Preparation and Characterization of Bis(fluoroxy)perfluoroalkanes. II. Bis(fluoroxy)perfluoromethane[1,2]

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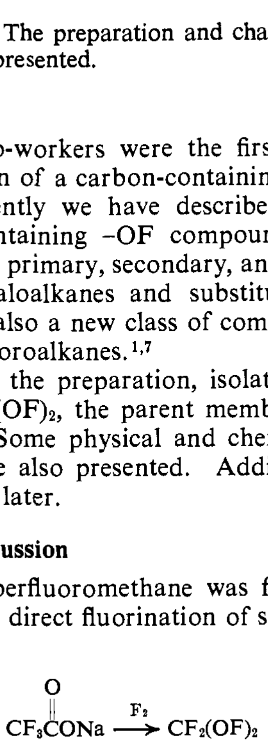
Abstract: The preparation and characterization of the first member of the bis(fluoroxy)perfluoroalkanes, $CF_2(OF)_2$, are presented.

Cady and co-workers were the first to report the preparation of a carbon-containing hypofluorite,[3] CF_3OF.[4] Recently we have described a number of new carbon-containing -OF compounds.[1,6–7] These include not only primary, secondary, and tertiary mono(fluoroxy)polyhaloalkanes and substituted derivatives thereof,[5–7] but also a new class of compounds, the bis(fluoroxy)perfluoroalkanes.[1,7]

In this paper the preparation, isolation, and identification of $CF_2(OF)_2$, the parent member of this class, are reported. Some physical and chemical properties of $CF_2(OF)_2$ are also presented. Additional reactions will be reported later.

Results and Discussion

Bis(fluoroxy)perfluoromethane was first obtained in low yield by the direct fluorination of salts of trifluoroacetic acid.



$$CF_3\overset{\overset{O}{\|}}{C}ONa \xrightarrow{F_2} CF_2(OF)_2$$

Somewhat higher yields are obtained by the direct fluorination of sodium oxalate.[8] In both cases, the

$$Na_2C_2O_4 \xrightarrow{F_2} 2CF_2(OF)_2 + 2NaF$$

reaction temperature and fluorine concentration were studied over wide ranges. The major factor in obtaining higher yields appears to be control of the reaction so that excessive exotherms do not occur. Nonreactive solid diluents such as NaF have also been employed as described previously,[5] but their use does not appear to offer significant advantages and at times actually results in lower yields of $CF_2(OF)_2$.

The fluorination of sodium trifluoroacetate also gives many other volatile products in varying amounts. The predominant products are C_2F_5OF[5] and $CF_3CF(OF)_2$.[1,7] Other products include CF_3OF, CF_3OOF, C_2F_5OOF, CF_3OOOCF_3, and $CF_3OOOC_2F_5$.[7,9]

Bis(fluoroxy)perfluoromethane was separated by vacuum-line techniques and was purified by gas chromatography. The infrared spectrum of $CF_2(OF)_2$ is shown in Figure 1; the complex band structure between 10.5 and 11.3 μ is assigned to the OF groups but may include C–O vibrations also. Structure confirmation of bis(fluoroxy)perfluoromethane by the assignment and analysis of the fluorine nuclear magnetic resonance is illustrated in Figure 2. The triplet at -159.2 ϕ^* is assigned to the two equivalent -OF groups upon consideration of the shielding value and spin–spin analysis.[10] The $-CF_2-$ group signal (triplet) is at 84.2 ϕ^*. The peak areas were found to be in the ratio of 1.0:1.0. The coupling constant is 39.0 cps.

It is again noted that F^{19} nuclear magnetic resonance spectroscopy is an extremely useful method for the structural characterization of fluoroxyperfluoroalkanes. Consideration of the chemical shifts together with simple first-order analysis of the fine structure caused by spin–spin interaction as well as the relative area ratios has permitted an unequivocal assignment of structure to the OF compound in many instances.

Various physical properties of bis(fluoroxy)perfluoromethane are presented in Table I. From the calorimetric results[11] one can calculate that the OF groups in $CF_2(OF)_2$ are bound less strongly than the OF group in CF_3OF by about 4 kcal/mole per group.

Bis(fluoroxy)perfluoromethane has been found to be exceptionally stable compared to other fluoroxy compounds. Several samples, stored in sealed glass nmr tubes with $CFCl_3$ as internal reference and solvent, showed only minor decomposition after approximately 5 years at ambient temperatures of 20–25°. No decomposition has been observed with samples stored in fluorine-passivated steel or Monel cylinders. Differential thermal analysis showed that an exothermic reaction occurred smoothly when $CF_2(OF)_2$ was heated

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(1) Part I of this series: P. G. Thompson and J. H. Prager, *J. Am. Chem. Soc.*, in press.

(2) This research was supported by the Advanced Research Projects Agency under Contract NOrd 18688 and was monitored by the Bureau of Naval Weapons.

(3) The term "hypofluorite" is used to emphasize the -OF structural group in analogy to the universally recognized hypochlorite group -OCl, not to imply that the fluorine atom is positive relative to the oxygen atom. In accordance with the recommendations of the ACS Committee on Nomenclature of Highly Fluorinated Molecules, we have established the functional group name for the OF group as the fluoroxy group.

(4) K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

(5) J. H. Prager and P. G. Thompson, *ibid.*, **87**, 230 (1965).

(6) J. H. Prager, *J. Org. Chem.*, **31**, 392 (1966).

(7) P. G. Thompson, "Oxygen Fluorides and Hypofluorites," The Fluorine Symposium of the Inorganic Division of the American Chemical Society, Ann Arbor, Mich., June 27, 1966.

(8) Private communications from (a) J. K. Ruff and M. Lustig, (b) R. Cauble and G. H. Cady, and (c) J. Shreeve reveal that these three laboratories have recently discovered independently a convenient method involving alkali fluoride catalyzed fluorination of carbon dioxide which gives very high yields of $CF_2(OF)_2$.

(9) P. G. Thompson, to be published.

(10) See ref 5 for discussion on nmr spectra of fluoroxypolyfluoroalkyl compounds.

(11) Performed by G. D. Foss and D. A. Pitt of these laboratories; See "Calorimetric Studies of Bis(fluoroxy)perfluoromethane, $CF_2(OF)_2$," to be published.

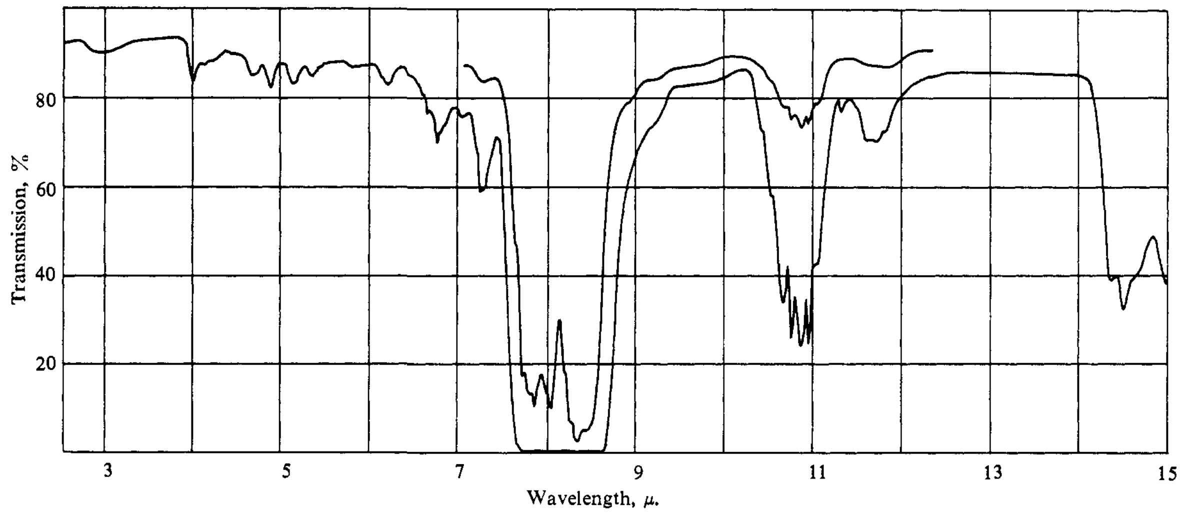

Figure 1. Infrared spectrum of $CF_2(OF)_2$: 180 and 30 mm pressure, 25-mm cell.

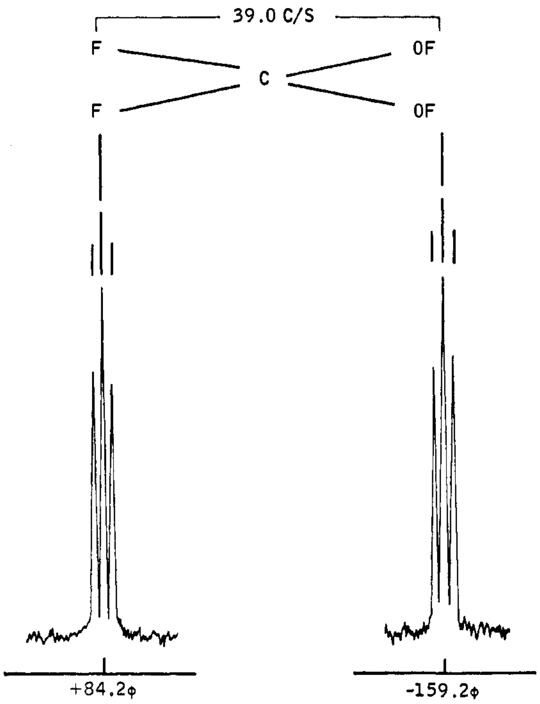

Figure 2. Nmr spectrum of $CF_2(OF)_2$.

above 250°. An infrared spectrum of the products showed COF_2, CO_2, a small amount of CF_3OF, and a trace of SiF_4. As in the case with $CF_3CF(OF)_2$,[1] the products formed indicate that some reductive defluorination may have resulted by reaction of $CF_2(OF)_2$ with the metal cup and/or other materials in the DTA apparatus. When $CF_2(OF)_2$ is flashed or ignited, quantitative analysis of the products formed indicates that thermal decomposition proceeds predominantly by the following reaction.

$$CF_2(OF)_2 \xrightarrow{\Delta} COF_2 + 0.5O_2 + F_2$$

The results of additional stability tests on the rate of decomposition in glass at elevated temperatures are given in Table II.

The thermal stability of $CF_2(OF)_2$ is remarkable when compared to other fluoroxy compounds; the only known fluoroxyperfluoroalkane of comparable thermal stability is CF_3OF, which exists in reversible equilibrium with COF_2 and F_2 above 275°.[12] It is proposed that the absence of a carbon–carbon bond in these two compounds accounts for the exceptional thermal stability of $CF_2(OF)_2$ and CF_3OF. This precludes the chain reductive decomposition discussed previously.[1,5,7] A

Table I. Physical Properties of $CF_2(OF)_2$

Melting point:	No crystalline phase evident at −196° (glass)	
Boiling point:	−64°	
Critical temperature:	+47.5°	
Vapor pressure:	$\log P_{mm} = 7.530 - 971.6/T$ (T is in °K)	
Heat of vaporization:	4445 cal/mole	
Trouton's constant:	21.3	
Density:	Temp, °C	d, g/cc
	−64	1.62
	0	1.34
	+25	1.20
	+40	1.08
	+45	1.02
	$\beta = 22 \times 10^{-4}$ deg^{-1} (−70 to −49°)	
	$= 125 \times 10^{-4}$ deg^{-1} (+40 to +45°)	
Heat of formation:	−130.5 kcal/mole (calorimetry)	

Table II. Thermal Stability Tests of $CF_2(OF)_2$

Temp, °C	Time, hr	% unchanged
150	6	~100
200	14	~80
250	3	~40
275	13	<3
300	3.5	<12

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

discussion of the factors believed to be responsible for the observed relative stabilities of the various fluoroxy compounds reported to date will be the subject of a later paper.

The decomposition of $CF_2(OF)_2$ can also be brought about by certain chemical initiators or fragmentizing agents as discussed previously for other fluoroxy compounds.[1,5] However, $CF_2(OF)_2$ is not as susceptible to hydrocarbon fragmentizing agents as are fluoroxy compounds containing a carbon–carbon bond.

Bis(fluoroxy)perfluoromethane is strongly oxidizing toward reducing agents such as mercury, potassium iodide, and aqueous alkali. With excess potassium iodide (in water or in acetonitrile–water solution), the over-all reduction of $CF_2(OF)_2$ as shown by quantitative analysis of the products can be expressed by the equation

$$CF_2(OF)_2 + 4KI \longrightarrow 2I_2 + CO_2 + 4KF$$

The corresponding reaction also occurs rapidly in aqueous sodium hydroxide.

$$CF_2(OF)_2 + 6NaOH \longrightarrow O_2 + Na_2CO_3 + 4NaF + 3H_2O$$

Experimental Section

Fluorination procedures, isolation, purification, analysis, and characterization of bis(fluoroxy)perfluoromethane were similar to procedures discussed previously.[1,5] Differential thermal analysis and measurement of physical properties were carried out using the apparatus and procedures developed in these laboratories for potentially explosive fluorine-containing compounds.[13]

Safety Precautions. Although $CF_2(OF)_2$ has exceptional thermal stability, it is potentially hazardous because of its high energy content, high reactivity, and very strong oxidizing properties. However, it does not appear to be exceptionally sensitive to phase changes. Still, explosions of considerable force and brisance have occurred in the course of this work, and it is recommended that suitable protective equipment[1,5] be used when preparing, reacting, or storing $CF_2(OF)_2$. No detailed toxicity studies have been carried out on $CF_2(OF)_2$, but it appears advisable to avoid exposure to any OF-containing compound in view of the known toxicity of OF_2.[14]

Fluorination of Sodium Trifluoroacetate. Sodium trifluoroacetate was prepared by neutralization of trifluoroacetic acid (3M Co.) with sodium carbonate or sodium hydroxide. A 2.97-g (21.8 mmoles) sample of finely divided dry salt in a monel sintered-plate reactor was treated with 0.32 mole of fluorine at 22°; the fluorine concentration was increased from 0 to 33% over a 1-hr period and maintained for an additional 3-hr period. The residual material in the reactor was found to weigh 1.24 g; it consisted principally of $NaHF_2$ together with small amounts of NaF. The volatile products condensed in the liquid oxygen trap (14.9 mmoles) were analyzed by gas chromatography. The OF-containing products consisted of 55% $CF_3CF(OF)_2$, 35% C_2F_5OF, 2% $CF_2(OF)_2$, and 2% CF_3OF.

Fluorination of Sodium Oxalate Using the Static-Bed Process. Sodium oxalate was prepared by neutralization of oxalic acid with sodium carbonate, dried in a vacuum oven, and stored over silica gel until used. A 1.67-g (12.5-mmoles) sample of finely divided dry salt in the monel sintered-plate reactor was treated with 0.27 mole of fluorine at 21°; the fluorine concentration was increased from 0 to 20% over a 45-min period and maintained for an additional 2.5-hr period. The residual material in the reactor was found to weigh 1.60 g; it consisted principally of unreacted sodium oxalate together with smaller amounts of sodium bifluoride and sodium fluoride. The volatile products condensed in the liquid oxygen trap were found to oxidize ferrocene.[5] They were analyzed by infrared spectroscopy and gas chromatography. The products consisted of approximately 90% carbon dioxide and 10% $CF_2(OF)_2$. The amount obtained corresponded to somewhat over 10% conversion of the sodium oxalate. Other runs gave high conversion of the sodium oxalate, but yields of $CF_2(OF)_2$ were consistently in the 1–15% range.

Bis(fluoroxy)perfluoromethane. Bis(fluoroxy)perfluoromethane was purified by gas chromatography at −30°. Its retention time was found to be 40 relative to dichlorodifluoromethane and 9 relative to fluorotrichloromethane. Elemental analyses were obtained on a sample of chromatographed $CF_2(OF)_2$. A molecular weight determination (vapor density) on this material gave a value of 122 (calculated, 120).

Anal. Calcd for CF_4O_2: C, 10.0; F, 63.3. Found: C, 10.3; F, 63.2.

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(13) R. L. Bohon, *Anal. Chem.*, 33, 1451 (1961).

(14) D. Lester and W. R. Adams, *Am. Ind. Hyg. Assoc. J.*, 26, 562 (1965).