McCarthy, J. R. Holmes, R. F. Stahl, and R. Juurik, *Inorg. Chem.*, **7**, 2064 (1968).

(2) W. B. Fox, C. A. Wamser, R. Eibeck, D. K. Huggins, J. S. MacKenzie, and R. Juurik, *ibid.*, **8**, 1247 (1969).

(3) C. A. Wamser and B. B. Stewart, *Rev. Sci. Instr.*, **36**, 397 (1965).

(4) S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," Columbia University, New York, N. Y., June 20, 1944. AEC Declassified, March 20, 1947 (MDDC).

The adducts of $F_3NO$ with Lewis acids were formed by direct combination of the components. With the exception of the $F_3NO$–$SbF_5$ adduct (*vide infra*), this involved successive condensation, at −196°, of measured amounts of the components in a suitable reaction vessel, followed by warming to temperatures within the range of stability of the particular adduct. The $F_3NO \cdot BF_3$ complex forms when the condensed phases are being warmed from −196 to −78° and is stable only at temperatures below about −50°; at higher temperatures, it dissociates into its components, the dissociation being essentially complete at room temperature. Dissociation is negligible at temperatures of −78° (well above the boiling point of either component) or below. The $F_3NO$–$AsF_5$ adduct, stable at 25°, could be formed as above or simply by mixing the gaseous components at room temperature.

However, in the case of the $F_3NO$–$SbF_5$ adduct, the low vapor pressure of $SbF_5$ and the incomplete reaction of gaseous $F_3NO$ with liquid $SbF_5$ (caused by solid formation at the interfacial surface) necessitated a modification in procedure. The synthesis of pure $F_3NO \cdot SbF_5$ in bulk was most conveniently effected by passing an excess of gaseous $F_3NO$ through a solution of $SbF_5$ in liquid anhydrous HF at −50°. The subsequent removal of the reaction medium by volatilization under reduced pressure at room temperature left white microcrystalline $F_3NO \cdot SbF_5$. The $SbF_5$ adduct has no detectable dissociation pressure at 25°, while $F_3NO \cdot AsF_5$ at this temperature dissociates slightly (5 mm of $F_3NO$ + 5 mm of $AsF_5$).

The 1:1 compositions of the $F_3NO$–Lewis acid adducts were confirmed by chemical analysis and/or by tensimetric measurement of reacted gases.[2] There is some evidence, in the $F_3NO$–$BF_3$ system, for the existence of a $F_3NO \cdot 2BF_3$ complex, which, unlike the 1:1 compound, is unstable at −78°.[2]

Solutions were formed by condensing appropriate quantities of the solvent on the complexes at −196° in Plaskon tubes, followed by gradual warming to the melting point of the solvent. Solutions were examined by nmr spectroscopy (Varian Model V-4302 spectrometer) at a variety of temperatures down to the freezing range. Fluorine-19 chemical shifts were determined by the substitution method, using $CFCl_3$ as reference. Certain solutions could not be prepared; thus, the high melting points of $IF_5$ and $AsF_3$ precluded the preparation of solutions of the relatively unstable complex $F_3NO \cdot BF_3$ in these solvents.

Infrared spectra of the solid $F_3NO$ complexes were obtained by a technique similar to that reported by Geichman, *et al.*[5] In the cases of $F_3NO \cdot AsF_5$ and $F_3NO \cdot SbF_5$, the complexes were deposited on $BaF_2$ or AgCl windows by combining low pressures of the gaseous components (1:1) at room temperature inside Monel Metal gas infrared cells. The $F_3NO \cdot BF_3$ complex was formed by combining the components in a low-temperature infrared cell with an internal $BaF_2$ window held at −196°. In this case, a 1:1 gaseous mixture of $F_3NO$ and $BF_3$ was discharged slowly from a Monel storage bulb into the cell and allowed to impinge on the cold $BaF_2$ window. Infrared spectra were recorded at various intervals while the window containing the condensed solid was allowed to warm slowly from −196°. By this technique, the appearance of the gaseous dissociation products in the spectra (above −50°) could be monitored and served to provide information on the extent of dissociation as a function of temperature.

Liquid infrared spectra of *solutions* of $F_3NO \cdot AsF_5$ and $F_3NO \cdot SbF_5$ in $IF_5$ and $BrF_5$ were obtained at room temperature with the aid of a cell which could be assembled with $BaF_2$ or $CaF_2$ windows and Halon-TFE spacers and gaskets. Samples of the solutions were transferred in a drybox into the cell by injection from a Halon-TFE syringe through capillary openings in the cell gasket. No difficulties were experienced with $IF_5$ solutions, but the higher vapor pressure of the $BrF_5$ solutions caused some difficulties in introducing samples into the cell.

A few measurements of the electrolytic conductance of $F_3NO$, $BF_3$, and combinations thereof in anhydrous HF were made at −78° in a Plaskon cell with small platinum electrodes. No detectable change in conductance was observed when $F_3NO$ or $BF_3$ alone was dissolved in HF, but the combination of the two at the same concentrations (about 0.6 *M*) caused a considerable increase in conductance, indicating the presence of ionic species.

## Results and Discussion

**Nmr Characterization of $F_2NO^+$.**—The $F^{19}$ nmr spectrum of pure $F_3NO$ (liquid at −78°) consists of a sharply defined 1:1:1 triplet with a chemical shift ($CFCl_3$ reference) of −363 ppm and $J_{N-F}$ = 136 Hz. The spectrum is not significantly different for solutions of $F_3NO$, since an average chemical shift of −362 ± 3 ppm was observed for $F_3NO$ in the solvents HF, $CFCl_3$, $SO_2F_2$, $CF_3COCF_3$, $CF_3CN$, $BrF_5$, $ClF_3$, $N_2O_4$, and $SO_2$ over the temperature range −78–0°.

In contrast to pure $F_3NO$, which tends to be more soluble in nonpolar or moderately polar solvents, the $F_3NO$–Lewis acid complexes are quite soluble in certain polar solvents and give rise to the nmr spectral data summarized in Table I. The solutions in HF, $IF_5$, and $BrF_5$ were indefinitely stable, while the solutions in liquid $AsF_3$ showed some tendency to decompose, probably involving oxidation of As(III). Typical nmr spectra for three selected systems are shown schematically in Figure 1.

TABLE I

$F^{19}$ NMR SPECTRAL DATA FOR SOLUTIONS OF $F_3NO$–LEWIS ACID COMPLEXES

| Lewis acid | Solvent | Temp, °C | Resonance and chem shift ($CFCl_3$ ref),[i] ppm | Assignment and rel area | Notes |
|---|---|---|---|---|---|
| $BF_3$ | HF | −78 | −331 (triplet) | $F_2NO^+$ (1) | *a* |
| | | | +154 (singlet) | $BF_4^-$ (2) | |
| $AsF_6$ | HF | −20 | −333 (triplet) | $F_2NO^+$ (1) | *b* |
| | | | +60 (singlet) | $AsF_6^-$ (3) | |
| $SbF_5$ | HF | −20 | −333 (triplet) | $F_2NO^+$ (1) | *b* |
| | | | +135 (singlet) | $SbF_6^-$ (3) | |
| $AsF_5$ | $AsF_3$ | 0 | −331 (triplet) | $F_2NO^+$ | *c* |
| $SbF_6$ | $IF_5$ | 0 | −332 (triplet) | $F_2NO^+$ (1) | *d* |
| | | | +117 (singlet) | $SbF_6^-$ (3) | |
| $BF_3$ | $BrF_6$ | −60 | −321 (singlet) | $F_2NO^+$ (1) | *e* |
| | | | +152 (singlet) | $BF_4^-$ (2) | |
| $SbF_5$ | $BrF_6$ | −20 to | −325[f] | $F_2NO^+$ (1) | *h* |
| | | +25 | +122[g] | $Sb_2F_{11}^-$ (5) | |

[a] Also trace "free" $F_3NO$ at −364 ppm; HF resonance (doublet) at +200 ppm. [b] HF resonance (doublet) at +200 ppm. [c] Identical spectrum for $SbF_5$ complex; anionic species not resolved. [d] $IF_5$ resonances at −50 ppm (quintet), −7 ppm (doublet). [e] Also trace "free" $F_3NO$ at −363 ppm; $BrF_5$ resonances at −269 ppm (quintet), −141 ppm (doublet). [f] Singlet at lower temperatures changing toward triplet at 25°. [g] Broad singlet with some poorly defined triplet structure. [h] $BrF_5$ resonances at −270 ppm (quintet), −141 ppm (doublet). [i] All $J_{N-F}$ values for $F_2NO^+$ resonances are 250 ± 3 Hz.

The nmr spectra of the solutions of the $F_3NO$ complexes in HF, $AsF_3$, and $IF_5$ exhibit a 4:5:4 triplet $F^{19}$ resonance centered at −331 ± 3 ppm with $J_{N-F}$ = 250 Hz. This represents a change in chemical shift in excess of 30 ppm to higher magnetic field and a nearly twofold increase in the N–F coupling constant on comparison with the solutions of $F_3NO$ itself. There is also a characteristic broadening of the individual peaks of the triplet, with the outer members appreciably broader than the central member. ($BrF_5$ is unique as a solvent

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(5) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *Inorg. Chem.*, **1**, 661 (1962).

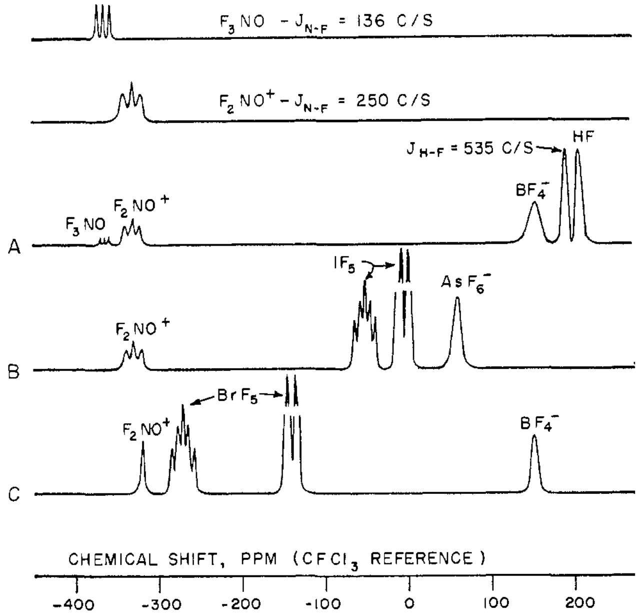

Figure 1.—Schematic representation of typical fluorine-19 nmr spectra of solutions of $F_3NO$ adducts: (A) solution of $F_3NO \cdot BF_3$ in HF at −80°; (B) solution of $F_3NO \cdot AsF_5$ in $IF_5$ at 0°; (C) solution of $F_3NO \cdot BF_3$ in $BrF_5$ at −60°.

in that the $F^{19}$ resonance for the dissolved complexes consists of a *singlet* at −321 ppm; $F_3NO$ itself in this solvent, however, presents the usual 1:1:1 triplet with the same chemical shift as in other solvents.)

Evaluation of the other fluorine-containing species which are observed in the $F^{19}$ nmr spectra affords compelling evidence that the solutions contain the ionic species $F_2NO^+$. Thus, the spectra of solutions of $F_3NO \cdot BF_3$ in HF, of which the one shown in Figure 1 is typical, indicate three major fluorine-containing species: (a) the N–F species at −331 ppm derived from $F_3NO$; (b) a species at +154 ppm (precisely the chemical shift observed for the $BF_4^-$ ion in HF); and (c) an intense doublet centered at about +200 ppm with a splitting of about 535 Hz, corresponding to the solvent HF. In all such solutions, the areas of the −331 and +154 ppm peaks were found to be in the ratio 1:2, as required for $F_2NO^+$:$BF_4^-$, the values deviating less than 10% from this ratio. It would appear, therefore, that these solutions contain principally $F_2NO^+$ and $BF_4^-$ in equimolar amounts. These solutions also contain a small amount of "free" $F_3NO$ as indicated by the weak triplet signal at −364 ppm. This suggests that there is an equilibrium established among $F_3NO$, $BF_3$, $F_2NO^+$, and $BF_4^-$ in HF solutions, which in turn may be related to the relative Lewis acidities of HF, $BF_3$, and $F_2NO^+$. The extensive solvolysis of $BF_4^-$ in HF (to $BF_3$ and $F^-$)[6] may also be a contributing factor, little or no "free" $F_3NO$ having been observed in similar solutions of $F_3NO \cdot AsF_5$ or $F_3NO \cdot SbF_5$ ($SbF_6^-$ and presumably $AsF_6^-$ undergo negligible solvolysis in HF[6]).

The $F^{19}$ nmr spectra of the $F_3NO$ complexes of $AsF_5$ and $SbF_5$ in HF, as well as the complexes in $IF_5$ and $BrF_5$, similarly indicate the presence of $F_2NO^+$ and the corresponding $MF_6^-$ anion as the principal ionic species. However, in some cases the chemical exchange of fluoride ion between solvent and anion could not be slowed sufficiently to allow full resolution of the anion resonance. In all cases where spectral resolution could be attained, the anion resonances were observed to lie close to the expected chemical shifts (+154 ppm for $BF_4^-$, +60 ppm for $AsF_6^-$, and +117 to +135 ppm for $SbF_6^-$ [7]). Furthermore, the area of the peak attributed to $F_2NO^+$ was very nearly one-third that of the $AsF_6^-$ or $SbF_6^-$ peak.

$BrF_5$ appears to be unique as a solvent for the $F_3NO$ adducts. The nmr spectra of solutions of $F_3NO \cdot BF_3$ or $F_3NO \cdot AsF_5$ in $BrF_5$ indicate the presence of $F_2NO^+$ and the corresponding anion ($BF_4^-$ or $AsF_6^-$) with the expected intensity ratios. However, the $F_2NO^+$ exhibits a *singlet* resonance rather than the triplet observed in other media. The 10-ppm increase in the $F^{19}$ shielding constant, relative to shifts observed in the other solvents, is an order of magnitude too large to be attributed to a bulk diamagnetic susceptibility effect. Moreover, the anion resonances are observed at the same positions as in the other solvents used. The increased shielding may be the result of ion pairing ($BrF_5$ is usually considered to be a poorly ionizing solvent) or a specific solvation interaction with the cation or possibly a combination of both effects. An analogous effect has been observed in the proton resonance spectra of $LiB(CH_3)_4$ in ether solutions, the change from a multiplet to singlet with decreasing temperature being attributed to increased quadrupolar interaction accompanying the slower rate at which equilibrium between the contact and solvent-separated ion pairs is attained.[8] In the case of $F_3NO \cdot SbF_5$ in $BrF_5$, some anion–solvent interaction appeared to exist also, as indicated by the unexpectedly high anion-to-cation intensity ratios in this system. This effect was not explored further but may result from the presence of anionic species of the type $Sb_2F_{11}^-$ which have been postulated on the basis of nmr data on HF–$SbF_5$ systems.[9]

The differences between the N–F resonances of the parent molecule $F_3NO$ and its cationic derivative $F_2NO^+$ (which is isoelectronic with $COF_2$) are consistent with a change from an $sp^3$-hybridized tetrahedral structure to an $sp^2$-hybridized planar-trigonal geometry for the cation. The higher N–F coupling constant observed for $F_2NO^+$ may be attributed to increased s character of the N-bonding orbital in the N–F bond. The line shape of the $F_2NO^+$ resonance signal is consistent with a lower degree of electronic symmetry about the N atom of $F_2NO^+$ compared with that of $F_3NO$. The 4:5:4 triplet component intensities resemble that observed for the planar-trigonal molecule $FNO_2$.

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(6) A. F. Clifford and S. Kongpricha, *J. Inorg. Nucl. Chem.*, **20**, 147 (1961).

(7) Unlike those of $BF_4^-$ and $AsF_6^-$, the chemical shift of $SbF_6^-$ appears to vary considerably with the particular solvent, an effect confirmed by nmr measurements on solutions of known $SbF_6^-$ sources. For solutions of $KSbF_6$, the following shifts were observed in the solvents noted: HF, +135 ppm; $IF_5$, +117 ppm; $BrF_5$, +122 ppm.

(8) K. C. Williams and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4134 (1966).

(9) H. H. Hyman, L. A. Quarterman, M. Kilpatrick, and J. J. Katz, *J. Phys. Chem.*, **65**, 123 (1961); Technical Progress Report No. 7, Stanford Research Institute, Menlo Park, Calif., Jan 1–March 31, 1965.

**Infrared Spectral Characterization of $F_2NO^+$.**—The infrared spectra of the solid complexes of $F_3NO$ with $SbF_5$, $AsF_5$, and $BF_3$ are presented in Figure 2 and provide further evidence for the presence of $F_2NO^+$ in these compounds.

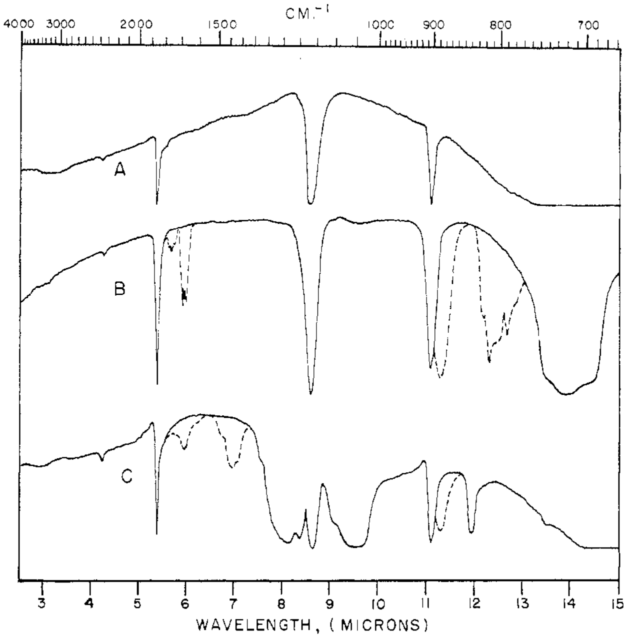

Figure 2.—Infrared spectra of solid $F_3NO$–Lewis acid adducts: (A) $F_3NO \cdot SbF_5$ at 25° ($BaF_2$ windows); (B) $F_3NO \cdot AsF_5$ at 25° (AgCl windows); (C) $F_3NO \cdot BF_3$ at −120° ($BaF_2$ internal window, NaCl external windows).

All three spectra disclose a common pattern of three absorption bands not found in the spectra of any of the components in the gaseous or condensed phases (low temperature). These bands and their probable assignments are: 1857 $cm^{-1}$, N–O str; 1162 $cm^{-1}$, N–F sym str; 905 $cm^{-1}$, N–F asym str.

The presence of major absorptions characteristic of $AsF_6^-$ (700-$cm^{-1}$ region) and $BF_4^-$ (1050 $cm^{-1}$) in the spectra of the corresponding $F_3NO$ complexes supports the assignment of the above bands to $F_2NO^+$. (The absorption in the 650-$cm^{-1}$ region, which should be characteristic of $SbF_6^-$, is just beyond the wavelength region studied and would furthermore be obscured by the $BaF_2$ window cutoff which begins at even shorter wavelengths.) Accordingly, these solid complexes appear to possess ionic structures of the form $F_2NO^+BF_4^-$, $F_2NO^+AsF_6^-$, and $F_2NO^+SbF_6^-$.

Since the $F_3NO \cdot AsF_5$ complex is slightly dissociated at 25°, all spectra of this solid compound at room temperature contain absorptions characteristic of the gaseous components, $F_3NO$ and $AsF_5$, as indicated by the dashed lines in Figure 2. It has been estimated from such spectra that the equilibrium dissociation pressure of $F_3NO \cdot AsF_5$ at 25° is about 10 mm, comprising 5 mm each of $F_3NO$ and $AsF_5$. In accord with the stronger Lewis acidity of $SbF_5$, the $F_3NO \cdot SbF_5$ complex is negligibly dissociated at 25°, as confirmed by the absence of any detectable $F_3NO$ or $SbF_5$ in the spectrum of the solid. This is further demonstrated by the fact that the spectrum of the $SbF_5$ complex undergoes no appreciable change on extended vacuum pumping of the infrared cell at room temperature, while the spectrum of the corresponding $AsF_5$ complex gradually vanishes by this treatment.

Spectra of the solid $F_3NO \cdot BF_3$ complex were recorded at a variety of temperatures from −196 to about −40° where dissociation was extensive. As the temperature increases above −60°, the bands attributed to $F_2NO^+$ and $BF_4^-$ recede progressively, while bands characteristic of gaseous $F_3NO$ and $BF_3$ develop in the spectra. The spectra of the solid complex contain additional bands believed attributable to $B_2F_7^-$,[10] indicating the presence of some 1:2 complex (*i.e.*, $F_2NO^+B_2F_7^-$) as well as the 1:1 complex. The bands characteristic of $B_2F_7^-$ occur at 1220, 1099, 1053, 1020, and 833 $cm^{-1}$,[10] and absorptions close to these wavelengths have been noted in the low-temperature spectra of $F_3NO$–$BF_3$ complexes.

Infrared spectra of *solutions* of $F_2NO^+AsF_6^-$ and $F_2NO^+SbF_6^-$ in $IF_5$ and $BrF_5$ also showed the characteristic bands of the $F_2NO^+$ cation at 1857, 1162, and 905 $cm^{-1}$, thus corroborating the $F^{19}$ nmr characterization of the species $F_2NO^+$ in such solutions.

It appears likely that the N—O bond strength in $F_2NO^+$ is comparable to that in ONF or NO itself and the bond probably possesses considerably more $\pi$ character than the N—O bond in $F_3NO$. The N—O stretching frequency has increased to a value within the accepted range for a full N=O double bond. This is consistent with the requirement for an expected planar structure with bond angles close to 120° and approximately $sp^2$ hybridization of the nitrogen atom.

**Chemical Properties of $F_2NO^+$.**—The $F_3NO$–Lewis acid complexes were found to be considerably more reactive than $F_3NO$ itself. Most carbon-containing compounds suffer oxidative degradation (often violently), although some compounds containing carbon–carbon double bonds undergo smooth fluorine addition.

$F_2NO^+$ hydrolyzes vigorously in accordance with the reaction

$$F_2NO^+AsF_6^- + 2H_2O \longrightarrow 2HF + HAsF_6 + HNO_3$$

Anhydrous HF solutions containing $F_2NO^+$ and $HF_2^-$ as the principal ionic species were prepared by metathetical reaction of solutions of $F_2NO^+BF_4^-$ and $K^+HF_2^-$ in HF at −60°. Approximately 85% of the $BF_4^-$ was precipitated as $KBF_4$ (identified by X-ray diffraction). The $F^{19}$ nmr spectra of the filtrates confirmed the survival of the $F_2NO^+$ and 85% reduction in $BF_4^-$ concentration. Such solutions were employed in some studies as convenient sources of $F_2NO^+$ in metathetical reactions.

Since $F_2NO^+$ and $HF_2^-$ are the ions which would be expected to result if $F_3NO$ itself could be induced to ionize in HF, attempts were made to effect such ionization. These attempts, which were all unsuccessful, included pressurizations of $F_3NO$–HF systems in

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(10) S. Brownstein and J. Paasivirta, *Can. J. Chem.*, **43**, 1645 (1965).

the absence and presence of additives (traces of $F^-$, $H_2O$, Lewis acids, etc.).

A considerable effort was directed toward the synthesis of compounds containing $F_2NO^+$ with oxidizing anions such as $ClO_4^-$, $ClO_3^-$, $NO_3^-$, etc., since such compounds would be expected to be highly energetic solid oxidizers. The general approach involved metathesis as exemplified by the generalized equation

$$F_2NO^+A^- + M^+ClO_4^- \xrightarrow{\text{solvent}} F_2NO^+ClO_4^- + M^+A^-$$

where $A^-$ represents a Lewis acid ligand ($AsF_6^-$, $SbF_6^-$, or $BF_4^-$) and $M^+$ represents an alkali metal or other salt form of the desired oxidizing anion (usually perchlorate as shown). Various solvent media, such as HF, $IF_5$, or $BrF_5$, were employed.

These attempts were generally unsuccessful in that no compounds of the type $F_2NO^+ClO_4^-$ could be isolated from any of the reaction mixtures. Instead, when perchlorates were involved, the reaction products were identified as $FClO_3$ and $FNO_2$, possibly from decomposition of the desired compound or other interaction of the ions $F_2NO^+$ and $ClO_4^-$ (*i.e.*, $F_2NO^+ + ClO_4^- \rightarrow FClO_3 + FNO_2$).

Similarly, combination of solutions containing $F_2NO^+$ and $ClO_3^-$ or $SO_3F^-$, led to the formation of $FClO_2$ and $SO_2F_2$, respectively, along with $FNO_2$ in both cases.

In the earlier phases of the study, the reactions were thought to proceed *via* anion solvolysis, since it has been observed in separate experiments that $ClO_4^-$ and $ClO_3^-$ salts, for example, would yield $FClO_3$ and $FClO_2$, respectively, upon interaction with HF, $IF_5$, or $BrF_5$ in the presence of strong Lewis acids.[11] However, no $SO_2F_2$ could be formed from $SO_3F^-$ in this manner, nor did $ClO_4^-$ yield any $FClO_3$ when treated with $BF_3$ in HF, yet under similar conditions $SO_2F_2$ was formed by the reaction of $F_2NO^+$ and $SO_3F^-$, and $FClO_3$ was formed by the interaction of $F_2NO^+BF_4^-$ and $ClO_4^-$, in HF.

Analogous reaction products were observed in attempted metathesis reactions of $N_2F^+AsF_6^-$ with $ClO_4^-$ and $SO_3F^-$ in HF medium, namely, $FClO_3$ and $SO_2F_2$, respectively, along with $N_2O$.[12]

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# The Difluoronitronium Cation, $NF_2O^+$

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Nitrogen oxide trifluoride forms white crystalline 1:1 adducts with the Lewis acids $BF_3$, $AsF_5$, and $SbF_5$. In addition to the 1:1 complex, $BF_3$ can form at $-126°$ a 2:1 adduct with $NF_3O$. The thermal stability of these complexes decreases in the order: $NF_3O \cdot SbF_5 > NF_3O \cdot AsF_5 > NF_3O \cdot BF_3 > NF_3O \cdot 2BF_3$. The dissociation pressure–temperature relation has been measured and thermodynamic data are calculated for the process $NF_3O \cdot BF_3(s) = NF_3O(g) + BF_3(g)$. Hydrolysis of $NF_3O \cdot AsF_5$ results in the formation of $NO_2^+AsF_6^-$. Infrared and Raman measurements show that $NF_3O \cdot SbF_5$, $NF_3O \cdot AsF_5$, $NF_3O \cdot BF_3$, and $NF_3O \cdot 2BF_3$ have the ionic structures $NF_2O^+SbF_6^-$, $NF_2O^+AsF_6^-$, $NF_2O^+BF_4^-$, and $NF_2O^+B_2F_7^-$, respectively. The $NF_2O^+$ cation (point group $C_{2v}$) has a structure similar to that of isoelectronic $CF_2O$. All fundamentals have been observed for $NF_2O^+$.

## Introduction

Several independent disclosures have been made on the synthesis, properties, and chemistry of $NF_3O$.[1-5] In addition, one paper[6] dealing with the infrared spectrum and thermodynamic properties of $NF_3O$ has been published.

The capability of $NF_3O$ to form adducts with strong Lewis acids has been recognized by all three groups[1-6] investigating this compound. Thus, Fox and coworkers[4] reported the existence of 1:1 adducts between $NF_3O$ and $AsF_5$ or $SbF_5$. They suggested the ionic structures $NF_2O^+AsF_6^-$ and $NF_2O^+SbF_6^-$, respectively, for these adducts based on $^{19}F$ nmr and incomplete infrared data. Similarly, Bartlett and coworkers[5] reported the existence of the complex $NF_3O \cdot AsF_5$. They also proposed the ionic structure $NF_2O^+AsF_6^-$ based on incomplete infrared data. Some of the chemistry of the $NF_3O \cdot BF_3$ adduct has been developed in showing that this adduct can add at low temperature

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