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The Chemistry of Trifluoramine Oxide. II. Reactions with Inorganic Substrates

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Trifluoramine oxide oxidizes N_2F_4, N_2O_4, Cl_2, and SF_4 to NF_3, NO_2F, ClF, and SF_6, respectively, the F_3NO being reduced to NOF in each case. These and other reaction studies indicate that oxidations by F_3NO involve primarily fluorination rather than oxygenation. Trifluoramine oxide is not readily hydrolyzed by water or aqueous base but is attacked by sulfuric acid. The interaction of F_3NO with fluorinated Lewis acids is also described.

Introduction

As part of a broader study of the chemistry of compounds containing N–F bonds, we have investigated the unusual new compound trifluoramine oxide, F_3NO, in some detail. Earlier papers from this laboratory[1,2] and elsewhere[3] have described the synthesis and physical properties of F_3NO and given a preliminary account of its chemical behavior. In the present work, reactions of F_3NO with a variety of inorganic substrates were investigated, particular attention being given to those capable of oxidation in order to determine whether F_3NO would function as a fluorinating agent, an oxygenating agent, or both. The behavior of F_3NO toward Lewis acids was also examined, since the binary nitrogen fluorides[4–7] (except NF_3) and oxyfluorides[8,9] have been found to form complexes with such materials.

Results and Discussion

The general pattern that emerges from the reaction studies reported herein is that of trifluoramine oxide behaving as a strong oxidizing agent, as expected of a nitrogen(V) compound. However, the mode of oxidative attack by F_3NO seems to be predominantly one of substrate fluorination to the exclusion of substrate oxygenation. Thus, the relatively straightforward oxidations (fluorinations) of N_2F_4, N_2O_4, Cl_2, and SF_4 by F_3NO produce NF_3, NO_2F, ClF, and SF_6, respectively, with the F_3NO being reduced to NOF in each case. In other cases (see results summarized in Table I) the reactions were sufficiently complex that complete product characterization was not possible, and no reasonable stoichiometry could be inferred from the data. Still, the absence of binary nitrogen fluoride products and the plethora of nitrogen–oxygen products in all cases tended to confirm the thesis that F_3NO behaves more as a fluorinating than an oxygenating agent toward oxidizable materials. This behavior is consistent with the results of thermochemical[10] and spectroscopic[11] investigations which indicate a very strong N–O bond and relatively weak N–F bonds in F_3NO.

It is of interest that reactions of F_3NO with even very readily oxidizable substrates (CO, SO_2, N_2F_4, SF_4) generally required heating or the application of ultraviolet radiation, indicating a high activation energy for attack by F_3NO. In this sense, the behavior of F_3NO resembles that of NF_3[12] and OF_2[13] which also frequently require considerable activation to undergo thermodynamically favorable reactions. A further manifestation of kinetically—rather than thermodynamically—derived stability may be seen in the relative inertness of F_3NO to hydrolysis. Trifluoramine oxide showed no tendency to react with water and hydrolyzed only very slowly in the presence of strong aqueous NaOH at 90°, though thermochemical data for F_3NO indicate that the heat of hydrolysis (*e.g.*, $F_3NO + 2H_2O \rightarrow HNO_3 + 3HF$) should be around -75 kcal/mol.[10] Hydrolysis of F_3NO occurs more readily in strong sulfuric acid solutions, which may be related to the ability of strong Lewis acids (*vide infra*) to abstract fluoride ion from F_3NO, thereby generating the very reactive and hydrolyzable F_2NO^+ ion.

Trifluoramine oxide forms isolable 1:1 complexes with SbF_5, AsF_5, and BF_3, but not with PF_5. The data show that the order of acidities toward F_3NO is, as expected, $SbF_5 > AsF_5 > BF_3 > PF_5$. The ability of F_3NO to form stable complexes with the strong Lewis acids SbF_5 and AsF_5 is analogous to the ability of the binary nitrogen fluorides N_2F_2[4,5] and N_2F_4[6,7] to form complexes with these acids.[14] However, the fact that F_3NO also forms a 1:1 complex with the weaker acid BF_3 (contrary to an earlier report[3c]) indicates that F_3NO may be a somewhat stronger base (fluoride donor) than N_2F_2 and N_2F_4. (The latter show no evidence of interaction with BF_3 at $-78°$ and only weak association below $-120°$.[15,16]) The $F_3NO-BCl_3$ study, which was aimed at providing further comparison of the basicities

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TABLE I

REACTIONS OF F_3NO WITH INORGANIC SUBSTANCES

Reactant[a]	Conditions	Products and results
SO_2	*b*	SO_3, SO_2F_2, SOF_4, SiF_4, N_2O, NO_2, $(NO)_2SiF_6$, $NOSO_3F$
CO	*b*	COF_2, CO_2, CF_4, NO_2, SiF_4, $(NO)_2SiF_6$
$Fe(CO)_5$	F_3NO gas added slowly to liquid $Fe(CO)_5$ at 25°	Series of mildly explosive flashes; brown solids formed in liquid; volatile products CO, COF_2, SiF_4
COF_2	10,800 psi, 300°, 4 hr	CF_4, CF_3OOCF_3, NOF, NO_2
CF_3I	*b*	C_2F_6, COF_2, CF_4, NO_2
COS	*b*	SO_2, NO, NO_2, NOF
SO_3	*b*	$S_2O_5F_2$, SO_2F_2, $NOSO_3F$, NO_2SO_3F
$LiClO_4$	1600 psi, 100°, 4 hr	$FClO_3$, NO_2Cl, NO_2, NO_2F, solids
$Mg(ClO_4)_2$	4400 psi, 100°, 4 hr	$FClO_3$, NO_2F, NO_2, NOF, solids
H_2SO_4	5 min, 25°	HF, NO_2^+, SO_3F^-

[a] Reactant and F_3NO in a 1:1 mole ratio. [b] Ultraviolet irradiation in a quartz bulb at atmospheric pressure with a high-pressure mercury lamp for 2–3 hr.

of F_3NO and N_2F_4 (the latter shows no evidence of interaction with BCl_3 at $-78°$[15]), unfortunately did not provide an unequivocal result. Though it is likely that the solid observed at $-78°$ in the F_3NO–BCl_3 system was the expected 1:1 complex, which would further indicate that F_3NO is a stronger base than N_2F_4, the extensive secondary reactions which followed made definite characterization of the solid impossible. The behavior of F_3NO toward BCl_3 in this instance (*i.e.*, facile oxidation of chloride to elemental chlorine) illustrates the enhancement of F_3NO reactivity as an oxidant in a highly acidic environment. A further example of this is the facile oxidation of HCl to Cl_2 by F_3NO when BF_3 is added to the system. We have observed numerous instances in which vigorous oxidations by F_3NO were catalyzed by small amounts of BF_3, AsF_5, or SbF_5. It is possible that an underlying mechanism for these oxidations involves initial formation of the F_3NO–acid complex which contains the powerfully electrophilic F_2NO^+ cation.

Experimental Section

Apparatus and Procedures.—Standard high-vacuum techniques were used throughout the investigation. Pressures of oxidizing gases were measured as described earlier,[1] and relative amounts of volatile products, if not readily separable by fractionation, were determined by comparison of their infrared spectra with standard calibrated spectra obtained with a Perkin-Elmer Infracord spectrophotometer. Nmr data were obtained with a Varian V-4302 spectrometer.

Reaction of F_3NO with SF_4.—A mixture of F_3NO and SF_4 in a nickel infrared cell (BaF_2 windows) was subjected to 0.5 hr of irradiation with a high-pressure mercury lamp. Infrared analysis of the cell contents showed that half of the F_3NO had been consumed and the only products were NOF (1.2 mmol) and SF_6 (1.3 mmol). The results are best described by the equation $F_3NO + SF_4 \rightarrow NOF + SF_6$.

Reaction of F_3NO with Chlorine.—A mixture of chlorine and F_3NO (25 mmol each) was brought to 400° and 5850 psi in a well-fluorinated nickel autoclave. After 2 hr, the products were separated by vacuum-line fractionation and found by infrared analysis to be a mixture of ClF (40 mmol, 80% yield) and NOF (22 mmol, 88% yield). The reaction can be represented by the equation $F_3NO + Cl_2 \rightarrow 2\,ClF + NOF$.

Reaction of F_3NO with N_2O_4.—A solution containing 2.5% by weight of F_3NO in N_2O_4 (under 2.3 atm of F_3NO pressure) was formed at 0° in an nmr sample tube. Over a period of several hours at 0°, the F_3NO signal intensity (triplet at $\phi - 364$, $J_{NF} = 136$ Hz) diminished as new signals attributable to NOF (broad at ϕ -480) and NO_2F (broad triplet centered at ϕ -393, $J_{NF} = 115$ Hz) appeared in the solution. Qualitative area measurements indicated that the total resonances of NOF and NO_2F accounted for the decreased F_3NO signal and that the NO_2F concentration was twice that of the NOF. The reaction occurring was therefore $F_3NO + N_2O_4 \rightarrow NOF + 2NO_2F$.

Reaction of F_3NO with N_2F_4.—In a run typical of several experiments, F_3NO (1.00 mmol) and N_2F_4 (0.50 mmol) in a 100-ml quartz bulb were completely consumed after 1 hr of irradiation with a high-pressure mercury lamp. The observed products were NF_3 (*ca.* 1 mmol) and an unresolved mixture of NO_2, SiF_4, and solid $(NO)_2SiF_6$. The latter materials undoubtedly arose through attack of NOF, an expected product, on the silica vessel. When a similar F_3NO–N_2F_4 mixture (2:1 molar ratio) was placed in a well-passivated nickel cell with BaF_2 windows and irradiated for 0.5 hr, only unused F_3NO, NF_3, and NOF (approximately 1:2:1 molar ratio) were observed as products. These data are consistent with the equation $F_3NO + N_2F_4 \rightarrow 2NF_3 + NOF$.

Reaction of F_3NO with H_2O.—Gaseous F_3NO was virtually unaffected by contact with liquid water at 25° and was only slowly attacked by 50% aqueous $NaOH$ at 90° (25% hydrolysis in 8 hr). In later work, 50% aqueous $NaOH$ or solid KOH pellets at 25° were used for scrubbing F_3NO to remove impurities such as SiF_4, NO_2, NOF, and NO_2F. The F_3NO recoveries were 95–100%.

Reaction of F_3NO with Iodide Ion.—A measured quantity of F_3NO (0.457 mmol) was added to an excess of deaerated aqueous KI acidified with phosphoric acid. After the mixture was shaken for 5 min at 25°, liberated iodine was titrated with standard thiosulfate solution in the usual manner. Results showed that 1.412 mequiv of I^- had been consumed (3.08 mequiv of I^-/mmol of F_3NO) in good agreement with the equation $3I^- + F_3NO \rightarrow NO + 3F^- + 1.5I_2$.

Reaction of F_3NO with SbF_5.—In a typical experiment, SbF_5 (1.0 mmol) was dissolved in 3 ml of anhydrous HF and cooled to $-78°$. The addition of F_3NO (1.0 mmol) to this solution caused rapid formation of a white precipitate, and subsequent removal of volatile material left a quantitative yield of white microcrystalline $F_3NO \cdot SbF_5$. *Anal.* Calcd for $F_3NO \cdot SbF_5$: F, 50.04; Sb, 40.08; N, 4.60. Found: F, 48.30; Sb, 41.35; N, 4.70. The sample underwent no change on heating to 100° but reacted violently with water at 25°.

Reaction of F_3NO with AsF_5.—When equimolar amounts of gaseous F_3NO and AsF_5 were allowed to mix at 25°, a white solid formed immediately in the reactor. Elemental analysis of the solid reaction product gave the following results. *Anal.* Calcd for $F_3NO \cdot AsF_5$: F, 59.17; As, 29.17; N, 5.44. Found: F, 58.70; As, 29.17; N, 5.60. The material exhibited dissociation pressures at 25° of around 10 mm, the gas phase being comprised of equal amounts of F_3NO and AsF_5. The solid fumed in moist air and reacted violently with water.

Reaction of F_3NO with BF_3.—Measured amounts of F_3NO (1.00 mmol) and BF_3 (3.00 mmol) were combined in a 30-cm^3 glass ampoule at $-196°$. Repeated warming to $-130°$ and chilling to $-196°$ produced a considerable amount of white solid which persisted at $-130°$, well above the melting points of the reactants. The readily available vapor over the solid at $-130°$, recovered by vacuum pumping into a collection bulb at $-196°$ for 5 min, was found to be 0.98 mmol of pure BF_3. No perceptible BF_3 was recovered by an additional 5 min of pumping, 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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