

In a subsequent publication, a more detailed model for LiF-BeF₂ solutions will be compared with the present data, a model in which polymeric anions Be_aF_b^{(b-2a)-} are assumed. These will extend in composition and structure from the monomer BeF₄²⁻—the principal species when \bar{X}_{BeF_2} is less than 0.33—through increasingly polymeric anions as \bar{X}_{BeF_2} increases, to very large networks or chain structures as pure BeF₂ is approached. For the present it may be useful to point out that since in such a model Li⁺ is the only

cation present in solution, its ion fraction is unity and its activity might be approximated as unity. In this case the activity of LiF given by the present results (Table II) should approximate the activity of F⁻ ion

$$a_{\text{LiF}} = (a_{\text{Li}})(a_{\text{F}^-}) \sim a_{\text{F}^-}$$

The rapid drop in γ_{LiF} (Figure 7a)—*i.e.*, in a_{LiF} —as BeF₂ is added to LiF thus may be viewed as corresponding to the depletion of free F⁻ ions as Be_aF_b^{(b-2a)-} polymers are formed.

Notes

CONTRIBUTION FROM THE MORRISTOWN LABORATORY,
INDUSTRIAL CHEMICALS DIVISION, ALLIED CHEMICAL
CORPORATION, MORRISTOWN, NEW JERSEY 07960

N,N-Difluoro-O-fluorocarbonylhydroxylamine, FC(O)ONF₂, and N,N-Difluoro-O-trifluoromethylhydroxylamine, CF₃ONF₂

BY W. B. FOX, G. FRANZ, AND L. R. ANDERSON

Received August 28, 1967

Recent publications have described the synthesis of the novel N-fluorinated hydroxylamines FSO₂ONF₂,¹ SF₆ONF₂,^{2,3} and CF₃ONF₂.^{3,4} through reactions of tetrafluorohydrazine with (FSO₂O)₂, SF₆OF, and CF₃OF, respectively. Presumably these reactions proceed *via* simple coupling of difluoramino radicals with the intermediate oxy radicals (FSO₂O·, SF₅O·, and CF₃O·) generated from the substrates.¹⁻⁴

In the light of these reports and our recent esr studies of the oxy radicals generated by homolytic cleavage of the peroxides FC(O)OOC(O)F⁵ and CF₃OOCF₃,⁶ it was of interest to examine the reactions of these peroxides with tetrafluorohydrazine. The anticipated synthesis of the corresponding N-fluoro-O-substituted hydroxylamines is described below.

Experimental Section

Materials.—Bis(fluorocarbonyl)peroxide was prepared by a published method⁷ and fractionated on the vacuum line through traps at -111, -130, and -196°. The peroxide collected at -130° was used after its identity was confirmed by infrared and mass spectral analysis. Bis(trifluoromethyl) peroxide from Peninsular ChemResearch and tetrafluorohydrazine from E. I. du Pont de Nemours and Co. were sufficiently pure to be used without further treatment.

Preparation of FC(O)ONF₂.—The most satisfactory procedure for preparing FC(O)ONF₂ is illustrated by the following example. An evacuated 200-ml Pyrex bulb was charged with 150 mm of gaseous N₂F₄ (1.60 mmol) at 25°, and an equal amount of FC(O)OOC(O)F was then added from a high-pressure reservoir. Within 1 min after the addition, a rapid reaction occurred as evidenced by formation of a white "mist" in the reactor. The bulb was then cooled to -78° and volatile products were pumped off through traps at -111 and -196°. The product FC(O)ONF₂ was collected at -111° and a mixture of NF₃, CO₂, COF₂, and SiF₄ was found in the -196° trap. The FC(O)ONF₂ fraction (0.40 mmol) was contaminated with small amounts of NO₂ and unused peroxide from which it could be separated by fractional codistillation.⁸ *Anal.* Calcd for FC(O)ONF₂: N, 12.2; F, 49.5. Found: N, 11.8; F, 48.7. In nearly a dozen runs conducted in this fashion, yields of FC(O)ONF₂ ranged from 10 to 15%.

An unusual requirement of these runs was that a fresh, unused reaction bulb was required for each experiment to ensure reasonable yields of the desired product. Subsequent experiments conducted in bulbs after their initial use produced NF₃, COF₂, NO₂, and oxygen, but no detectable amount of FC(O)ONF₂. No manner of rinsing or cleaning restored the apparent catalytic activity of the Pyrex reactor walls. With one exception, experiments conducted in vessels of quartz, nickel, Monel, and stainless steel were unrewarding and led to mixtures of COF₂, NF₃, NO₂, and noncondensable material. In one case, equimolar amounts of N₂F₄ and FC(O)OOC(O)F in a reactor of Type 316 stainless steel produced a quantitative yield of FC(O)ONF₂, but this result could not be reproduced in numerous subsequent trials.

Preparation of CF₃ONF₂.⁹—The reactor used was a 30-ml Hoke cylinder (316 stainless steel) fitted with a 323A Hoke valve. Tetrafluorohydrazine (2.5 mmol) and bis(trifluoromethyl) peroxide (2.4 mmol) were combined in the tube and heated to 130° for 10 days. Vacuum-line fractionation of products through traps at -130, -142, and -196° afforded unused CF₃OOCF₃ (1.7 mmol) in the first two traps. A mixture of CF₃ONF₂, N₂F₄, NF₃ (trace), and COF₂ in the third trap was refractionated through -158 and -196° traps which isolated a CF₃ONF₂-COF₂ mixture at -158° and N₂F₄ (2.2 mmol, contaminated with minor amounts of COF₂, CF₃ONF₂, and NF₃) at -196°. Pure CF₃ONF₂⁸ (0.5 mmol) was recovered from the -158° fraction after removing the COF₂ (0.5 mmol) by absorption on finely ground CsF. Based on CF₃OOCF₃ consumed (0.7 mmol), the pure CF₃ONF₂ recovered (0.5 mmol) represents a 36% yield (83% based on N₂F₄ consumed). No significant reaction between CF₃OOCF₃ and N₂F₄ occurred when mixtures were heated

(1) M. Lustig and G. H. Cady, *Inorg. Chem.*, **2**, 388 (1963).

(2) J. Ruff, *ibid.*, **4**, 1788 (1965).

(3) W. H. Hale and S. M. Williamson, *ibid.*, **4**, 1342 (1965).

(4) J. M. Shreeve and L. C. Duncan, *ibid.*, **4**, 1516 (1965).

(5) W. B. Fox and G. Franz, *ibid.*, **5**, 946 (1966).

(6) N. Vanderkooi and W. B. Fox, to be published.

(7) (a) A. J. Arvia, P. J. Aymonino, C. Waldow, and H. J. Schumacher, *Angew. Chem.*, **72**, 169 (1960); (b) A. J. Arvia, P. J. Aymonino, and H. J. Schumacher, *Z. Anorg. Allgem. Chem.*, **316**, 327 (1962).

(8) G. H. Cady and D. P. Siegarth, *Anal. Chem.*, **31**, 618 (1959).

(9) Following completion of this work, a similar preparation of CF₃ONF₂ was reported by G. N. Sausen, U. S. Patent 3,214,465 (Oct 26, 1965).

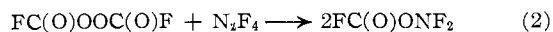
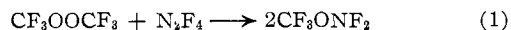
to 90° for 16 hr or 140° for 4 hr. Reactions conducted in Pyrex vessels and subjected to ultraviolet irradiation by a high-pressure mercury lamp were attended by extensive attack on the glass and formation of NO₂, NF₃, COF₂, SiF₄, CO₂, and CF₄. No evidence for CF₃ONF₂ was found in these studies.

Nmr and Infrared Spectra.—The infrared spectrum of FC(O)ONF₂ was obtained with a Beckman IR-8 spectrophotometer. The F¹⁹ nmr spectrum of FC(O)ONF₂ as a 10–20% solution in SF₆ was recorded at –78° with a Varian spectrometer, Model V-4302. Chemical shifts are reported in ϕ units, here defined as ppm relative to CFCl₃.

Mass Spectrum.—A Consolidated Electrodynamics Corp. Model 21-202 spectrometer with an ionization potential of 70 V was used to obtain the fragmentation pattern of FC(O)ONF₂. The mass number, species, and relative abundance (in parentheses) of the most prominent peaks are as follows: 28, CO⁺ (36.7); 30, NO⁺ (44.0); 33, NF⁺ (30.8); 44, CO₂⁺ (56.6); 47, FCO⁺ (100.0); 49, NOF⁺ (0.4); 52, NF₂⁺ (58.3); 63, FCO₂⁺ (0.3); 68, ONF₂⁺ (0.3); 77, FCO₂N⁺ (0.2); 96, FCO₂NF⁺ (0.1). No peaks at higher mass numbers were observed.

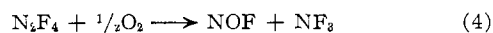
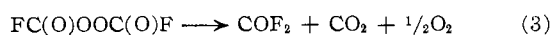
Results and Discussion

The formation of the N,N-difluorohydroxylamine products in this study can be represented by

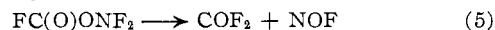


Both reactions probably involve primary fission of the peroxide O–O bonds and subsequent addition of the resultant oxy radicals to the NF₂· radicals known to exist in equilibrium with N₂F₄.¹⁰ The much greater reactivity of FC(O)OC(O)F than of CF₃OOCF₃ toward N₂F₄ may be a manifestation of weaker O–O bonding in the fluorocarbonyl peroxide compared with trifluoromethyl peroxide. This would be consistent with the much lower thermal stability of FC(O)OC(O)F⁷ compared with CF₃OOCF₃.¹¹

The synthesis of CF₃ONF₂ according to eq 1 offers some advantage over the synthesis of this material from CF₃OF and N₂F₄,^{3,4} since undesirable by-product formation (COF₂, NF₃, CF₄, NOF) is minimized and more efficient utilization of starting materials results. The formation of FC(O)ONF₂ according to eq 2 appears to be a facile process but the experimental results indicate a number of equally facile competing reactions in the system. The variations in yields of FC(O)ONF₂ and the erratic influences of reactor history and type are reminiscent of the irregular behavior observed in the synthesis of SF₅ONF₂.² The by-products (COF₂, CO₂, O₂, and NF₃) formed here during the synthesis of FC(O)ONF₂ may have arisen partly through thermal decomposition of the peroxide, eq 3,⁷ followed by oxidation of the N₂F₄ as reported by Beach¹²



Thermal decomposition of the desired product FC(O)ONF₂ according to the equation



probably occurred to some extent during synthesis,

(10) (a) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **82**, 2400 (1960); (b) L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961).

(11) R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 5628 (1957).

(12) L. K. Beach, *J. Inorg. Nucl. Chem.*, **26**, 2033 (1964).

since isolated samples of FC(O)ONF₂ which decomposed during storage or when heated formed mainly COF₂ and NOF (or products of the latter's attack on glass¹³). Hale and Williamson³ have observed this mode of thermal decomposition (*e.g.*, NOF elimination) for CF₃ONF₂ and SF₅ONF₂. It is of interest that photochemical decomposition of FC(O)ONF₂ at –196° in the resonance cavity of an esr spectrometer produced the previously reported⁶ anisotropic doublet spectrum of the FCO₂· radical. This indicates that photochemical decomposition of FC(O)ONF₂ differs from thermal decomposition in proceeding by O–N bond cleavage rather than C–O rupture.

The infrared spectrum of FC(O)ONF₂ in the sodium chloride region is entirely consistent with its formulation as a fluorinated hydroxylamine derivative. Very strong absorptions at 1890 and 1215 cm⁻¹ arise from C=O and C–F stretching vibrations of the FCO group.^{14,15} Strong bands at 1037 and 906 cm⁻¹ may be assigned to symmetric and asymmetric N–F stretches, respectively, in view of their similarity to such vibrations in CF₃ONF₂ (1027 and 933 cm⁻¹)³ and FSO₂ONF₂ (1032 and 913 cm⁻¹).¹ Bands found at 887 (s) and 870 (vs) cm⁻¹ in FC(O)ONF₂ are assignable to singly bonded C–O and N–O stretches, since these modes appear at 892 and 865 cm⁻¹, respectively, in CF₃ONF₂.³ The general shape of the absorption envelope over the range 1050–850 cm⁻¹ in the FC(O)ONF₂ spectrum bears a striking resemblance to that of CF₃ONF₂ in this region. Bands in the FC(O)ONF₂ spectrum at 675 (w) and 740 (w) cm⁻¹ have not been definitely assigned, but the 740-cm⁻¹ band may be associated with the NF₂O symmetric deformation.

Additional evidence for the proposed structure of FC(O)ONF₂ may be derived from the nmr spectrum. A broad triplet at ϕ –110 is attributable to quadrupole-broadened NF resonance of the ONF₂ group, with $J_{\text{NF}} = 158$ Hz. (The nmr spectrum of CF₃ONF₂ exhibits a similar NF triplet at ϕ –124° with $J_{\text{NF}} = 126$ Hz.³) A high-field resonance at ϕ +40, assignable to C–F of the FC(O)O group⁵ appeared to be a narrow, incompletely resolved triplet, the fine structure arising from coupling between the CF and NF fluorines. Since the line width of the band at half-height was around 10 Hz, it could only be estimated that $J_{\text{CF-NF}}$ was less than 10 Hz and greater than 3 Hz. This range appears reasonable, since CF₃ONF₂ has $J_{\text{NF-CF}} = 3.4$ Hz⁴ and FSO₂ONF₂ has $J_{\text{NF-CF}} = 4.6$ Hz.¹ The area of the CF resonance was half that of the NF resonance.

N,N-Difluoro-O-fluorocarbonylhydroxylamine was found to be stable as a liquid stored in glass for weeks at –78°, but gaseous samples at room temperature generally underwent sudden decomposition after periods ranging from several minutes to several days. The compound was rapidly decomposed by moisture and mercury, the latter tendency preventing accurate gas

(13) O. Ruff, W. Menzel, and W. Neumann, *Z. Anorg. Allgem. Chem.*, **208**, 293 (1932).

(14) J. Simons, "Fluorine Chemistry," Vol. II, Academic Press, New York, N. Y., 1954, p 485.

(15) K. Loos and R. Lord, *Spectrochim. Acta*, **21**, 119 (1965).

density and molecular weight measurements. However, crude measurements with a Monel Bourdon gauge, as well as the behavior of FC(O)ONF₂ during vacuum line manipulations, suggested a normal boiling point in the vicinity of 0°.

Caution! Although no explosions occurred during the course of this work, the materials are potentially hazardous and proper shielding should be used.

Acknowledgments.—The authors thank Dr. B. B. Stewart for the nmr spectra, Mr. E. McCarthy for the mass spectroscopic results, and Miss R. Juurik for the chemical analyses. This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Research Missile Command, Redstone Arsenal, Huntsville, Ala., under Contracts DA-30-069-ORD-2638 and DA-01-021-AMC-12264(Z).

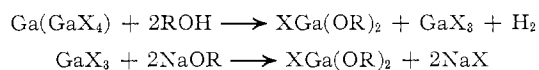
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF RAJASTHAN, JAIPUR, INDIA

Reactions of Gallium Alkoxides with Acyl Halides

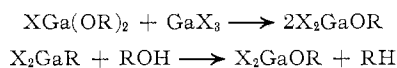
By S. R. BINDAL, P. N. KAPOOR, AND R. C. MEHROTRA

Received February 1, 1967

Halide alkoxides of a number of elements (*e.g.*, Ti,¹ Zr,² Al,³ Fe,⁴ and V⁵) have been synthesized by the reactions of their alkoxides with acyl halides. In a recent communication Mogelet⁶ has reported the preparation of halide alkoxides of gallium by reactions of the type



where X = Cl or Br and R = CH₃ or C₂H₅. These monohalide derivatives were found to be insoluble in organic solvents and were assumed to be coordinatively polymeric. Dihalide monoalkoxy derivatives could not be prepared by similar reactions, since the dihalide derivatives initially formed were found to yield the monohalide derivatives. The dihalide derivatives could finally be prepared by reactions of the type



where X = Cl or Br and R = CH₃ or C₂H₅.

(1) D. C. Bradley, D. C. Hancock, and W. Wardlaw, *J. Chem. Soc.*, 2773 (1952).

(2) D. C. Bradley, F. M. Halim, R. C. Mehrotra, and W. Wardlaw, *ibid.*, 4609 (1952).

(3) R. C. Mehrotra and R. K. Mehrotra, *J. Indian Chem. Soc.*, **39**, 23 (1962).

(4) P. P. Sharma, Ph.D. Thesis, University of Rajasthan, Jaipur, India, 1966.

(5) R. C. Mehrotra and R. K. Mittal, *Z. Anorg. Allgem. Chem.*, **332**, 189 (1964).

(6) L. Mogelet, "Proceedings, 9th International Conference on Coordination Chemistry," Verlag Helvetica Chimica Acta, Basle, 1966.

TABLE I

INFRARED BANDS OF THE COMPOUNDS^a

Compound	Bands, cm ⁻¹											
Ga(<i>t</i> -C ₃ H ₇ O) ₂ Cl (distd) ^{b,c}	3700 vw	3645 w	3650 w	3580 w	3445 vw	3100 s	3080 s	3070 s (A)	3025 s	2985 s (A)	2980 s (A)	2905 s
Ga(<i>t</i> -C ₃ H ₇ O)Cl ₂ (distd) ^{b,d}	3700 w	3650 w	3600 vw	3610 vw	3445 vw	3080 s	3070 s (A)	3035 s	3040 s	2985 s (A)	2980 s (A)	2915 s
GaCl ₂ · <i>i</i> -C ₃ H ₇ OOCCH ₃ ^{e,d}	3700 w	3650 w	3600 vw	3610 vw	3445 vw	3080 s	3070 s (A)	3035 s	3040 s	2985 s (A)	2980 s (A)	2915 s
Ga(<i>t</i> -C ₃ H ₇ O) ₂ Cl	2605 w	2375 m	2370 w	2330 w	2210 w	2010 w	1960 m	1810 s	1810 s	1755 w	1705 w (C)	1670 w
Ga(<i>t</i> -C ₃ H ₇ O)Cl ₂	2600 w	2375 m	2370 w	2330 w	2210 w	2000 vw	1955 m	1805 s	1805 s	1755 w	1705 w (C)	1670 w
GaCl ₂ · <i>i</i> -C ₃ H ₇ OOCCH ₃	1365 m	1295 s	1245 w	1254 s	1245 w	1218 s, b	1180 m (E)	1155 w (E)	1155 w (E)	1122 w	1064 vw	1028 w
Ga(<i>t</i> -C ₃ H ₇ O) ₂ Cl (D)	1360 s	1295 s	1245 w	1254 s	1245 w	1218 s, b	1180 m (E)	1155 w (E)	1155 w (E)	1122 w	1064 vw	1028 w
Ga(<i>t</i> -C ₃ H ₇ O)Cl ₂	933 w	883 w	843 w	843 w	815 w (E)	753 s, b	717 s (E)	685 s	615 w (F)	593 w (F)	593 w (F)	593 w (F)
GaCl ₂ · <i>i</i> -C ₃ H ₇ OOCCH ₃	925 w	883 w	843 w	843 w	815 w (E)	768 w	717 s (E)	685 s, b	610 sh (F)	605 m (F)	605 m (F)	605 m (F)
Ga(<i>t</i> -C ₃ H ₇ O) ₂ Cl	1465 s (D)	1445 m (D)	1465 s (D)	1465 s (D)	1460 m (D)	1460 m (D)	1460 m (D)	1460 m (D)	1460 m (D)	1460 m (D)	1460 m (D)	1460 m (D)
Ga(<i>t</i> -C ₃ H ₇ O)Cl ₂	1385 m (D)	1385 m (D)	1385 m (D)	1385 m (D)	1385 m (D)	1385 m (D)	1385 m (D)	1385 m (D)	1385 m (D)	1385 m (D)	1385 m (D)	1385 m (D)
GaCl ₂ · <i>i</i> -C ₃ H ₇ OOCCH ₃	942 m	942 m	942 m	942 m	942 m	942 m	942 m	942 m	942 m	942 m	942 m	942 m
Ga(<i>t</i> -C ₃ H ₇ O) ₂ Cl	2660 w	2660 w	2660 w	2660 w	2660 w	2660 w	2660 w	2660 w	2660 w	2660 w	2660 w	2660 w
Ga(<i>t</i> -C ₃ H ₇ O)Cl ₂	2895 w (B)	2895 w (B)	2895 w (B)	2895 w (B)	2895 w (B)	2895 w (B)	2895 w (B)	2895 w (B)	2895 w (B)	2895 w (B)	2895 w (B)	2895 w (B)
GaCl ₂ · <i>i</i> -C ₃ H ₇ OOCCH ₃	2830 w	2830 w	2830 w	2830 w	2830 w	2830 w	2830 w	2830 w	2830 w	2830 w	2830 w	2830 w
Ga(<i>t</i> -C ₃ H ₇ O) ₂ Cl	1500 s	1500 s	1500 s	1500 s	1500 s	1500 s	1500 s	1500 s	1500 s	1500 s	1500 s	1500 s
Ga(<i>t</i> -C ₃ H ₇ O)Cl ₂	1520 w	1520 w	1520 w	1520 w	1520 w	1520 w	1520 w	1520 w	1520 w	1520 w	1520 w	1520 w
GaCl ₂ · <i>i</i> -C ₃ H ₇ OOCCH ₃	1515 w	1515 w	1515 w	1515 w	1515 w	1515 w	1515 w	1515 w	1515 w	1515 w	1515 w	1515 w
Ga(<i>t</i> -C ₃ H ₇ O) ₂ Cl	1605 w	1605 w	1605 w	1605 w	1605 w	1605 w	1605 w	1605 w	1605 w	1605 w	1605 w	1605 w
Ga(<i>t</i> -C ₃ H ₇ O)Cl ₂	1615 w	1615 w	1615 w	1615 w	1615 w	1615 w	1615 w	1615 w	1615 w	1615 w	1615 w	1615 w
GaCl ₂ · <i>i</i> -C ₃ H ₇ OOCCH ₃	945 m (E)	945 m (E)	945 m (E)	945 m (E)	945 m (E)	945 m (E)	945 m (E)	945 m (E)	945 m (E)	945 m (E)	945 m (E)	945 m (E)
Ga(<i>t</i> -C ₃ H ₇ O) ₂ Cl	957 m (E)	957 m (E)	957 m (E)	957 m (E)	957 m (E)	957 m (E)	957 m (E)	957 m (E)	957 m (E)	957 m (E)	957 m (E)	957 m (E)
Ga(<i>t</i> -C ₃ H ₇ O)Cl ₂	1035 s	1035 s	1035 s	1035 s	1035 s	1035 s	1035 s	1035 s	1035 s	1035 s	1035 s	1035 s
GaCl ₂ · <i>i</i> -C ₃ H ₇ OOCCH ₃	1032 s	1032 s	1032 s	1032 s	1032 s	1032 s	1032 s	1032 s	1032 s	1032 s	1032 s	1032 s

^a s = strong, m = medium, w = weak, vw = very weak, b = broad, sh = shoulder. ^b Most of the unclassified peaks may be assigned to the solvent used. ^c Solvent: chloroform. ^d Solvent: benzene.