

[CONTRIBUTION FROM THE CHEMISTRY SECTION, ROCKETDYNE, A DIVISION OF NORTH AMERICAN AVIATION, INC., CANOGA PARK, CALIF.]

The Synthesis and Reactions of Difluoramine¹

BY EMIL A. LAWTON AND JOHN Q. WEBER

RECEIVED JULY 19, 1963

The direct fluorination of urea yields liquids containing up to 20% fluorine bound to nitrogen and which evolve difluoramine spontaneously at ambient temperature. Difluoramine forms weak adducts with ethers and is readily converted to tetrafluorohydrazine by disproportionation or oxidation. With HCl or phosgene, chlorodifluoramine is formed.

The fluorination of urea at 0° yields a complex yellow to pink liquid (I) which on distillation at reduced pressure yields difluoramine, HNF₂. Physical properties of difluoramine and methods of preparation have been described elsewhere¹⁻³ as well as some of its reactions. We now wish to present more details of the fluorination procedures as well as some of the new reactions of difluoramine.

The fluorination of urea was first reported by Glemser and Ludemann⁴ in which they reported the formation of CO₂, COF₂, biurea, biuret, and a small amount of liquid which was not identified. Dissolution of the solid product in water yielded ammonium fluoride. No mention was made of any new oxidizing fluorine species.

We have found that a fluorine-nitrogen mixture reacts with urea at 0° to form a complex mixture of gaseous products as well as I which is retained in the reactor. The gaseous products have not all been identified but contain CO₂, CF₄, COF₂, (CF₃)₂NF, (CF₃)₃N, HF, HNF₂, HCN, and higher boiling constituents. The liquid contains varying amounts of fluorine (30-70%) and up to 20% active fluorine (oxidizes HI) by weight. The liquid may be stored for months in polyethylene containers at reduced temperatures, but is catalytically converted to a solid quite rapidly in Pyrex. Solution of the liquid in water and evaporation to dryness yield biurea, ammonium fluoride, and a refractory white solid which is probably a polymeric triazine.

The slow distillation of the fluorinated liquid from Kel-F or polyethylene into glass under vacuum yields a mixture of gases by decomposition, principally CO₂, SiF₄, and HNF₂, and a solid residue remains which contains difluorourea.⁵ When NaF is added to the liquid prior to distillation HNCO is also obtained. Difluoramine is easily obtained pure by fractional condensation. Yields of difluoramine have been as high as 30% based on fluorine.

Difluoramine is extremely shock sensitive as a liquid and even more so as a solid. The liquid is at least as detonable as nitroglycerin. The solid will detonate spontaneously when a large quantity is frozen by liquid nitrogen.

Difluoramine is readily converted to N₂F₄ in high yield by a variety of reagents according to the reaction



Effective catalysts are stainless steel, copper, urea, solid decomposition residues of the liquid, and lithium hydride. Only in the last case was hydrogen involved and this is now believed to be due to the action of HF on the

hydride. Oxidants such as Br₂, FClO₃, and O₂ also react to form N₂F₄ but large quantities of the last two yield nitrogen oxides. Difluoramine is soluble in water, in which it hydrolyzes quite slowly.

The electronegative effect of the fluorine atoms makes the molecule a weak acid. With ethers 1:1 adducts are obtained. The physical properties of the adducts of dimethyl and diethyl ethers and with ethylene oxide are given in Table I. The composition of the dimethyl ether adduct was proved by a vapor-liquid phase diagram which displayed a pronounced minimum near equimolar composition. These adducts were completely dissociated at room temperature.

TABLE I
ADDUCTS OF HNF₂ WITH ETHERS

Ether	B. p., °C. (extrap.)	Δ <i>H</i> _{vap}	Trouton's constant	Vapor pressure eq. log <i>p</i> _{mm}
Dimethyl	0	7.66	28.1	(-1674/ <i>T</i>) + 9.005
Diethyl	36	7.41	24.0	(-1619/ <i>T</i>) + 8.124
Ethylene oxide	22	6.92	23.5	(-1512/ <i>T</i>) + 8.015

Difluoramine reacted in the gas phase with carbonyl chloride to form a mixture of N₂F₄ and the recently reported ClNF₂.⁶ We postulated HCl to be an intermediate in this reaction; therefore the reaction of HNF₂ and anhydrous HCl was examined in the gas phase. The compounds reacted slowly forming ClNF₂ by the reaction



Yields as high as 78% based on this reaction were obtained, however, the reaction was not always reproducible. Some tetrafluorohydrazine is often formed which is extremely difficult to separate from ClNF₂.

Experimental

With the exception of the fluorinations, most of the reactions were carried out in a Pyrex high vacuum line using stopcocks lubricated with Halocarbon grease.⁷ All gaseous volumes are given in cc. STP, all liquid volumes in ml.

Fluorination of Urea.—Reagent grade urea was placed on a steel grid in the cylindrical reactor which was cooled with an ice bath. Fluorine, diluted with 4 to 10 volumes of nitrogen, was introduced below the grid at rates of 0.1 to 0.25 mole per hour and the liquid which formed collected below the grid but above the fluorine inlet. The best yields of liquid were obtained with about one mole of fluorine per mole of urea, the yield falling with longer fluorination. A typical example of fluorination follows. Urea (36.3 g., 0.60 mole) was treated for 4 hr. with fluorine (18.4 g., 0.48 mole), diluted 10:1 with nitrogen. The product (50.3 g.) was a pink fuming liquid, I, which contained 35.0% total hydrolyzable fluorine and 15.0% active fluorine. A trap

(1) Preliminary communication: E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **81**, 4755 (1959).

(2) A. Kennedy and C. B. Colburn, *ibid.*, **81**, 2906 (1959).

(3) J. P. Freeman, A. Kennedy, and C. B. Colburn, *ibid.*, **82**, 5304 (1960).

(4) O. Glemser and H. Ludemann, *Z. anorg. allgem. Chem.*, **286**, 168 (1956).

(5) E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. Warner, *J. Inorg. Nucl. Chem.*, **17**, 188 (1961).

(6) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

(7) Halocarbon Products Corp., 82 Burlews Court, Hackensack, N. J.

at -125° , following HF absorbers, contained only a small amount of SiF_4 and NO_2 . However, in other runs, HNF_2 , COF_2 , and HCN were identified in the mixtures in the trap; other liquids and gases containing some CF and NF bonds were present but not identified.

Fluorine Analyses.—Active fluorine was determined by addition to KI in 90% acetic acid, reducing the NF_2 groups to ammonium ions, and titrating evolved iodine with thiosulfate to the iodine end point. The total fluorine was determined by hydrolyzing the sample with dilute base for a day. In neutral or acid solution the oxidizing species present persisted indefinitely and interfered with the amperometric end point employed with the lead chlorofluoride technique for the determination of fluoride ion.

Preparation of Difluoramine.—Samples of I were distilled from polyethylene thimbles or Kel-F coated glassware at 1–4 mm. at room temperature. The vapors were condensed at -142° after passage through Pyrex wool to convert HF to SiF_4 . The distillations were conducted for 2–4 hr. after which difluoramine was purified by fractional condensation. Solids, occasionally with oxidizing power, condensed at -112° , pure difluoramine at -126° , and difluoramine contaminated with CO_2 and SiF_4 at -142° .

The compound I (3.7 g.) containing 15% active fluorine yielded 113 cc. of pure HNF_2 which represented 35% of the active fluorine. Comparable yields of HNF_2 were obtained when sodium fluoride was added to I prior to distillation, in which case the HNF_2 was free of SiF_4 but contaminated with considerable isocyanic acid which was difficult to remove.

Density of Difluoramine.—The density of difluoramine was measured in a pycnometer with a volume of 0.0343 ml. which was calibrated with mercury. The weight of difluoramine was determined by vaporization of the liquid into a calibrated volume and use of the perfect gas laws. A small correction was made for the quantity in the vapor phase above the liquid. The densities measured are given in Table II and may be represented by $d = 1.424 - 0.00202t$ where $t = ^{\circ}\text{C}$.

TABLE II

DENSITY OF DIFLUORAMINE

Temp., °C.	Density (obsd.), g./ml.	Density (calcd.), ^a g./ml.	Temp., °C.	Density (obsd.), g./ml.	Density (calcd.), ^a g./ml.
-80.5	1.587	1.586	-49.5	1.513	1.524
-64.5	1.553	1.554	-42.5	1.513	1.510
-52.2	1.538	1.530	0	...	1.424

^a From above equation.

Melting Point of Difluoramine.—Difluoramine was condensed as an easily visible ring of white opaque frost in a small tube and immersed in a partially silvered dewar flask, which was then permitted to warm, with stirring, at about $2^{\circ}/\text{min}$. The melting point was taken as the temperature at which the ring became translucent, -117.1 to -116.4° (av. of -115.7 to -114.5° and -118.6 to -118.4°). Further measurements were not attempted because of the explosive nature of the solid.

Explosive Nature of Difluoramine.—Difluoramine, in quantities up to 1 g., has been condensed over 100 times as the solid at -142° without incident. However, more than 10 explosions have occurred when quantities as small as 50 mg. were condensed at -196° , the explosions usually occurring within a few seconds after the liquid nitrogen bath was removed.

Difluoramine in Water.—A 0.015 M solution of difluoramine in 0.10 M sulfuric acid was thermostated at 35° and after 66 hr. 14% of the difluoramine had been lost. The HNF_2 content of the solution was determined by reaction of HI. Addition of urea before titration did not change the titer, indicating nitrous acid was not a hydrolysis product. Portions of the above 0.015 M solution were treated with silver nitrate and cupric nitrate; however, no precipitates formed, even upon making the solutions neutral.

Difluoramine Complexes with Ethers.—Mixtures of difluoramine with dimethyl ether or diethyl ether were stable on long standing. However, with ethylene oxide, slow polymerization of the oxide occurred to form a white nonvolatile solid leaving the HNF_2 unchanged. Dioxane was not formed as with BF_3 and other Lewis acids.⁸ A plot of vapor pressure vs. composition at -80° of HNF_2 and $(\text{CH}_3)_2\text{O}$ displayed a minimum of 3 mm. (26.5 mm. for an ideal solution) near equimolar composition. The data for vapor pressure vs. temperature of 1:1 mixtures with the ethers are listed in Tables III, IV, and V and the properties derived are in Table I. The dimethyl and diethyl ethers were dried over CaH_2 and all components of these mixtures were freshly

TABLE III

VAPOR PRESSURES OF DIFLUORAMINE-DIMETHYL ETHER

Temp., °C.	<i>p</i> (obsd.), mm.	<i>p</i> (calcd.), ^a mm.	Temp., °C.	<i>p</i> (obsd.), mm.	<i>p</i> (calcd.), ^a mm.
-79.4	2	2.5	-41.4	59	58.9
-74.0	4	4.0	-47.5	38	37.2
-67.1	8	7.6	-39.4	72	67.6
-63.2	11	10.5	-36.8	82	81.3
-58.0	16	16.2	-34.0	99	100.0
-51.0	28	28.2			

^a From eq. in Table I.

TABLE IV

VAPOR PRESSURES OF DIFLUORAMINE-DIETHYL ETHER ADDUCT,
1:1

Temp., °C.	<i>p</i> (obsd.), mm.	<i>p</i> (calcd.), ^a mm.	Temp., °C.	<i>p</i> (obsd.), mm.	<i>p</i> (calcd.), ^a mm.
-32.6	26	25.2	-0.2	157	158
-27.5	35	33.4	+2.4	191	191
-27.3	32	34.7	8.5	233	234
-23.0	46	45.7	19.9	381	398
-11.7	88	85.1			

^a From eq. in Table I.

TABLE V

VAPOR PRESSURES OF DIFLUORAMINE-ETHYLENE OXIDE ADDUCT,
1:1

Temp., °C.	<i>p</i> (obsd.), mm.	<i>p</i> (calcd.), ^a mm.	Temp., °C.	<i>p</i> (obsd.), mm.	<i>p</i> (calcd.), ^a mm.
-69.0	3	4.0	-34.5	50	47.5
-62.3	6	6.7	-29.0	67	64.6
-49.8	16	17.0	-23.0	95	96.5
-45.5	23	23.0	-15.1	140	145
-39.0	34	37.0	-11.2	161	174

^a From eq. in Table I.

fractionated in the vacuum line. The ethylene oxide-difluoramine mixture was fractionated immediately before use to ensure 1:1 composition.

Any error in the ethylene oxide data is probably small, since polymerization would be slight during the 2-hr. period when the vapor pressures were being measured. Even after standing overnight at room temperature the mixture contained 59 mole % HNF_2 (iodimetric titration), indicating 18% polymerization of the oxide.

Preparation of Chlorodifluoramine.—Difluoramine did not react with carbonyl chloride in diethyl ether. When pyridine was added, all the difluoramine was consumed with the formation of tetrafluorohydrazine and a black tar. Heating HNF_2 (19.7 cc.) with COCl_2 (8.4 cc.) for 27 hr. at 105° caused the formation of chlorodifluoramine (6.7 cc.). The other reaction products were a white solid, CO_2 , and SiF_4 . The ClNF_2 was identified by its molecular weight of 89.5 (calcd. 87.5), by the agreement of the vapor pressure equation we determined ($\log p_{\text{mm}} = (-980/T) + 7.665$) with the literature, and the identity of the infrared spectrum with that of an authentic sample.⁹ Chlorodifluoramine (12.7 cc.) was formed from a mixture of HNF_2 (29.6 cc.) and HCl (22.6 cc.) after 22 hr. at room temperature. Also present were SiF_4 , NH_4Cl (by qualitative tests), and unreacted HCl and HNF_2 (5.3 cc.). The ClNF_2 was obtained pure by addition of dimethyl ether prior to fractionation to complex the acidic contaminants whose vapor pressures are close to that of ClNF_2 .

Preparation of Tetrafluorohydrazine from Difluoramine.— HNF_2 and urea exhibited no interaction at room temperature; however, when 20.2 cc. of HNF_2 was allowed to stand over 3 g. of finely powdered urea at -80° the pressure fell to 11.5 mm. When equilibrium was approached from the low pressure side the pressure finally rose to 9.5 mm. after 3 hr. All of the HNF_2 was promptly recovered when the mixture was allowed to warm

(8) M. Schmeisser and H. Jenkner, *Z. Naturforsch.*, **7h**, 583 (1962).

(9) We are indebted to Dr. C. B. Colburn, Rohm and Haas Co., for furnishing us the infrared spectra of both N_2F_4 and ClNF_2 .

to room temperature. Urea (21 mg.) and HNF_2 (24.6 cc.) were held at 0° for 68 hr. in a 7-ml. high pressure ampoule; HNF_2 (10.1 cc.) was recovered but the remainder had been converted to N_2F_4 (5.5 cc.) in 95% yield according to (1). The solid remaining gave qualitative tests for NH_4^+ and F^- . HNF_2 (4.5 cc.) was condensed into an 80-ml. stainless steel ampoule. After 6

days at room temperature the ampoule contained 1.1 cc. of HNF_2 and 0.8 cc. of N_2F_4 . This represents a 59% yield of N_2F_4 based on 1.

Acknowledgment.—We are indebted to the Office of Naval Research for support of this work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y., AND NATIONAL BUREAU OF STANDARDS, WASHINGTON 25, D. C.]

The Structure of Gaseous Copper(II) Nitrate as Determined by Electron Diffraction

BY R. E. LAVILLA^{1a,b} AND S. H. BAUER^{1a}

RECEIVED JUNE 7, 1963

Anhydrous copper(II) nitrate has a sufficient vapor pressure at 180 – 200° to permit the recording of electron diffraction photographs. That this gas is monomeric has been demonstrated by Addison, *et al.*, by means of vapor density measurements and confirmed with mass spectrometry; its range of stability has also been ascertained. Visually estimated intensities of the electron diffraction patterns were used for the Fourier inversion to a radial density function and were compared with computed intensity curves for many models. The analysis indicates the molecular structure of gaseous copper(II) nitrate to be of the bidentate form with the copper atom occupying the center of inversion. The central copper atom has four nearest oxygen atoms at $2.00 \pm 0.02 \text{ \AA}$. and two Cu–N distances of $2.30 \pm 0.03 \text{ \AA}$, $\angle \text{O–N–O} = 120 \pm 2^\circ$ and $\angle \text{O–Cu–O} \approx 70^\circ$.

A. Introduction

Addison and Hathaway² reported the preparation of anhydrous copper(II) nitrate and found it to have an unexpected volatility. When heated to 150 – 225° , it sublimes with a vapor pressure of 0.3 to 3.5 mm.; the vapor density corresponds to monomeric $\text{Cu}(\text{NO}_3)_2$. An analysis of the mass spectrum³ of gaseous copper(II) nitrate with the solid sample at 88° supports the monomeric nature of the molecular gas and suggests that the nitrogen and oxygen atoms are bonded as in the nitrate groups. The infrared spectra⁴ of the solid and vapor phases are typical of covalently bonded nitrate groups, but there are significant differences between the spectra of the two phases. A preliminary report⁵ of the crystal structure of anhydrous $\text{Cu}(\text{NO}_3)_2$ lends further support to the presence of covalent bonding in the solid phase.

Of considerable interest are the recently prepared anhydrous ferric and mercuric nitrates^{6a} and copper perchlorate^{6b} which also show high volatilities. Thus, it appears that copper(II) nitrate is a typical member of an interesting group of compounds.

We hope that this preliminary electron diffraction investigation of copper(II) nitrate vapor provides a structural basis for the interpretation of its interesting properties. Owing to an unfortunate error in the reduction of photographic intensities between the third and sixth maxima, an incorrect structure was at first deduced for gaseous copper(II) nitrate.⁷ The diffraction pattern predicted for that structure differs substantially from the experimental one, following correct reduction of data, and hence may be dismissed from further consideration.

B. Experimental

Anhydrous $\text{Cu}(\text{NO}_3)_2$ was furnished by C. C. Addison in sealed glass vials. These were opened in a nitrogen-filled dry-box and the sample transferred to the reservoir of a special designed nozzle assembly. Nonsectored electron diffraction photographs were taken with the camera described by Hastings and Bauer,⁸ with the nozzle assembly maintained between 175 and 185°

TABLE I

Max.	Min.	q_{obs}	I_{vis}	$q[\text{V}_h\text{-}(22\text{T})]$	$q[\text{V}_h\text{-}(22\text{T})]$	$q[\text{V}_d\text{-}(19\text{T})]$	$q[\text{V}_d\text{-}(19\text{T})]$
					q_{obs}	q_{obs}	q_{obs}
1		11.9	7.5	12.0	1.008	12.0	1.008
	1	16.0	–8.9	16.0	1.000	15.8	0.988
2		20.2	8.5	20.5	1.015	20.8	1.030
Shoulder		22.2	3.0	23.0	1.036	23.0	1.036
	2	27.5	–7.5	26.3	0.956	26.2	0.953
3		30.7	5.0	31.1	1.013	31.0	1.010
	3	33.0	–3.4	33.0	1.000	33.0	1.000
4		35.4	7.0	34.8	0.983	34.8	0.983
	4	37.9	–1.7	38.0	1.003	37.9	1.000
5		40.1	1.3	41.2	1.027	40.6	1.013
	5	43.2	–2.6	43.0	0.995	43.0	0.995
6		46.0	2.5	45.2	.983	45.6	.991
	6	49.0	–2.4	48.2	.984	48.0	.980
7		52.3	6.0	52.6	1.006	52.3	1.000
Shoulder		54.1	1.8	55.0	1.017	54.5	1.007
	7	58.2	–5.2	58.1	0.998	58.4	1.003
8		63.5	7.0	62.9	.991	63.2	0.995
	8	68.6	–4.5	67.8	.988	68.2	.994
9		74	6.0	72.5	.980	72.7	.982
	9	79	–5.5	77.0	.975	77.0	.975
10		84	7.0	82.1	.977	82.1	.977
				Mean	0.997		0.996
				Av. dev.	0.015		0.014

(vapor pressure 0.6 to 1.0 mm.). Photographs were taken over a period of 6 days, with different loadings of sample. No differences were noted in the diffraction patterns. The Medium Lantern Slide Kodak plates which were used were processed in Kodak D-76, and the exposures ranged from 0.3 to 8.0 min. The sample–plate distance was ≈ 18 cm., electron wave length $\approx 0.053 \text{ \AA}$; gold foil served for calibration patterns.

C. Analysis of the Photographs

The positions of the maxima and minima in the diffraction pattern of ten selected photographs were measured with an optical comparator. The intensities of all the diffraction features were estimated visually. In addition, three plates selected for proper density were microphotometered to supplement the visual estimate of the intensities between the third and sixth halos, whose narrow breadth and close spacing made a reliable visual estimate difficult. The results are summarized in Table I.

- (1) (a) Cornell University; (b) National Bureau of Standards.
- (2) C. C. Addison and B. J. Hathaway, *J. Chem. Soc.*, 3099 (1958).
- (3) R. F. Porter, R. C. Schoemaker, and C. C. Addison, *Proc. Chem. Soc.*, 11 (1959).
- (4) C. C. Addison and B. M. Gatehouse, *Chem. Ind. (London)*, 464 (1958).
- (5) S. C. Wallwork, *Proc. Chem. Soc.*, 311 (1959).
- (6) (a) C. C. Addison, B. J. Hathaway, and N. Logan, *ibid.*, 51 (1958); (b) B. J. Hathaway, *ibid.*, 344 (1958).
- (7) S. H. Bauer and C. C. Addison, *ibid.*, 251 (1960).

- (8) J. M. Hastings and S. H. Bauer, *J. Chem. Phys.*, **18**, 13 (1950).