In a subsequent publication, a more detailed model for LiF–BeF$_2$ solutions will be compared with the present data, a model in which polymeric anions Be$_a$F$_b^{(b-2a)-}$ are assumed. These will extend in composition and structure from the monomer BeF$_4^{2-}$—the principal species when $X_{\mathrm{BeF_2}}$ is less than 0.33—through increasingly polymeric anions as $X_{\mathrm{BeF_2}}$ increases, to very large networks or chain structures as pure BeF$_2$ 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

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

The rapid drop in γ_{LiF} (Figure 7a)—*i.e.*, in a_{LiF}—as BeF$_2$ is added to LiF thus may be viewed as corresponding to the depletion of free F$^-$ ions as Be$_a$F$_b^{(b-2a)-}$ 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)ONF$_2$, and N,N-Difluoro-O-trifluoromethylhydroxylamine, CF$_3$ONF$_2$

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 FSO$_2$ONF$_2$,[1] SF$_5$ONF$_2$,[2,3] and CF$_3$ONF$_2$[3,4] through reactions of tetrafluorohydrazine with (FSO$_2$O)$_2$, SF$_5$OF, and CF$_3$OF, respectively. Presumably these reactions proceed *via* simple coupling of difluoramino radicals with the intermediate oxy radicals (FSO$_2$O·, SF$_5$O·, and CF$_3$O·) 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)F[5] and CF$_3$OOCF$_3$,[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 method[7] 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)ONF$_2$.—The most satisfactory procedure for preparing FC(O)ONF$_2$ is illustrated by the following example. An evacuated 200-ml Pyrex bulb was charged with 150 mm of gaseous N$_2$F$_4$ (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)ONF$_2$ was collected at −111° and a mixture of NF$_3$, CO$_2$, COF$_2$, and SiF$_4$ was found in the −196° trap. The FC(O)ONF$_2$ fraction (0.40 mmol) was contaminated with small amounts of NO$_2$ and unused peroxide from which it could be separated by fractional codistillation.[8] *Anal.* Calcd for FC(O)ONF$_2$: 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)ONF$_2$ 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 NF$_3$, COF$_2$, NO$_2$, and oxygen, but no detectable amount of FC(O)ONF$_2$. 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 COF$_2$, NF$_3$, NO$_2$, and noncondensable material. In one case, equimolar amounts of N$_2$F$_4$ and FC(O)OOC(O)F in a reactor of Type 316 stainless steel produced a quantitative yield of FC(O)ONF$_2$, but this result could not be reproduced in numerous subsequent trials.

Preparation of CF$_3$ONF$_2$.[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 CF$_3$OOCF$_3$ (1.7 mmol) in the first two traps. A mixture of CF$_3$ONF$_2$, N$_2$F$_4$, NF$_3$ (trace), and COF$_2$ in the third trap was refractionated through −158 and −196° traps which isolated a CF$_3$ONF$_2$–COF$_2$ mixture at −158° and N$_2$F$_4$ (2.2 mmol, contaminated with minor amounts of COF$_2$, CF$_3$ONF$_2$, and NF$_3$) at −196°. Pure CF$_3$ONF$_2$[3] (0.5 mmol) was recovered from the −158° fraction after removing the COF$_2$ (0.5 mmol) by absorption on finely ground CsF. Based on CF$_3$OOCF$_3$ consumed (0.7 mmol), the pure CF$_3$ONF$_2$ recovered (0.5 mmol) represents a 36% yield (83% based on N$_2$F$_4$ consumed). No significant reaction between CF$_3$OOCF$_3$ and N$_2$F$_4$ 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. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

(9) Following completion of this work, a similar preparation of CF$_3$ONF$_2$ 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 NO_2, NF_3, COF_2, SiF_4, CO_2, and CF_4. No evidence for CF_3ONF_2 was found in these studies.

Nmr and Infrared Spectra.—The infrared spectrum of $FC(O)ONF_2$ was obtained with a Beckman IR-8 spectrophotometer. The F^{19} nmr spectrum of $FC(O)ONF_2$ as a 10–20% solution in SF_6 was recorded at $-78°$ with a Varian spectrometer, Model V-4302. Chemical shifts are reported in ϕ units, here defined as ppm relative to $CFCl_3$.

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 $FC(O)ONF_2$. 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, CO_2^+ (56.6); 47, FCO^+ (100.0); 49, NOF^+ (0.4); 52, NF_2^+ (58.3); 63, FCO_2^+ (0.3); 68, ONF_2^+ (0.3); 77, FCO_2N^+ (0.2); 96, FCO_2NF^+ (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

$$CF_3OOCF_3 + N_2F_4 \longrightarrow 2CF_3ONF_2 \qquad (1)$$

$$FC(O)OOC(O)F + N_2F_4 \longrightarrow 2FC(O)ONF_2 \qquad (2)$$

Both reactions probably involve primary fission of the peroxide O–O bonds and subsequent addition of the resultant oxy radicals to the $NF_2\cdot$ radicals known to exist in equilibrium with N_2F_4.[10] The much greater reactivity of $FC(O)OOC(O)F$ than of CF_3OOCF_3 toward N_2F_4 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 $FC(O)OOC(O)F$[7] compared with CF_3OOCF_3.[11]

The synthesis of CF_3ONF_2 according to eq 1 offers some advantage over the synthesis of this material from CF_3OF and N_2F_4,[3,4] since undesirable by-product formation (COF_2, NF_3, CF_4, NOF) is minimized and more efficient utilization of starting materials results. The formation of $FC(O)ONF_2$ 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 $FC(O)ONF_2$ and the erratic influences of reactor history and type are reminiscent of the irregular behavior observed in the synthesis of SF_5ONF_2.[2] The by-products (COF_2, CO_2, O_2, and NF_3) formed here during the synthesis of $FC(O)ONF_2$ may have arisen partly through thermal decomposition of the peroxide, eq 3,[7] followed by oxidation of the N_2F_4 as reported by Beach[12]

$$FC(O)OOC(O)F \longrightarrow COF_2 + CO_2 + {}^1/_2O_2 \qquad (3)$$

$$N_2F_4 + {}^1/_2O_2 \longrightarrow NOF + NF_3 \qquad (4)$$

Thermal decomposition of the desired product $FC(O)ONF_2$ according to the equation

$$FC(O)ONF_2 \longrightarrow COF_2 + NOF \qquad (5)$$

probably occurred to some extent during synthesis, since isolated samples of $FC(O)ONF_2$ which decomposed during storage or when heated formed mainly COF_2 and NOF (or products of the latter's attack on glass[13]). Hale and Williamson[3] have observed this mode of thermal decomposition (*e.g.*, NOF elimination) for CF_3ONF_2 and SF_5ONF_2. It is of interest that photochemical decomposition of $FC(O)ONF_2$ at $-196°$ in the resonance cavity of an esr spectrometer produced the previously reported[5] anisotropic doublet spectrum of the $FCO_2\cdot$ radical. This indicates that photochemical decomposition of $FC(O)ONF_2$ differs from thermal decomposition in proceeding by O–N bond cleavage rather than C–O rupture.

The infrared spectrum of $FC(O)ONF_2$ 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 CF_3ONF_2 (1027 and 933 cm^{-1})[3] and FSO_2ONF_2 (1032 and 913 cm^{-1}).[1] Bands found at 887 (s) and 870 (vs) cm^{-1} in $FC(O)ONF_2$ are assignable to singly bonded C—O and N—O stretches, since these modes appear at 892 and 865 cm^{-1}, respectively, in CF_3ONF_2.[3] The general shape of the absorption envelope over the range 1050–850 cm^{-1} in the $FC(O)ONF_2$ spectrum bears a striking resemblance to that of CF_3ONF_2 in this region. Bands in the $FC(O)ONF_2$ 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 NF_2O symmetric deformation.

Additional evidence for the proposed structure of $FC(O)ONF_2$ may be derived from the nmr spectrum. A broad triplet at ϕ -110 is attributable to quadrupole-broadened NF resonance of the ONF_2 group, with $J_{NF} = 158$ Hz. (The nmr spectrum of CF_3ONF_2 exhibits a similar NF triplet at ϕ -124[4] with $J_{NF} = 126$ Hz.[3]) A high-field resonance at ϕ $+40$, assignable to C–F of the FC(O)O group[5] 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_{CF-NF} was less than 10 Hz and greater than 3 Hz. This range appears reasonable, since CF_3ONF_2 has $J_{NF-CF} = 3.4$ Hz[4] and FSO_2ONF_2 has $J_{NF-CF} = 4.6$ 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

---

(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).

(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 $FC(O)ONF_2$ 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 V[5]) have been synthesized by the reactions of their alkoxides with acyl halides. In a recent communication Mogele[6] has reported the preparation of halide alkoxides of gallium by reactions of the type

$$Ga(GaX_4) + 2ROH \longrightarrow XGa(OR)_2 + GaX_3 + H_2$$
$$GaX_3 + 2NaOR \longrightarrow XGa(OR)_2 + 2NaX$$

where X = Cl or Br and R = CH_3 or C_2H_5. 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

$$XGa(OR)_2 + GaX_3 \longrightarrow 2X_2GaOR$$
$$X_2GaR + ROH \longrightarrow X_2GaOR + RH$$

where X = Cl or Br and R = CH_3 or C_2H_5.

TABLE I

INFRARED BANDS OF THE COMPOUNDS[a]

Compound	Bands, cm^{-1}														
$Ga(i\text{-}C_3H_7O)_2Cl$ (distld)[b,c]	. . .	. . .	3580 w	. . .	. . .	. . .	3025 s	2965 s (A)	. . .	2905 s	. . .	. . .	. . .		
$Ga(i\text{-}C_3H_7O)Cl_2$ (distld)[b,d]	3700 vw	3645 w	3610 vw	. . .	3100 s	3080 s (A)	3040 s	2985 s (A)	. . .	2915 s	2890 w (B)	2830 vw	2660 w		
$GaCl_3\cdot i\text{-}C_3H_7OOCCH_3$[b,d]	3700 w	3650 w	3600 vw	3445 vw	3090 s	3070 s (A)	3035 s	2980 s (A)	2940 sh	. . .	2895 w (B)	2815 w	2655 w		
$Ga(i\text{-}C_3H_7O)_2Cl$	. . .	2375 m	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	1500 s	1445 m (D)	1395 s (D)
$Ga(i\text{-}C_3H_7O)Cl_2$	2605 w	2370 w	2330 w	2210 w	2010 w	1960 m	1810 s	1755 w	. . .	1670 w	1615 w	1580 w	1520 w	1465 s (D)	1385 m (D)
$GaCl_3\cdot i\text{-}C_3H_7OOCCH_3$	2600 w	. . .	2315 w	2205 w	2000 vw	1955 m	1805 s	. . .	1705 w (C)	. . .	1605 w	1580 w	1515 w	1460 m (D)	. . .
$Ga(i\text{-}C_3H_7O)_2Cl$	1365 m (D)	1295 s	. . .	. . .	1218 s, b	. . .	1155 w (E)	1122 w	1064 vw	1028 w	942 m				
$Ga(i\text{-}C_3H_7O)Cl_2$	. . .	. . .	. . .	1245 w	. . .	1173 w (E)	1140 s (E)	1117 w	. . .	1035 s	945 m (E)				
$GaCl_3\cdot i\text{-}C_3H_7OOCCH_3$	1360 s (D)	. . .	1254 s	1250 sh	. . .	1180 m (E)	1145 m (E)	1107 s	. . .	1032 s	957 m (E)				
$Ga(i\text{-}C_3H_7O)_2Cl$	933 s	883 w	843 w	. . .	753 s, b	665 s	615 w (F)	593 w (F)	. . .						
$Ga(i\text{-}(C_3H_7O)Cl_2$	925 w	. . .	843 w	814 w (E)	768 w	668 s, b	610 sh (F)	. . .	. . .						
$GaCl_3\cdot i\text{-}C_3H_7OOCCH_3$	. . .	885 w	845 w	815 w (E)	768 w	670 s, b	620 sh (F)	605 m (F)	422 w (F)						

[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.

---

(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. Mogele, "Proceedings, 9th International Conference on Coordination Chemistry," Verlag Helvetica Chimica Acta, Basle, 1966.