Fluorocarbonyl Hypofluorite

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Abstract: The new compound fluorocarbonyl hypofluorite, FC(O)OF, has been prepared by the reaction of bis-(fluorocarbonyl) peroxide, $(FCO)_2O_2$, and fluorine at room temperature under the influence of Pyrex-filtered ultraviolet light. The compound could be further oxidized by fluorine, in the presence of cesium fluoride, to produce the recently reported compound, bis(fluoroxy)difluoromethane, $F_2C(OF)_2$.

The only previously known substances which contain a hypofluorite group, O—F, attached to a carbonyl group, C=O, are the highly unstable acyl OF compounds, $CF_3C(O)OF$ and $C_2F_5C(O)OF$.[1] The preparation of the one-carbon homolog, fluorocarbonyl hypofluorite, FC(O)OF, is now reported.

Experimental Section

Materials. Bis(fluorocarbonyl) peroxide was prepared by flowing carbon monoxide, oxygen, and fluorine at 0.5, 3, and 1 l./hr, respectively, through a 1-l. Pyrex glass flask, and later pumping on the products in an acetone–Dry Ice bath until the infrared spectrum and molecular weight showed it to be pure.[2]

Carbon monoxide, sulfur hexafluoride, oxygen, fluorine, sulfur tetrafluoride, and cesium fluoride were commercial grade materials and were used directly from the containers. The chromatography column consisted of a 4-m length of 6.35-mm o.d. copper tubing packed with 42–60 mesh Chromosorb W which contained 42% perfluorotributylamine. While in use, the column was held at 0°. The fractional codistillation column was of the usual construction.[3]

Preparation of Fluorocarbonyl Hypofluorite. The reaction between bis(fluorocarbonyl) peroxide and fluorine was carried out in a 2-l. flask containing a Pyrex glass finger holding a water-cooled, medium pressure, 350-w mercury lamp. A typical reaction using 140 mm of the peroxide and 480 mm of fluorine, irradiated for 4 hr, converted about one-half of the peroxide to other products, 15% of which was the hypofluorite. The flask then contained in decreasing percentages the starting materials, CO_2, COF_2, CF_3OF, FC(O)OF, SiF_4, CF_3OOCF_3, $FC(O)OOCF_3$ (a new compound which will be the subject of a subsequent article), and CF_3OOOCF_3.[4,5] Fractional codistillation gave at best a mixture containing about 92% FC(O)OF and 8% CF_3OOCF_3. This mixture was then separated into its pure components by gas chromatography.

Fluorocarbonyl hypofluorite was also prepared in small yield (<5%) by the reaction at room temperature between the same starting materials but without using the ultraviolet lamp. In this case, about 2 weeks was required for the reaction to go to completion. CO_2, COF_2, SiF_4, BF_3, and an unidentified compound were also produced.

Chemical Analysis. The compound was analyzed by allowing 0.2882 g (3.439 mmoles) to react at room temperature with an excess of 1 *N* NaOH in a 60-cc Pyrex glass bulb. A vigorous reaction occurred according to the equation

$$FC(O)OF + 4OH^- \longrightarrow CO_3^{2-} + 2F^- + 2H_2O + 0.5O_2$$

The hydroxide and carbonate ions were titrated with a 0.1 *N* HCl solution. The gaseous oxygen was measured gravimetrically.

Anal. Calcd: C, 14.6; O, 39.0; F, 46.4. Found: C, 15.0; O, 40.1; F, 45.7.

Molecular Weight: The average molecular weight obtained from eight vapor density measurements was 82 g/mole (calculated for FC(O)OF, 82).

Melting Point. The melting point was obtained by freezing the sample in a 7-mm o.d. glass tube. Using a warming rate of 0.5°/min in an isopentane bath, the white crystals were observed to melt within a 0.5° range starting at $-141.4 \pm 0.8°$.

Volatility. Fractional codistillation indicated a boiling point within 10° of $-55°$.

Infrared Spectrum. The infrared spectrum shown was taken at gas pressures ranging from 1 to 80 mm using a Beckman Model IR10 spectrometer. A Monel metal cell, equipped with silver chloride windows, having a length of 10 cm, was used.

Table I. Infrared Spectrum[a]

Band, cm^{-1}	Type	Assignment	Comparative bands, cm^{-1}
3845 vvw		$2\nu_1$ (3860)	
2925 vvw	PR	$\nu_1 + \nu_3$ (2923)	
2373 vw	PR	$2\nu_2$ (2384)	
2174 vvw		$\nu_2 + \nu_3$ (2185)	
2096 vvw		$\nu_2 + \nu_4$ (2105)	
1986 sh	Q	$2\nu_3$ (1986)	
1930 vvs	PR	ν_1, C=O str	1928, COF_2;[b,c] 1919, $(FCO)_2O_2$[d,e]
1643 vvw		$\nu_3 + \nu_6$ (1651)	
1480 vw		$2\nu_5$ (1490)	
1314 vvw	PQR	$2\nu_6$ (1316)	
1261 s	PQR		
1224 sh	Q		
1216 sh	Q		
1192 vvs	PQR	ν_2, C–F str	1200, $(FCO)_2O_2$[d,e]
993 m	PR	ν_3, C–O str	985, $(FCO)_2O_2$;[d,e] 965, $(CF_3)_2O$[f]
943 sh	Q		
913 m	PQR	ν_4, O–F str	901, C_2F_5OF;[g] 888, SF_5OF_1;[h] 928, O_2NOF[i]
875 sh	Q		
749 m	Q		
745 s	Q	ν_5, C out of plane	749, $(FCO)_2O_2$[d]
738 m	Q		
658 w	PQR	ν_6, FC=O rocking	660, $(FCO)_2O_2$;[d] 626, COF_2[b]
508 vvw	PR		

[a] s, strong; m, medium; w, weak; sh, shoulder. [b] A. H. Nielsen, T. G. Burke, P. J. Woltz, and E. A. Jones, *J. Chem. Phys.*, **20**, 596 (1952). [c] The value given is the average between the symmetric and asymmetric stretches. [d] A. J. Arvia and P. J. Aymonino, *Spectrochim. Acta*, **18**, 1299 (1962). [e] The value given is the average between the two resonantly split bands. [f] J. H. Simons, "Fluorine Chemistry" Vol. II, Academic Press Inc., New York, N. Y., 1954, p 479. [g] J. H. Prager and P. G. Thompson, *J. Am. Chem. Soc.*, **87**, 230 (1965). [h] F. Dudley, G. Cady, and D. Eggers, *ibid.*, **78**, 1553 (1956). [i] R. H. Miller, D. L. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta*, **23**, 223 (1967).

It was difficult to know whether all three of the spikes at 749, 745, and 738 cm^{-1} should have been assigned to the C out-of-plane mode, but since the OF group may change position, more than one peak of that fundamental may be occurring. The strong triplet at

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(1) G. H. Cady and K. B. Kellogg, *J. Am. Chem. Soc.*, **75**, 2501 (1953).

(2) A. Arvia, P. Aymonino, and H. Schumacher, *Z. Anorg. Allgem. Chem.*, 316 (1962).

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

(4) L. R. Anderson and W. B. Fox, *J. Am. Chem. Soc.*, **89**, 4313 (1967).

(5) P. G. Thompson, *ibid.*, **89**, 1811 (1967).

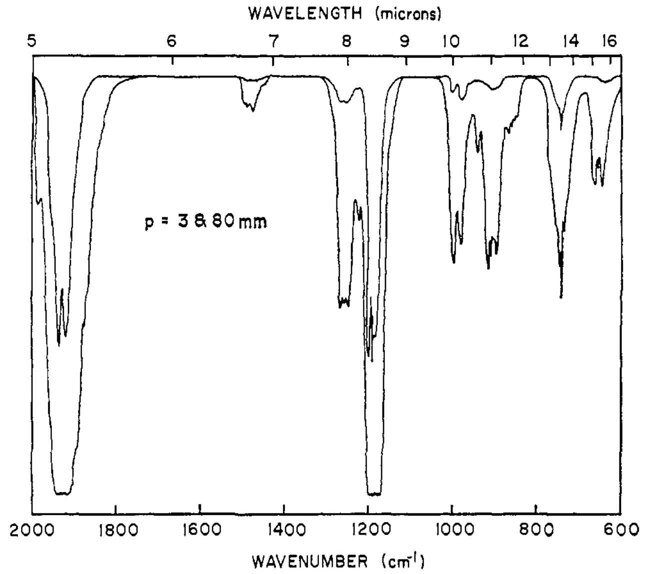

Figure 1.

1261 cm^{-1} was not assigned. All assignments should be considered to be tentative until a more detailed study is made. The infrared spectral data are shown in Table I and Figure 1.

Nmr Spectrum. To obtain F^{19} spectra, a Varian Associates high-resolution, 40-Mc nuclear magnetic resonance spectrometer with a Model No. V-4311 fixed-frequency radiofrequency transmitter was used. The sample to be analyzed was placed in a 5-mm o.d. glass tube with sulfur hexafluoride used as an internal standard.

The spectrum contained two sharply defined sets of doublets of equal area. The coupling constant was 141 cps, while the chemical shift was +94.4 ppm for the CF group and −151.8 ppm for the OF group. The only other hypofluorites whose OF shifts were measured using sulfur hexafluoride as an internal standard were CF_3OF (−92.5 ppm), SF_5OF (−131.2 ppm), and SO_3F_2 (−187.5 ppm).[6]

Stability. The compound reacted with and/or decomposed in Pyrex glass to give carbon dioxide, silicon tetrafluoride, and oxygen. Even a single transfer from one trap to another in a glass vacuum line produced some decomposition products. While no explosions occurred in this laboratory, since some hypofluorites are known to be unstable, care should be used when handling this material.

Reactions. When fluorocarbonyl hypofluorite was placed in a Monel bomb with excess fluorine and some cesium fluoride catalyst at room temperature, bis(fluoroxy)difluoromethane,[7] $F_2C(OF)_2$, was produced.

$$FC(O)OF + F_2 \xrightarrow[\text{room temp}]{CsF} F_2C(OF)_2$$

The product was identified by its characteristic infrared spectrum.

It is interesting to note that $F_2C(OF)_2$ was not produced when CO_2, FC(O)OF, and F_2 were irradiated with ultraviolet light, and FC(O)OF could not be synthesized by treating CO_2 with an equal amount of F_2 in the presence of CsF.[7]

When fluorocarbonyl hypofluorite was allowed to react with sulfur tetrafluoride under the influence of ultraviolet light, the following compounds were produced: CO_2, COF_2, SiF_4, SF_6, SO_2F_2, SOF_2, and a small amount of a new compound, pentafluorosulfur fluoroformate, $FC(O)OSF_5$.[8]

$$FC(O)OF + SF_4 \xrightarrow{h\nu} FC(O)OSF_5$$

The compound was identified by its infrared spectrum.

Iodine is liberated when the hypofluorite was brought into contact with KI solution.

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(6) G. Cady and C. Merrill, *J. Am. Chem. Soc.*, **84**, 2260 (1962).

(7) R. Cauble and G. Cady, *ibid.*, **89**, 1962 (1967).

(8) R. Czerepinski and G. Cady, to be published.