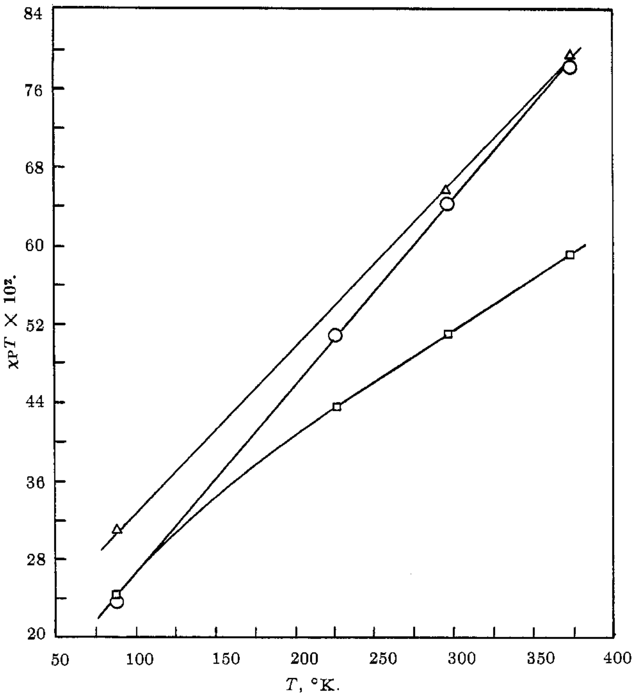

Figure 1.—Magnetic susceptibilities per gram-ion of Fe^{3+} ions times absolute temperature *vs.* absolute temperature for sample 1 (○), sample 2 (△), and sample 7 (□).

χ_P values are given in Table II. The plots for samples 1 and 2 closely approximate a straight line over the whole temperature range. The temperature dependence of χ_P is of the form

$$\chi_P - a = c/T \qquad (1)$$

where a and c are constants. The plot for sample 7 closely approximates a straight line only between 372 and 226°K. The slope is appreciably smaller than the slope of the other plots. Creer[8] has indicated that his preparations of β-ferric oxide monohydrate, of less than 50 Å. particles, almost obeyed a Curie law.

Takada, *et al.*,[9] have reported the Mössbauer spectrum for β-ferric oxide monohydrate. At 110°K. it shows magnetic splitting of the energy levels of the iron nucleus, while at 300°K. this splitting is not observed. Takada, *et al.*, have interpreted this as indicating an antiferromagnetic Curie point between 300 and 110°K. The details of preparation of their sample were not given but they state that their sample was of high purity. We assume that their sample and sample 7 were largely the same. The deviation of χ_PT *vs.* T from a straight line at 88°K. can be accounted for by the onset of antiferromagnetic behavior by sample 7 between 226 and 88°K. If sample 7 obeyed eq. 1 at 88°K., χ_P would be about 3180×10^{-6}.

The low magnetic dilution indicated by antiferromagnetic behavior can account for the low slope of the straight line portion of the plot for sample 7 and the corresponding low values of χ_P. An appreciable difference in magnetic dilution between sample 7 and other samples may be due to a need of the β-ferric oxide monohydrate lattice to find another source of stability as the amount of stabilizing impurity approaches zero. The onset of low magnetic dilution might provide this stability.

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Difluoraminocarbonyl Fluoride

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Trifluoronitrosomethane (CF_3NO) has been reported as a product derived from the fluorination of silver cyanide.[1] When the former contacted 8% aqueous sodium hydroxide, nearly quantitative conversion to its isomer, difluoraminocarbonyl fluoride (NF_2CFO), occurred.[2] This isomer was said to be a colorless, stable compound with a boiling point of −83.4°. However, although Haszeldine and Jander[3] have demonstrated that trifluoronitrosomethane may be slowly decolorized when heated with activated charcoal or when agitated with aqueous base to give several compounds, including hexafluoroazoxymethane ($CF_3{}^{+}N(O^{-})NCF_3$) and trifluoronitromethane (CF_3NO_2), no evidence was found to confirm the formation of difluoraminocarbonyl fluoride. It was concluded that the compound reported as the latter was either perfluoroethane (C_2F_6) or perfluoromethylamine (CF_3NF_2) and, therefore, that difluoraminocarbonyl fluoride was yet to be prepared.[3]

Bumgardner and Lustig[4] have reported the synthesis of difluoraminosulfuryl fluoride by the ultraviolet radiation of a mixture of tetrafluorohydrazine (N_2F_4) and sulfur dioxide. By a similar reaction involving tetrafluorohydrazine and carbon monoxide, it now has been possible to synthesize difluoraminocarbonyl fluoride with properties quite different from those reported heretofore.

Experimental

Reagents.—Tetrafluorohydrazine, obtained from Air Products, Inc., was used without further purification. Carbon monoxide, obtained from the Matheson Company, Inc., was passed through a tube at −183° to remove carbon dioxide and water. Reagents used for analyses were of analytical reagent grade.

Analytical Methods.—After sodium fusion, fluorine was determined through the use of a null-point method,[5,6] carbon was obtained as the carbonate formed by basic hydrolysis, and nitrogen was determined iodometrically. Vapor pressure measurements were made in a vacuum system of small volume by maintaining the compound in a liquid state at various low temperatures in appropriate slush baths and by reading the pressure on a mercury manometer. Vapor density was determined through the use of Regnault's method with a 244.4-ml. Pyrex flask

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equipped with a Teflon stopcock (Fischer and Porter Co.). Liquid densities were measured in a pycnometer of calibrated volume of 0.1–0.2 ml. Separation of reaction products and subsequent purification of the desired product were performed with a dry, fractional codistillation apparatus[7] using a coiled, unpacked, fluorinated copper column (12 ft. of 1/8-in. o.d. tubing). After separation, identification of known reaction products was made through infrared spectra. These spectra were obtained with a Perkin-Elmer Model 137B Infracord and a Pyrex cell with a 5-cm. path length and sodium chloride windows. The mass spectrum was recorded with a Consolidated Engineering Corp. Type 21-103 mass spectrometer. The nuclear magnetic resonance spectrum was obtained through the use of a Varian Model 4311B high-resolution spectrometer equipped with a 40-Mc. oscillator. Trichlorofluoromethane was used as an external reference. Since the compound is easily hydrolyzed, the synthesis and subsequent manipulations were carried out under anhydrous, vacuum conditions.

Reaction of Tetrafluorohydrazine and Carbon Monoxide.—Preliminary attempts to prepare difluoraminocarbonyl fluoride by mixing equimolar amounts of the starting materials at room temperature and at pressures not in excess of 1000 mm. and by slowly warming to various temperatures up to 200° in a static brass reactor resulted in a large number of decomposition products, including CF_4, N_2O, NO_2, CO_2, FNO, and COF_2. Some of these were present only as traces and all were not formed in every reaction. Reactions run in Monel tubes at pressures from 50 to about 200 atm. usually resulted in products similar to those in the lower pressure reactions described above.

In a typical run, 206 mm. of CO and 101 mm. of N_2F_4 were mixed in a 3-l. Pyrex bulb equipped with a quartz finger (water-cooled) and were irradiated for 2 hr. with a Hanau Type 81 high-pressure ultraviolet lamp. The yield of purified NF_2CFO was about 15% (2.6 mmoles) based on the initial amount of N_2F_4. Also recovered were about 15 mmoles of a roughly 50–50 mixture of N_2F_4 and COF_2. Large quantities of N_2F_2, accompanied by smaller amounts of SiF_4, NF_3, N_2O, and CO_2, were also found. These products suggest that the mechanism proposed for the reaction of N_2F_4 and SO_2[3] would be applicable in this case.

Physical Properties of Difluoraminocarbonyl Fluoride.—(a) Experimental measurements gave an average vapor density of 100.3 g./mole compared to 99.0 for NF_2CFO. (b) The melting point was not determined since the pure material supercools to a glass (below −130°) which is stable at −183° for several months without crystallization. (c) The density of the glass is roughly 2.00 g./ml. at −183°. Liquid densities are given in Table I. In the range of −130 to −60°, the density (g./ml.) may be expressed as a function of the absolute temperature by the equation $d = 2.331 - 0.003577T$. (d) The vapor pressure values, measured over the temperature range from −130.0 to −56.2°, are given in Table II. The extrapolated boiling point is −52.0°. In the range −100 to −56°, these points lie on a Clausius–Clapeyron curve given by the equation $\log P_{\mathrm{mm}} = 7.984 - 1129T^{-1}$. These data indicate a molar heat of vaporization of 5.17 kcal./mole and a Trouton constant of 23.4. (e) The infrared spectrum obtained at 10 mm. pressure consists of strong bands at 1900 (doublet, C–O stretch) and 1220 cm.$^{-1}$ (triplet, C–F stretch), moderate complex bands centered at 1045 and 968 cm.$^{-1}$ (N–F stretches), a weak triplet at 840 cm.$^{-1}$, and a moderate triplet at 768 cm.$^{-1}$. The latter two were not identified. (f) The nuclear magnetic resonance spectrum showed a sharp, well-resolved triplet (1:2:1) in the C–F region ($\delta_{CCl_3F} = 15.1$ p.p.m.; $J = 19.1$ c.p.s.) and a broad, single peak in the N–F region ($\delta_{CCl_3F} = -29.1$ p.p.m.). (g) In the mass spectrum, a parent peak, although weak, was observed at mass number 99. Extensive hydrolysis of the sample was also evident. Peaks attributed to the following species (with mass number and relative abundance) were observed: CO^+, N_2^+, 28, 18; NF^+, 33, 13; CO_2^+, 44, 39; CFO^+, SiF^+, 47, 100; NF_2^+, 52, 8.5; $FNCO^+$, 61, 1; F_2NC^+, 64, 1.7; SiF_2^+, 66, 2.3; F_2NCO, 80, 0.1; F_2NCF, 83, 0.05; SiF_3^+, 85, 3.3; F_2NCFO, 99, 0.05; SiF_4^+, 104, 0.08. (h) *Anal.* Calcd. for NF_2CFO: C, 12.1; N, 14.2; F, 57.6. Found: C, 11.7; N, 14.4; F, 53.5.

TABLE I

LIQUID DENSITIES OF NF_2CFO

T, °C.	Density, g./ml.	T, °C.	Density, g./ml.
−130.0	1.817	−77.2	1.627
−115.5	1.764	−69.2	1.599
−97.7	1.704	−60.0	1.571
−87.3	1.665		

TABLE II

VAPOR PRESSURES OF NF_2CFO

P, mm.	T, °K.	P, mm.	T, °K.
2	143.2	257.0	202.4
7.5	157.2	394.5	209.4
33.5	175.5	510.5	214.0
80.0	185.9	546	215.2
166.5	195.9	596	217.0
		(760)	(221.2)

Since the compound is hydrolyzed instantly by water, great care was exercised to maintain anhydrous conditions. An infrared spectrum indicated that HNF_2, CO_2, and SiF_4 were produced when a trace of water vapor was introduced into a sample of pure NF_2CFO. Hydrolysis apparently occurs according to

$$NF_2CFO + H_2O = HNF_2 + CO_2 + HF$$

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

Gaseous difluoraminocarbonyl fluoride is also hydrolyzed rapidly and quantitatively at room temperature by acidic iodide or 0.6 N sodium hydroxide solutions according to

$$NF_2CFO + 6I^- + 5H_3O^+ = 2I_3^- + NH_4^+ + 3HF + CO_2 + 4H_2O \tag{1}$$

$$2NF_2CFO + 8OH^- = N_2F_2 + 4F^- + 2CO_3^{2-} + 4H_2O \tag{2}$$

Equation 1 is analogous to the hydrolysis of HNF_2,[8] and the N_2F_2 produced by eq. 2 is not hydrolyzed after 19 hr. at room temperature.[9]

Gaseous NF_2CFO does not attack mercury at room temperature. A sample was stored in CCl_3F in a sealed Pyrex tube at room temperature for 2 months with no appreciable alteration. The pure compound is stable for 2 hr. in glass at 100°.

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The $B_9H_{13}NCS^-$ Ion

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We wish to correct an earlier[1] characterization of hydrolytic stability in $B_{10}H_{12}X^-$ anions. Reaction

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