capacity of the olefin with increasing alkyl substitution has been previously noted[34] and could arise from either steric effects or an electron-releasing inductive effect on the part of the alkyl substituent.

(34) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc., A,* 328 (1967).

The Chemistry of Trifluoramine Oxide. I. Synthesis and Characterization of F₃NO

By W. B. FOX, J. S. MacKENZIE, E. R. McCARTHY, J. R. HOLMES, R. F. STAHL, and R. JUURIK

Experimental procedures for the electric-discharge synthesis and subsequent purification of F₃NO are described in detail. The physical properties of F₃NO, including infrared, nmr, and mass spectral data, vapor pressures, and critical constants, are also recorded.

Introduction

In an earlier communication we presented a preliminary account of the synthesis and properties of the unusual new compound trifluoramine oxide, F₃NO.[1,2] This novel material is the third known oxyfluoride of nitrogen (FNO and FNO₂ being the only previously reported examples[3]) and the high degree of both electronic and steric symmetry of the oxygen and fluorine atoms about the central nitrogen atom of F₃NO appears to be unique in the chemistry of simple covalent nitrogen compounds. Although the structure of F₃NO is formally analogous to that of a typical tertiary amine oxide, (*e.g.*, trimethylamine oxide), the saltlike character of the latter (mp 208°) compared with the highly covalent nature of the former (mp −160°) suggests that the two materials may represent profoundly different classes of compounds. Moreover, the lessons of organic chemistry lead us to expect amine oxide formation by only the most strongly basic amines, so that the existence of the highly stable F₃NO, in view of the manifest lack of basicity of NF₃ in all cases studied,[4] is indeed surprising and further admits of an unusual bonding situation. For these reasons, and because of increasing interest in nitrogen–fluorine chemistry in recent years, we have conducted a thorough investigation of the physical and chemical properties of F₃NO. In this, the first of a series of papers dealing with trifluoramine oxide, we present a detailed account of the electric-discharge technique for synthesizing F₃NO and a description of some of its properties.

(1) W. B. Fox, *et al., J. Am. Chem. Soc.,* **88**, 2604 (1966).

(2) The independent discovery and brief examination of F₃NO has also been reported by others: N. Bartlett, J. Passmore, and E. J. Wells, *Chem. Commun.,* 213 (1966).

(3) It is consistent with accepted practice to regard as oxyhalides those compounds in which both oxygen and halogen atoms are bonded directly to the central atom. This provides a useful distinction between such compounds and those with oxygen–halogen bonds such as ClNO₃ and FNO₃.

(4) A. D. Craig, *Inorg. Chem.,* **3**, 1628 (1964).

Experimental Section

Apparatus.—Standard high-vacuum techniques were used throughout the investigation. Because of the reactivity of some of the compounds with mercury, pressures were measured through a sensitive all-nickel pressure transmitter connected to an appropriate pressure-balancing system and mercury manometer.[5] Calibrations showed that the device was accurate to ±0.1 mm over the range 0–760 mm.

Electric-Discharge Synthesis of F₃NO.—The apparatus used was similar to that employed by Kirshenbaum for the low-temperature electric-discharge preparation of O₃F₂,[6] except that our U-shaped Pyrex discharge tube was symmetrical, with a nickel electrode in each limb (spacing 12 cm). In a typical run, an equimolar mixture (77 mmol each) of gaseous NF₃ and oxygen was passed slowly at 10–15 mm pressure into the discharge tube (held at −196°) with continuous pumping on the exit side of the tube to remove noncondensable material and maintain the reactor pressure in the desired range. During a run, which generally required 1–2 hr for completion, the discharge current varied from 30 to 50 mA at 5 kV.

Upon completion of a run, the condensable material in the discharge tube was an amber solid–liquid mixture at −196° which became a reddish liquid on slight warming. Alternate warming to −78° and cooling to −196° caused all color to disappear and produced considerable noncondensable material, suggesting that the colored materials were lower oxygen fluorides (*e.g.*, O₂F₂ or O₃F₂) which decomposed subsequently to O₂ and F₂.[7] Subsequent fractionation through traps at −130, −183, and −196° yielded NF₃ (23.3 mmol, trapped at −196°), F₃NO (7.0 mmol, trapped at −183°), and an unresolved mixture (trapped at −130°) of NO₂, N₂O₃, and white solid which was probably (NO)₂SiF₆. From these data, the conversion of NF₃ was 71% and the yield of F₃NO was 13%. Dozens of similarly conducted runs, using either NF₃–OF₂–H₂ or NF₃–O₂ mixtures, produced essentially the same results, with yields of F₃NO in the range of 10–15%.

Experiments in which the discharge tube was maintained at

(5) 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).

(6) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.,* **81**, 1277 (1959).

(7) A. G. Streng, *Chem. Rev.,* **63**, 607 (1963).
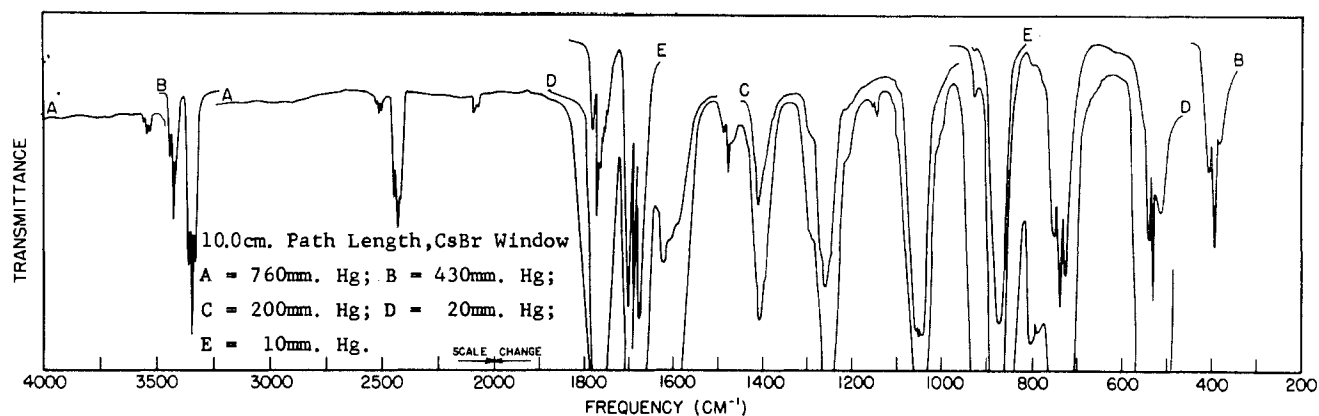
Figure 1.—Infrared spectrum of gaseous F_3NO.

−78° during the run, with a following −196° trap to collect products, yielded no F_3NO. Other experiments in which either the NF_3 or the O_2 alone was passed through a discharge zone and the other reagent was then added several centimeters downstream before collection at −196° also failed to produce F_3NO. This indicated that excitation of both reactants simultaneously provided the reactive precursors to F_3NO. Attempts chemically to oxidize NF_3 with O_2, O_3, peroxides, KO_2, etc., were equally unrewarding.

Purification of F_3NO.—The F_3NO as obtained in the discharge synthesis was usually contaminated with small amounts of N_2O, SiF_4, and NF_3. These impurities were effectively removed chromatographically using a 3-m, 0.25-in. o.d. column operated at 25° and filled with 1 m of 33% perfluorotributylamine[8a] and 2 m of Kel-F tetramer,[8b] both supported on Chromosorb P. The F_3NO retention times for several helium flow rates were: 370 sec at 14 cm³/min; 280 sec at 20 cm³/min; 220 sec at 29 cm³/min.

An alternative procedure, useful for larger quantities of material, involved addition of an excess of BF_3 to the crude mixture which was then maintained at around −120° for several hours. The impurities were then readily pumped away leaving behind a BF_3–F_3NO complex involatile at this low temperature.[9] Subsequent warming to room temperature decomposed the complex to F_3NO and BF_3 which were then shaken for several minutes with 1 N aqueous NaOH to remove BF_3, whereupon the unchanged F_3NO was stripped from the solution and recovered.

Analysis.—Nitrogen was determined by the Dumas technique. For the fluorine analysis, a measured quantity of F_3NO was digested with sodium in liquid ammonia at 25° in a sealed tube. Following removal of NH_3 and destruction of the excess sodium with ethanol, the fluoride was determined by the thorium nitrate method. *Anal.* Calcd for F_3NO: F, 65.5; N, 16.1. Found: F, 66.2; N, 16.0.

Infrared, Nmr, and Mass Spectra.—The infrared spectrum of F_3NO (Figure 1) was recorded with a Perkin-Elmer Model 521 spectrometer. The F^{19} nmr spectrum was obtained with a Varian Model V-4302 spectrometer using a 56.4-Mc probe. A Consolidated Electrodynamics Model 21-202 spectrometer operating at 70-V ionization potential was used for the mass spectrum.

Characterization of Trifluoramine Oxide

The formula F_3NO is supported unequivocally by the nitrogen and fluorine analyses, by the vapor density molecular weight (calcd for F_3NO, 87.0; found, 86.8), and by the mass spectrum shown in Table I. The relatively great intensities of F_2NO^+ and NO^+ fragments compared with the weak F_2N^+ peak (and undetected NF_3^+ ion) suggest relatively strong N–O

TABLE I
MASS SPECTRUM OF F_3NO

m/e	Rel abund	Ion	m/e	Rel abund	Ion
14	12.5	N^+	33	4.1	FN^+
16	3.7	O^+	49	1.6	FNO^+
19	9.8	F^+	52	1.3	F_2N^+
24.5	0.8	FNO^{2+}	68	78.1	F_2NO^+
30	100.0	NO^+	87	0.2	F_3NO^+

bonding in the molecule. This is consistent with the information revealed by the infrared spectrum (*vide infra*).

The F^{19} nmr spectrum of F_3NO is consistent with a highly symmetrical (psuedo-tetrahedral) amine oxide structure. Over the temperature range studied (−110 to −65°) the spectrum consists of a symmetrical and sharply defined 1:1:1 triplet centered at δ_{CCl_3F} −363 ± 2 ppm, with J_{NF} = 136 cps and line widths less than 10 cps. The narrow line widths and high symmetry of the triplet components are striking evidence of the high degree of electrical field symmetry around the nitrogen atom (as expected for the amine oxide structure), particularly when compared with N^{14} quadrupole-broadened spectra of less symmetrical N–F compounds (such as NF_3, N_2F_4, or NOF) recorded under similar conditions.

The nearly tetrahedral C_{3v} symmetry of F_3NO is clearly manifest by the infrared spectrum (Figure 1) in which the required six fundamental bands have been assigned.[1,10] The similarity of the molecular symmetry to T_d has also been recognized by others.[2] A noteworthy feature of the infrared spectrum is the occurrence of the N—O stretching vibration at 1687 cm⁻¹. Bartlett and coworkers[2] have suggested that the N—O bond of F_3NO may be formulated in a conventional way, with the oxygen joined to NF_3 by a semiionic bond $\equiv N^+$—O^-. However, the N—O stretching frequency of F_3NO is closer to that of the N=O double bond in FNO than to that of the familiar amine oxides and, in fact, has nearly 75% double-bond character.[10] This unexpectedly stable arrangement probably results from the high effective electronegativity of the nitrogen atom in F_3NO. The use of higher orbitals (antibond-

(8) Minnesota Mining and Manufacturing Co. products: (a) FC-43; (b) No. 8126.

(9) W. B. Fox, *et al.*, to be submitted for publication.

(10) A complete normal-coordinate analysis of the vibrational spectrum of F_3NO has been carried out and will be published separately.
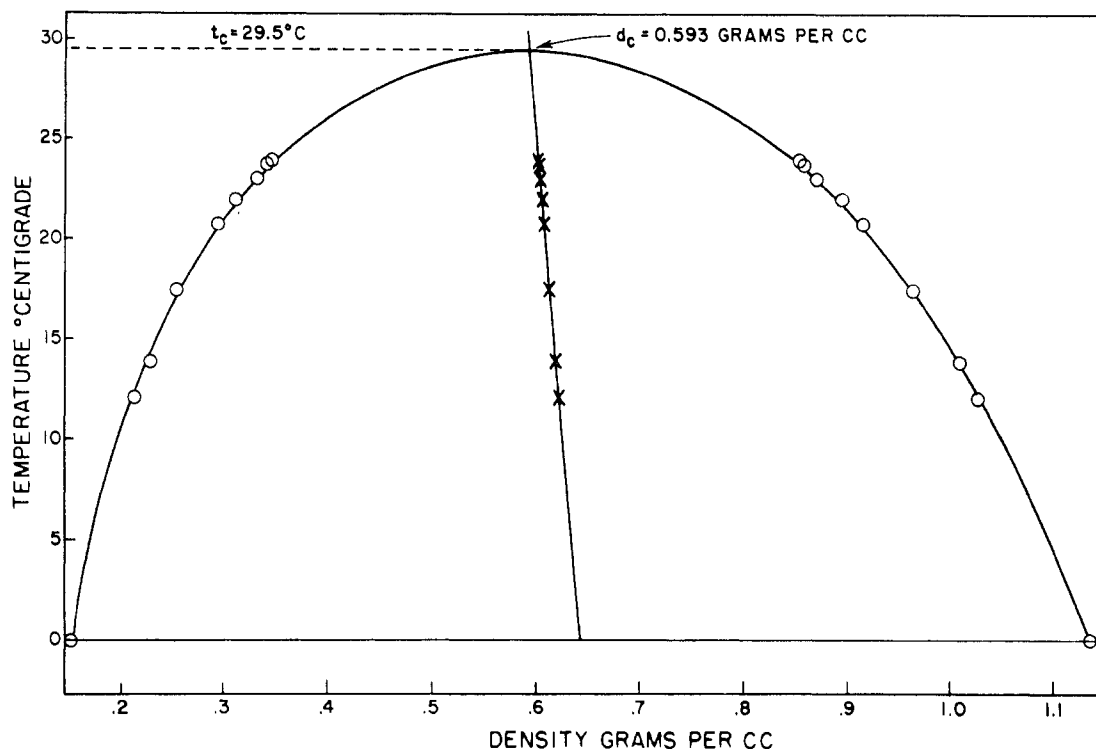
Figure 2.—Orthobaric density plot of F_3NO used to determine critical density.

ing) in the formation of double bonds in saturated molecules has been proposed convincingly by Lucken[11] and Williams[12] for molecules such as CF_4. The higher the effective nuclear charge on the central atom, the more important will be the contribution of these higher orbitals to the over-all bonding in the molecule. The F_3NO molecule would seem to represent an extreme case of this kind of behavior. The nitrogen atom is surrounded by one of the most highly electronegative groups of atoms possible (the only known exception being the recently reported NF_4^+ ion[13]) and the oxygen atom would have an enhanced tendency to back-donate lone-pair electrons into the nitrogen orbitals to such an extent that the N–O bond appears to have slightly greater than 70% double-bond character. This picture is compatible with the mass spectral cracking pattern, which suggests that the N–O bond is considerably more stable than the N–F bond. It is also compatible with the chemical behavior described below.

General Chemical Characteristics.—Trifluoramine oxide is a stable colorless gas which, when carefully purified, does not attack glass even when liquefied under pressures of around 65 atm at 25°. It is unreactive toward most metals but, in contrast to the report[2] of Bartlett and coworkers, we find that it reacts slowly with mercury at 25° when the latter is agitated to expose new surfaces, the products being mixed oxides of nitrogen and fluorides of mercury. The gas may be heated to 300° (atmospheric pressure) for short periods in nickel or Monel without change, but

prolonged heating (>1–2 hr) causes increasing degradation to nitrosyl fluoride and secondary products (NO_2, NO_2F, NO) of the latter's attack on the vessels. It is noteworthy that in hundreds of reaction studies conducted to date, decomposition to NF_3 and oxygen has never been observed; the dominant mode of reaction of F_3NO appears to be one of substrate fluorination with the N–O bond generally remaining intact.[9]

The ultraviolet spectrum of F_3NO shows the onset of very weak absorption at 2200 Å, the intensity increasing only slightly down to the limit of measurement at 2800 Å. Prolonged photolysis of F_3NO gas in a nickel cell (BaF_2 windows) with a 500-W high-pressure mercury lamp caused only minor decomposition, traces of NO_2, NO_2F, and NOF being formed. However, photolysis of solid F_3NO at −196° produced the $F_2NO \cdot$ radical in low concentration.[14]

Trifluoramine oxide is highly toxic. Experiments with albino rats showed that the LD_{50} concentration for 10-min exposure was between 200 and 500 ppm. From available data, this would place the toxicity of F_3NO between that of fluorine and oxygen difluoride,[15] but somewhat closer to the latter.

Physical Properties of F_3NO.—The vapor pressures of F_3NO at various temperatures are given in Table II.

A least-squares fit of the data to the equation

$$\log P_{mm} = -A + \frac{B}{T} + \frac{C}{T^2} + D \log T$$

was obtained with the IBM 7070 computer. Here $A = 10.391602$, $B = 180.04119$, $C = 49443.176$, $D =$

(11) E. A. C. Lucken, *J. Chem. Soc.*, 2954 (1959).

(12) J. F. A. Williams, *Trans. Faraday Soc.*, **57**, 2089 (1961).

(13) (a) K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, *Inorg. Chem.*, **6**, 533 (1967); (b) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *ibid.*, **6**, 1156 (1967).

(14) N. Vanderkooi, J. S. MacKenzie, and W. B. Fox, to be submitted for publication.

(15) "Oxygen Difluoride," Product Data Sheet, General Chemical Division, Allied Chemical Corp., Morristown, N. J.

Table II
Vapor Pressure of F$_3$NO

Temp, °K	Pressure, mm Obsd	Pressure, mm Calcd	Temp, °K	Pressure, mm Obsd	Pressure, mm Calcd
116.2	1.0	1.0	162.5	172.0	170.4
130.5	8.0	7.9	177.4	469.0	468.1
142.0	28.0	28.6	187.6	845.0	847.9
153.6	84.0	84.0	190.9	995.0	1013.4

6.0553102. The normal boiling point from the equation is −87.6°, Trouton's constant is 20.7, and the heat of vaporization is 3.85 kcal/mol.

The critical temperature of F$_3$NO was determined by the "disappearing meniscus" procedure. A heavy-walled Pyrex capillary tube was partially filled with F$_3$NO (98% purity) and sealed with a torch. The temperatures at which the meniscus disappeared on heating (29.8°) and reappeared on cooling (29.1°) were averaged to obtain the critical temperature, 29.5° (measured with a platinum resistance thermometer).

The critical density of F$_3$NO was determined by the method of Cailletet and Mathias.[16] Two heavy-walled Pyrex capillary tubes (calibrated for height *vs.* volume with weighed amounts of mercury) were partially filled with accurately weighed amounts of F$_3$NO and sealed off with a torch. The tubes were then immersed in a thermostatic bath controlled to ±0.1°, and the volumes of liquid and vapor at each temperature were obtained by measuring the heights of liquid

(16) Described in S. Glasstone, "Textbook of Physical Chemistry," 2nd ed D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p 431.

in the tubes with a cathetometer (to 0.001 cm). The equations[16]

$$W^{\mathrm{A}} = p_{\mathrm{g}}{}^{\mathrm{A}}V_{\mathrm{g}}{}^{\mathrm{A}} + p_{\mathrm{l}}{}^{\mathrm{A}}V_{\mathrm{l}}{}^{\mathrm{A}}$$
$$W^{\mathrm{B}} = p_{\mathrm{g}}{}^{\mathrm{B}}V_{\mathrm{g}}{}^{\mathrm{B}} + p_{\mathrm{l}}{}^{\mathrm{B}}V_{\mathrm{l}}{}^{\mathrm{B}}$$

were then solved simultaneously to give gas and liquid density as a function of temperature. These data were used to obtain a plot of the rectilinear diameter (average density of the two phases). Extrapolation of the rectilinear diameter to the critical temperature (29.5°) gave the critical density (0.593 g/ml). A graphic representation of the data is given in Figure 2. Liquid densities measured at temperatures down to −120° (not shown on the graph) were also measured. From the data, the temperature dependence of liquid density over the range −80 to −120° was found to be $d_t = 1.237 − 0.003544t$, where t is in degrees centigrade and d_t is in grams per milliliter.

From the critical density and critical temperature values, the critical pressure was calculated using the van der Waals equation applied to the critical state. The pertinent data are summarized as follows: $T_\mathrm{c} = 29.5°$, $d_\mathrm{c} = 0.593$ g/ml, $a = 4.0965$ l.^{2} atm, $b = 0.0489$ l., and $P_\mathrm{c} = 63.5$ atm. The critical pressure obtained by extrapolation of the vapor pressure equation was 64.0 atm, in excellent agreement with the value above.

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The Oxidation of Dimethylaminodifluorophosphine by Cyanogen Bromide

By JAMES E. CLUNE and KIM COHN

Cyanogen bromide will interact with (CH$_3$)$_2$NPF$_2$ to give (CH$_3$)$_2$NPF$_3$(CN) and (CH$_3$)$_2$NPFBr as products. These new compounds have been completely characterized by chemical analysis and infrared, nmr, and mass spectroscopy. Cyanogen bromide does not interact with PF$_3$.

Discussion

A fairly large number of halofluorophosphoranes and substituted halofluorophosphoranes have been prepared.[1-5] Some of these such as CCl$_3$PCl$_2$F$_2$[4] and (CH$_3$)$_2$NPF$_2$Cl$_2$[5] can be obtained by oxidation of the corresponding phosphine by an appropriate halogen. Pseudohalogens such as cyanogen or thiocyanogen and

pseudohalogen halides such as cyanogen chloride, cyanogen bromide, or thiocyanogen bromide have never been employed successfully as oxidizing agents with phosphines. Salthouse and Waddington[6] have recently reported that cyanogen chloride showed no oxidizing power toward phosphorus trichloride in liquid hydrogen chloride.

In addition, no pentacoordinate pseudohalofluoro-phosphoranes have been reported, although a pseudo-halofluorophosphine, PF$_2$CN, has recently been re-

(1) R. Baumgartner, W. Sawalny, and J. Gobeau, *Z. Anorg. Allgem. Chem.*, **333**, 171 (1964).
(2) Zh. M. Ivanova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **31**, 3991 (1961).
(3) Zh. M. Ivanova and A. V. Kirsanov, *ibid.*, **32**, 2592 (1962).
(4) J. F. Nixon, *J. Inorg. Nucl. Chem.*, **27**, 1281 (1965).
(5) K. Cohn and R. W. Parry, *Inorg. Chem.*, **7**, 46 (1968).

(6) J. A. Salthouse and T. C. Waddington, *J. Chem. Soc., A*, 1096 (1967).