# Fluorocarbon Peroxides.[1] Novel Peroxides Prepared from Bis(fluoroformyl) Peroxide

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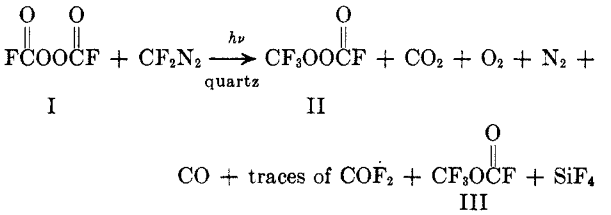
The photodecomposition of bis(fluoroformyl) peroxide in quartz apparatus gives fragments which have been trapped with difluorodiazirine to give fluoroformyl perfluoromethyl peroxide. Hydrolysis of the product affords either bis(perfluoromethyl) bis(peroxy)carbonate or perfluoromethyl hydroperoxide, depending on the reaction conditions. Fluorination of fluoroformyl perfluoromethyl peroxide and bis(perfluoromethyl) bis(peroxy)carbonate provides the corresponding fluoroxy compounds in high yields. The new peroxides prepared in this study are thermally stable at room temperature.

Bis(fluoroformyl) peroxide (I) is prepared by the reaction of fluorine, carbon monoxide, and oxygen[2] and is reported to be thermally unstable above room temperature and to decompose with explosive violence at 200°. The peroxide reacts with sulfur dioxide under photolytic conditions to give fluoroformylsulfuryl fluoride[3] and with fluorine under similar conditions to give the corresponding acyl fluoroxy compound.[4] Peroxide I has also served as an initiator for polymerization of tetrafluoroethylene.[5] The known chemistry of peroxide I has been explained on the basis of homolytic cleavage of the peroxide bond to give fluoroformate radicals,[2–5] which undergo further reactions. In the present work compound I has been found to be a convenient precursor for a series of fluorinated organic peroxides.

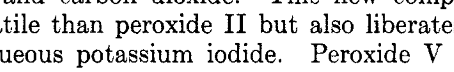
## Results

Photolysis of an equimolar gaseous mixture of peroxide I and difluorodiazirine[6] in a quartz vessel with a low-intensity ultraviolet light source has been found to give fluoroformyl perfluoromethyl peroxide (II, 18% yield),[7] along with liberation of nitrogen, oxygen, carbon monoxide, and carbon dioxide. Peroxide II was identified by its molecular weight and elemental analyses in addition to the spectral data and quantitative determination of the oxidizing power toward potassium iodide (see Experimental Section). An expected product, perfluoromethyl fluoroformate (III),[8] was found in only trace amounts (eq 1).



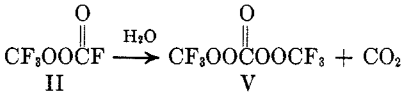
$$\underset{\mathrm{I}}{\mathrm{F\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}F}} + \mathrm{CF_2N_2} \xrightarrow[\text{quartz}]{h\nu} \underset{\mathrm{II}}{\mathrm{CF_3OO\overset{O}{\overset{\|}{C}}F}} + \mathrm{CO_2} + \mathrm{O_2} + \mathrm{N_2} + \mathrm{CO} + \text{traces of } \mathrm{COF_2} + \underset{\mathrm{III}}{\mathrm{CF_3O\overset{O}{\overset{\|}{C}}F}} + \mathrm{SiF_4} \quad (1)$$

In a control experiment neither peroxide II nor fluoroformate III was produced when a borosilicate glass vessel was substituted for the quartz vessel. Most of the starting peroxide (I) was recovered. When peroxide I was photolyzed alone in the quartz vessel under the same conditions but for a longer period of time, carbon dioxide was produced as the major component of the product mixture, along with bis(perfluoromethyl) peroxide (IV),[9] and traces of carbonyl fluoride, fluoroxyperfluoromethane, and silicon tetrafluoride. The yield of peroxide IV was approximately 50% of the theoretical amount based on the stoichiometry indicated in eq 2.



$$3\underset{\mathrm{I}}{\mathrm{F\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}F}} \xrightarrow[\text{quartz}]{h\nu} 4\mathrm{CO_2} + \underset{\mathrm{IV}}{\mathrm{CF_3OOCF_3}} + \mathrm{O_2} \quad (2)$$

Peroxide II is thermally stable at room temperature in the gas phase but hydrolyzes readily even in the presence of traces of water. Exposure of peroxide II at low pressures in the gas phase to a limited quantity of water vapor in glass apparatus for a limited period of time gave bis(perfluoromethyl) bis(peroxy)carbonate (V) and carbon dioxide. This new compound is less volatile than peroxide II but also liberates iodine from aqueous potassium iodide. Peroxide V is thermally stable at room temperature in carefully dried apparatus. The structure was shown by elemental analyses, the molecular weight, and the spectral data. The presence of a single peak in the fluorine nmr spectrum ($\phi^*$ +69.6) is convincing evidence for the equivalence of the perfluoromethyl groups.



$$\underset{\mathrm{II}}{\mathrm{CF_3OO\overset{O}{\overset{\|}{C}}F}} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{V}}{\mathrm{CF_3OO\overset{O}{\overset{\|}{C}}OOCF_3}} + \mathrm{CO_2} \quad (3)$$

Further hydrolysis of peroxide V in the vapor phase or hydrolysis of peroxide II with a stoichiometric amount or a molar excess of water vapor in the gas phase in glass apparatus gave the same product, perfluoromethyl hydroperoxide (VI). This material also liberates iodine from aqueous potassium iodide. Its structure is supported by the presence of infrared absorption at 2.80 $\mu$ (assigned to a hydroxyl group) and of a single fluorine nmr absorption peak (at $\phi^*$ +70.5) and the fact that carbon dioxide was the only other carbon-containing product from either reaction, in

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(1) Preceding paper in this series: R. L. Talbott, *J. Org. Chem.*, **30**, 1429 (1965).

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

(3) W. B. Fox and G. Franz, *Inorg. Chem.*, **5**, 946 (1966).

(4) R. L. Cauble and G. H. Cady, Abstracts of the Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., 1967, p 84; *J. Amer. Chem. Soc.*, **89**, 5161 (1967).

(5) A. J. Arvía, P. J. Aymonino, and H. J. Schumacher, *Z. Phys. Chem.* (Frankfurt am Main), **28**, 393 (1961).

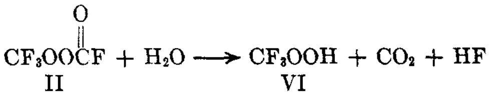
(6) R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 59 (1964); **3**, 245 (1966).

(7) The authors of ref 4 independently found peroxide II in low yields as a by-product of the reaction of peroxide I with fluorine: R. L. Cauble and G. H. Cady, *J. Org. Chem.*, **33**, 0000 (1968).

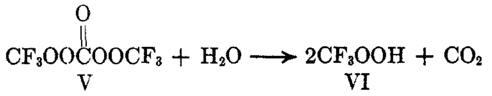
(8) (a) P. J. Aymonino, *Chem. Commun.*, 241 (1965); (b) B. C. Anderson and G. R. Morlock, U. S. Patent 3,226,418 (1965).

(9) F. Swarts, *Bull. Soc. Chim. Belg.*, **42**, 102 (1933); R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 5628 (1957).

addition to the mass cracking pattern, the molecular weight, and the elemental analyses. The stoichiometry of eq 4 and 5 (see Experimental Section) suggests that



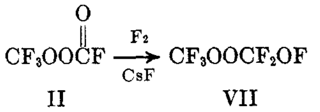
$$\underset{\mathrm{II}}{\mathrm{CF_3OO\overset{O}{\overset{\|}{C}}F}} + \mathrm{H_2O} \longrightarrow \underset{\mathrm{VI}}{\mathrm{CF_3OOH}} + \mathrm{CO_2} + \mathrm{HF} \tag{4}$$



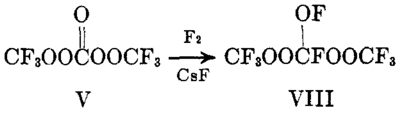
$$\underset{\mathrm{V}}{\mathrm{CF_3OO\overset{O}{\overset{\|}{C}}OOCF_3}} + \mathrm{H_2O} \longrightarrow \underset{\mathrm{VI}}{\mathrm{2CF_3OOH}} + \mathrm{CO_2} \tag{5}$$

the glass of the reaction vessel participates in the transformations shown in reactions 3 and 4, because less than the stoichiometric amount of water is needed for the reaction shown in eq 4 to give compound VI in high yields.

Peroxide II and peroxide V were readily fluorinated to give fluoroxy compounds under the conditions described in the literature[10] for the low-temperature fluorination of simple fluorinated acid fluorides and ketones. Peroxide II gave fluoroxyperfluoromethyl perfluoromethyl peroxide (VII, 90% yield). Peroxide V gave fluoroxybis(perfluoromethylperoxy)fluoromethane (VIII) in essentially quantitative yield.



$$\underset{\mathrm{II}}{\mathrm{CF_3OO\overset{O}{\overset{\|}{C}}F}} \xrightarrow[\mathrm{CsF}]{\mathrm{F_2}} \underset{\mathrm{VII}}{\mathrm{CF_3OOCF_2OF}} \tag{6}$$



$$\underset{\mathrm{V}}{\mathrm{CF_3OO\overset{O}{\overset{\|}{C}}OOCF_3}} \xrightarrow[\mathrm{CsF}]{\mathrm{F_2}} \underset{\mathrm{VIII}}{\mathrm{CF_3OO\overset{OF}{\overset{|}{C}}FOOCF_3}} \tag{7}$$

Compound VII was identified by its elemental analyses and its spectral data and comparison of the latter with the data for a sample prepared previously in an independent investigation.[11] The structure of compound VIII was characterized by its infrared, nmr, and mass spectra in addition to the elemental analyses. Both fluoroxy compounds are thermally stable for several months at room temperature. Compound VII was recovered essentially unchanged after 80 min at 195° in a stainless steel cylinder and after 60 min at 150° in a 20-fold excess of fluorine in the same cylinder. When compound VII was exposed to ferrocene,[12] a color change was observed in the ferrocene and carbonyl fluoride was produced. Peroxide II did not react with ferrocene under the same conditions.

## Discussion

Photolysis of peroxide I in quartz apparatus gives fragments which have been trapped to give fluorinated peroxides as derivatives. The mechanism of the dissociation is indicated to be complex by the variety of products formed, but the nature of the fragments is not clearly apparent from the structures of the products. In one experiment (eq 1) the trapping agent was difluorodiazirine or its cleavage product (difluorocarbene[6]) formed *in situ*, and in another experiment (eq 2) the decomposition fragments were apparently captured by peroxide I itself (or by other fragments formed *in situ*, which then recombined).[13] The control experiment presented evidence that the decomposition of peroxide I does not occur in the same manner when the higher energy ultraviolet light from the light source is filtered out of the light path. These results are not necessarily consistent with the proposed dissociation of peroxide I to fluoroformate radicals alone.

The reaction of peroxide I with difluorodiazirine (reaction 1) provides a useful synthetic route to a key intermediate to other novel fluorinated peroxides. With the exception of the starting material the peroxides prepared in this study are thermally stable at room temperature, although compounds II and V are exceptionally sensitive to hydrolysis. Compounds II, V, VI, VII, and VIII are the first reported members of families of fluorinated oxidants, whose chemistry is as yet scarcely examined. The structure of compound VIII is especially interesting in that the central carbon atom is bonded to two peroxide groups and one fluoroxy group, yet the compound is stable at room temperature.

The differences between the conditions required for the hydrolysis reactions shown in reactions 3, 4, and 5 (see Experimental Section) are rather subtle. Isolation of peroxide V rather than hydroperoxide VI from hydrolysis of compound II was reproducibly achieved at lower over-all pressure in the gas phase, at a charge of somewhat less water vapor in apparatus rigorously dried beforehand, and after limited reaction times. These results suggest a substantial difference in over-all rates of reaction for the transformations indicated by reactions 3 and 4. The stoichiometry observed requires that the glass of the reaction vessel was involved in both instances. The rates of the reactions were actually observed to vary, depending on the selection of the glass vessel used for the experiment. Although the evacuated vessels were carefully dried before use, residual traces of absorbed water on the inside surface of the glass could have contributed significantly to the variation in observed rate. Furthermore, etching of the glass by the by-product hydrogen fluoride provides an ever changing surface and also supplies additional water for the reaction. The results do not rule out the possibility that reactions 3 and 4 may take place by different mechanisms, although an advantageous rate difference is presently favored as the explanation, because of the ability of peroxide V to serve as an intermediate in eq 4 as shown by the ready hydrolysis of peroxide V to hydroperoxide VI (eq 5).

Equations 6 and 7 depict examples of selective fluorination of carbonyl groups to fluoroxy groups at low temperatures in the presence of peroxide groups in the same molecule. It was further shown that compound VII was stable toward dissociation at 195° and toward fluorination at 150°. Compound VII reacted with a reducing agent (ferrocene)[12] at room temperature with cleavage of both the fluoroxy group and the peroxide group. The control experiment with peroxide II showed that the reduction reaction does not involve peroxide II as an intermediate.

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[10] J. K. Ruff, A. R. Pitochelli, and M. Lustig, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

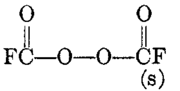
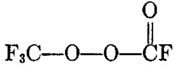
[11] J. H. Prager and P. G. Thompson of this laboratory have prepared members of the class R′fOOCFRfOF by other techniques. Publication is planned.

[12] The reaction of fluoroxy compounds with ferrocene is discussed by J. H. Prager and P. G. Thompson, *J. Amer. Chem. Soc.*, **87**, 230 (1965).

[13] The authors in ref 2b also observed bis(perfluoromethyl) peroxide as one of the products from photolysis of peroxide I.

Fluorine nmr spectroscopy was particularly helpful in the structural characterization of the new peroxides described in this work (see Table I). All six compounds studied having the trifluoromethylperoxy group ($CF_3OO-$) exhibit absorptions in the region between $\phi^*$ +68 and $\phi^*$ +71 in the fluorine nmr spectra.[14] In the three compounds where coupling constants could be observed in the absorption for the perfluoromethylperoxy group (compounds II, VII, and VIII), the values were less than 5 cps. Furthermore the spectra of peroxide I[3] and of bis(fluoroxy)-perfluoromethane[15] provide convenient models for comparison with the spectra of peroxide II and fluoroxy compound VII, respectively. The positions of the absorptions in the nmr spectra for compounds VII and VIII may be further compared with the spectrum of fluoroxyperfluoromethane[12] ($\phi^*$ +72.3 for the perfluoromethyl group and $\phi^*$ −147.1 for the fluoroxy group). Successive replacement of the fluorines on the carbon atom of fluoroxyperfluoromethane by perfluoromethylperoxy groups results in a shift in the absorption for the fluoroxy group of 9–12 $\phi^*$ units (per fluorine replaced) in the direction of lower field. There is a simultaneous shift of almost equal magnitude (8–10 $\phi^*$ units per fluorine replaced) in the direction of higher field in the absorption for the residual fluorine on the original carbon atom. The over-all consistency of these results contributes to the certainty of the structural assignments.

TABLE I
F[19] NMR SPECTRAL DATA FOR FLUORINATED PEROXIDES

| Compd | | |
|---|---|---|
| I[a,b] | |  $F\overset{\overset{O}{\|}}{C}—O—O—\overset{\overset{O}{\|}}{C}F$ (s) |
| | $\phi^*$ | +34.1 |
| II | Cps | \|——2——\| |
| | |  $F_3C—O—O—\overset{\overset{O}{\|}}{C}F$ (d) (q) |
| | $\phi^*$ | +69.5 +32.4 |
| IV[c] | | $F_3C—O—O—CF_3$ (s) |
| | $\phi^*$ | +69.0 |
| V | | $(F_3C—O—O—)_2CO$ (s) |
| | $\phi^*$ | +69.6 |
| VI | | $F_3C—O—O—H$ (s) |
| | $\phi^*$ | +70.5 |
| VII | Cps | \|——1.4——\|<br>\|—3.4—\|\|—35.1—\| |
| | | $F_3C—O—O—CF_2—O—F$ (d,t) (d,q) (t, unresolved) |
| | $\phi^*$ | +69.0 +80.6 −156.7 |
| VIII[d] | Cps | \|——< 3——\|<br>\|—3.5—\|\|—25—\| |
| | | $(F_3C—O—O—)_2CF—O—F$ |
| | $\phi^*$ | +68.7 +90.6 −168.0 |

[a] The spectra of compounds I and IV are given as models for reference purposes. [b] Lit. $\phi$ +34.4, ref 3. [c] Ref 14. [d] All peaks for compound VIII were over-all doublets with further unresolved fine structure.

## Experimental Section

**Apparatus.**—All experiments were carried out in well-ventilated areas,[16] and suitable barricades and personal safety equipment, such as face shields, heavy leather gloves, and heavy leather jackets, were used at all times for personnel protection. Wherever possible the samples were handled as gases and the manipulations were carried out by standard vacuum line techniques using a borosilicate glass vacuum line free from mercury vapor and lubricated with Kel-F No. 90 grease. A Wallace and Tiernan differential pressure gauge was used to measure gas pressures. Deliberate limitations of sample sizes were observed for personnel protection.

The infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam infrared spectrophotometer on gas samples in a 2.5-cm cell with sodium chloride windows. The mass-cracking patterns were obtained on a Consolidated Electrodynamics Corp. mass spectrometer, Type 21-103C, with an ionization potential of 70 V and an ionization chamber temperature of 250°. The nmr spectra were obtained on a Varian V-4300-2 nmr spectrometer at 40.00 Mcps with trichlorofluoromethane as solvent and internal reference.[17] Values are reported in $\phi^*$ units. For all spectra reported with more than one absorption the area ratios are consistent with the structure assignments within the limits of experimental error. The nmr results are given in Table I.

**Elemental Analyses.**—Analyses for carbon and fluorine were carried out on gas samples by combustion of the samples in a stream of moist oxygen at 1100–1200° according to the procedure developed in these laboratories for highly fluorinated compounds.[18] With only one or two exceptions the analyses for carbon were repeatedly satisfactory, but analyses for fluorine consistently gave slightly lower values than the calculated values. The reasons for this deviation are not well understood. The mass-cracking pattern was obtained independently for each compound analyzed to provide further information about the elemental composition in support of the combustion analyses. The fluorine analyses are included here, although the limitations of these data taken independently are recognized.

**Bis(fluoroformyl) Peroxide** (I).—A modification of the procedure described in the literature[2] was used. (*Caution. Numerous explosions in the cylinder were experienced with this procedure during changing of carbon monoxide. Although none of these resulted in rupture of the cylinder under the described conditions, proper precautions should be exercised.*) A clean, dry 3-l. Hoke stainless steel cylinder which had been pretreated with fluorine was evacuated and then charged to a pressure of 120 mm with fluorine (19.3 mmol), to a total pressure of 600 mm with oxygen (77.4 mmol), and then to a total pressure of 740 mm with carbon monoxide (22.5 mmol). The cylinder was kept at room temperature for 6 hr, and the contents were then subjected to fractional distillation–condensation at about 0.1 mm pressure, employing a trap cooled by a slush bath of ethyl bromide–liquid nitrogen (−119°). In a typical preparation the trap was found to contain 6.40 mmol of pure bis(fluoroformyl) peroxide (57% yield), although the yield was variable, depending on the total elapsed time at room temperature. The peroxide was stored in a glass ampoule packed in a chest of solid carbon dioxide until used and was purified by repeated fractional distillation–condensation on the vacuum line prior to each experiment. The purity of the peroxide was monitored by its infrared spectrum before each experiment.

**Fluoroformyl Perfluoromethyl Peroxide** (II).—A clean, dry, evacuated quartz tube of 83-cc volume, sealed at one end and equipped with a Fischer and Porter polytetrafluoroethylene valve at the other end, was charged with 0.50 mmol of peroxide I and 0.50 mmol of difluorodiazirine[5] and then irradiated with a Hanovia 140-W ultraviolet lamp for 6 hr with the lamp 2–3 in. from the reaction tube. The product was subjected to fractional distillation–condensation on the vacuum line, whereby nitrogen,

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(14) The absorptions for the fluorines of the $CF_3OO-$ group in a series of several perfluoroalkyl trifluoromethyl peroxides and trioxides are found in the region of $\phi^*$ +68–69: P. G. Thompson, *J. Amer. Chem. Soc.*, **89**, 4316 (1967).

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

(16) Toxicity studies of fluorinated peroxides have not been made, but their aggressive oxidizing capability makes exposure appear inadvisable. In this work all samples were assumed to be possible explosion hazards, although no violent explosions were encountered with any of the compounds described except peroxide I.

(17) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(18) H. E. Freier, B. W. Nippoldt, P. B. Olson, and D. G. Weiblen, *Anal. Chem.*, **27**, 146 (1955).

oxygen, and carbon monoxide were removed. The remaining product was chromatographed at −30° on the perfluorotributylamine column described previously.[1] There was obtained 0.091 mmol of pure fluoroformyl perfluoromethyl peroxide (II, 18% yield). The major by-product was carbon dioxide. Small amounts of carbonyl fluoride, silicon tetrafluoride, and trifluoromethyl fluoroformate (III)[8] were also isolated and identified by their infrared and nmr spectra.

Peroxide II is a colorless gas at room temperature, which liberated 0.0133 equiv of iodine from potassium iodide solution per gram of sample (calcd for a two-electron change, 0.0135 equiv) but did not produce a color change in ferrocene.[12] The infrared spectrum shows strong absorptions at 5.21 (assigned to a carbonyl group), 7.72, 8.05, and 8.56 μ and medium intensity absorptions at 9.95, 10.77, and 13.35 μ. The fluorine nmr spectrum is given in Table I. The mass spectrum displays prominent peaks at mass numbers 28 ($CO^+$), 44 ($CO_2^+$), 47 ($COF^+$), 63 ($CO_2F^+$), 66 ($CF_2O^+$), and 69 ($CF_3^+$). The highest two mass numbers observed are at mass numbers 129 ($C_2F_3O_3^+$, parent ion less one fluorine atom) and 148 ($C_2F_4O_3^+$, parent ion).

*Anal.* Calcd for $C_2F_4O_3$: C, 16.23; F, 51.34; mol wt, 148. Found: C, 16.1; F, 50.1; mol wt, 144 (by gas density), 138 (by effusion rate in the mass spectrometer), 148 (parent ion).

Neither peroxide II nor fluoroformate III was produced when a borosilicate glass vessel of the same size was substituted for the quartz tube in this procedure with approximately the same charges of starting materials, even after several hours additional irradiation. The difluorodiazirine was consumed after 22 hr but most of the peroxide was recovered.

**Photolysis of Bis(fluoroformyl) Peroxide.**—A sample of pure peroxide I (0.99 mmol) was charged into the quartz tube described in the preceding experiment and irradiated with the same lamp for 20 hr with the lamp 2–3 in. from the tube. The product mixture was then subjected to fractional distillation–condensation on the vacuum line, whereby any molecular oxygen formed in the reaction was removed. The remaining product (1.44 mmol) was found to be chiefly carbon dioxide and bis(perfluoromethyl) peroxide (IV) with small amounts of carbonyl fluoride and silicon tetrafluoride. The product was chromatographed on the perfluorotributylamine column and the components of the product mixture were identified by comparison of their infrared spectra and retention times with those of authentic samples. Traces of other products were observed but these materials were not isolated. The chromatographic data showed that the peroxide was present as approximately 10% of the product mixture (50% of the theoretical amount). The long reaction time was needed in this reaction. In an experiment conducted for only 2 hr under the same conditions most of the starting material was recovered.

**Hydrolysis of Fluoroformyl Perfluoromethyl Peroxide. A. Preparation of Perfluoromethyl Hydroperoxide (VI).**—A clean, dry, 15-cc borosilicate glass ampoule equipped with a Fischer and Porter polytetrafluoroethylene valve was charged with 0.745 mmol of peroxide II and 0.375 mmol of water vapor and allowed to stand at room temperature for 1 day. The product was then isolated by fractional distillation–condensation on the vacuum line at less than 1 mm pressure with traps cooled at −78°, −110, and −196°. From the trap cooled at −110° was recovered 0.59 mmol (80% yield) of perfluoromethyl hydroperoxide (VI). The trap cooled at −78° contained traces of water and compound VI and the trap cooled at −196° contained 0.90 mmol of carbon dioxide and silicon tetrafluoride plus traces of compound VI. Compound VI is a clear liquid with a boiling point near room temperature at 760 mm pressure and was stable for several months at room temperature when stored in a glass ampoule in the gas phase, even in the presence of small amounts of water. Compound VI rapidly liberates iodine from aqueous potassium iodide solution. The infrared spectrum for compound VI exhibits a sharp absorption at 2.80 μ (m), complex absorptions at 7.22 (m), 7.85 (vs), 8.14 (vs), and 8.95 μ (vw), and a broad absorption at 10.58 μ (vw). The fluorine nmr spectrum shows only one absorption (Table I). The mass spectrum exhibits prominent peaks at mass numbers 28 ($CO^+$), 44 ($CO_2^+$), 47 ($CFO^+$), 66 ($CF_2O^+$), 67 ($CF_2HO^+$), and 69 ($CF_3^+$, largest peak). The highest mass numbers observed were at mass numbers 83 ($CF_2HO_2^+$, parent ion less one fluorine atom), 85 ($CF_3O^+$), and 102 ($CF_3HO_2^+$, parent ion).

*Anal.* Calcd for $CF_3HO_2$: C, 11.77; F, 55.87; mol wt, 102. Found: C, 11.9; F, 54.8; mol wt, 105 (by gas density), 102 (parent ion).

**B. Preparation of Bis(perfluoromethyl) Bis(peroxy)carbonate (V).**—The ampoule described in part A was charged with 0.28 mmol of peroxide II and a trace of water vapor (distilled from 0.005 ml of liquid water) by vacuum transfer and allowed to stand at room temperature for 15 hr. The product was isolated by fractional distillation–condensation on the vacuum line at less than 1 mm pressure with traps cooled at −63, −110, and −196°. From the trap cooled at −110° was recovered 0.11 mmol of bis(perfluoromethyl) bis(peroxy)carbonate (V). The only other products were carbon dioxide and silicon tetrafluoride. Compound V is a clear, colorless liquid at room temperature with a vapor pressure of 150–200 mm (estimated bp 60° (760 mm)). It readily liberates iodine from aqueous potassium iodide solution and is stable in the gas phase at low pressures in carefully dried apparatus at room temperature. The infrared spectrum shows absorptions at 5.24 (m, assigned to the carbonyl group), 7.70 (s), 8.03 (vs), 8.18 (s), 8.77 (s), 8.95 (vs), 10.60 (vw), and 13.65 μ (w). The fluorine nmr spectrum exhibits only one absorption (Table I). The mass spectrum exhibits prominent peaks at mass numbers 28 ($CO^+$), 44 ($CO_2^+$), 47 ($CFO^+$), 66 ($CF_2O^+$), 69 ($CF_3^+$, largest peak), 113 ($C_2F_3O_2^+$), and 129 ($C_2F_3O_3^+$). The intensity of the peak at mass number 129 is approximately 20% of the peak intensity at mass number 69.

*Anal.* Calcd for $C_3F_6O_5$: C, 15.66; F, 49.56; mol wt, 230. Found: C, 15.1; F, 48.1; mol wt, 231 (by gas density).

**Hydrolysis of Bis(perfluoromethyl) Bis(peroxy)carbonate (V).**—A clean, dry, borosilicate glass nmr tube equipped with a Fischer and Porter polytetrafluoroethylene valve was charged with 0.01 mmol of pure peroxide V and 0.001 ml of liquid water. The tube was allowed to stand at room temperature for 15 hr. The product was then subjected to fractional distillation–condensation on the vacuum line with traps cooled at −78, −110, and −196°. The contents of each trap were transferred completely to separate infrared cells. The product from the trap at −110° had a spectrum identical with that of hydroperoxide VI. The product from the trap at −196° consisted only of carbon dioxide, while the trap at −78° contained only traces of water.

This reaction was also carried out in a 2.5-cm gas infrared cell, and the course of the reaction was followed by the spectra at convenient time intervals. The results were the same.

**Preparation of Fluoroxyperfluoromethyl Perfluoromethyl Peroxide (VII).**—The fluorination technique described in the literature[10] utilizing alkali metal fluorides as catalysts was used for this reaction. The reactions were carried out in a 75-cc Hoke stainless steel cylinder (rated at 1800 psi) containing 3.0 g of finely ground cesium fluoride which had been dried at 150° under reduced pressure and pretreated with fluorine. The cylinder was cooled in a bath of liquid nitrogen and charged with 0.56 mmol of pure peroxide II and 1.02 mmol of fluorine *via* the vacuum line. The cylinder was placed in a −78° bath and left there for 20 hr. During this time the bath warmed slightly. The cylinder was again cooled in a bath of liquid nitrogen and the volatile contents at this temperature were removed (excess fluorine). The cylinder was then allowed to warm to room temperature, and the volatile contents were transferred to the vacuum line and found to be pure fluoroxyperfluoromethyl perfluoromethyl peroxide (VII, 0.50 mmol, 90% yield).

Peroxide VII exhibits absorptions in the infrared spectrum at 7.78 (s), 7.97 (s), 8.22 (shoulder), 8.33 (m), 8.67 (s), and 10.67 μ (vw, assigned to the fluoroxy group). The fluorine nmr spectrum shows three peaks, as shown in Table I. The absorptions for the $-OCF_2OF$ group are found at approximately the same positions as the corresponding absorptions in the nmr spectrum of bis(fluoroxy)perfluoromethane[15] ($\phi^*$ +84.2 and $\phi^*$ −159.2 with a coupling constant of 39.0 cps). The mass-cracking pattern exhibits no peaks assignable to fragments with carbon–carbon bonds. The largest intensity peak appears at mass number 69 ($CF_3^+$). Strong peaks appear at mass numbers 47 ($CFO^+$), 66 ($CF_2O^+$), and 85 ($CF_3O^+$). Medium intensity peaks appear at mass numbers 28 ($CO^+$), 31 ($CF^+$), 35 ($FO^+$), 44 ($CO_2^+$), 50 ($CF_2^+$), 63 ($CFO_2^+$), 101 ($CF_3O_2^+$), and 151 ($C_2F_5O_2^+$, parent ion less one oxygen atom and one fluorine atom). Lower intensity peaks appear at mass numbers 16 ($O^+$), 19 ($F^+$), 32 ($O_2^+$), 82 ($CF_2O_2^+$), and 148 ($C_2F_4O_3^+$, parent ion less two fluorine atoms). No parent ion is observed.

*Anal.* Calcd for $C_2F_6O_3$: C, 12.91; F, 61.28; mol wt, 186. Found: C, 13.0; F, 59.6; mol wt, 183 (by gas density).

Peroxide VII was rapidly reduced by ferrocene to give carbonyl fluoride.

**Preparation of Fluoroxybis(perfluoromethylperoxy)fluoromethane (VIII).**—The procedure was the same as the procedure for the preparation of peroxide VII. The same reaction vessel was charged with 0.51 mmol of pure peroxide V and 1.02 mmol of fluorine, and the cylinder was then kept overnight in the −78° bath. Recovery of the product gave 0.52 mmol of pure fluoroxybis(perfluoromethylperoxy)fluoromethane (VIII, quantitative yield within experimental error). Peroxide VIII exhibits very strong, complex absorption in the infrared spectrum between 7.70 and 8.10 $\mu$ with peaks at 7.71, 7.87, and 8.00 $\mu$, as well as other peaks at 8.60 (s), 8.85 (vs), and 10.62 $\mu$ (w, broad). The fluorine nmr spectrum shows three complex peaks, as shown in Table I. The mass spectrum of peroxide VIII shows prominent peaks at mass numbers 44 ($CO_2^+$), 47 ($COF^+$, largest peak), and 69 ($CF_3^+$); medium intensity peaks at mass numbers 28 ($CO^+$), 63 ($CFO_2^+$), and 66 ($CF_2O^+$); and lower intensity peaks at mass numbers 16 ($O^+$), 19 ($F^+$), 31 ($CF^+$), 32 ($O_2^+$), 50 ($CF_2^+$), 85 ($CF_3O^+$), 113 ($C_2F_3O_2^+$), and 129 ($C_2F_3O_3^+$). No parent ion or ions near the molecular weight of the parent molecule were observed. The absence of peaks in the pattern attributable to fragments containing carbon–carbon bonds or elements other than carbon, fluorine, and oxygen is further support for the structure. Compound VIII liberates iodine from aqueous potassium iodide solution but is thermally stable at room temperature. The nmr sample in trichlorofluoromethane showed no decomposition after storage at room temperature in the nmr tube for several months.

*Anal.* Calcd for $C_3F_8O_6$: C, 13.43; F, 56.72. Found: C, 13.1; F, 55.5.

**Registry No.**—I, 692-74-0; II, 16118-40-4; V, 16156-35-7; VI, 16156-36-8; VII, 16156-37-9; VIII, 16156-38-0.

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# *Notes*

## Fluorocarbonyl Trifluoromethyl Peroxide

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A recent article[1] reporting the synthesis of FC(O)OF by the photochemical reaction of $(FCO)_2O_2$ with fluorine stated that the new compound $FC(O)OOCF_3$ was formed as a by-product. The yield was about 5%, based upon the quantity of $(FCO)_2O_2$ consumed. This new compound is the same as one now described by Talbott, who has used the name fluoroformyl perfluoromethyl peroxide and clearly established the formula.[2] In our work, samples of the pure compound were obtained through separation either by gas chromatography using the column described in ref 1 or by fractional codistillation. The observed properties are given below.

**Molecular Weight.**—The average molecular weight obtained from four vapor density measurements was 148 g/mol (theory for $FC(O)OOCF_3$, 148).

**Volatility.**—Fractional codistillation indicated a boiling point within 10° of −16°.

**Infrared Spectrum.**—The infrared spectrum of the gas as observed with a Beckman Model IR10 spectrometer is shown in Figure 1. The substance was in a cell 10 cm long with silver chloride windows. Absorption bands (cm$^{-1}$) were found at 1918, vs, C=O stretch; 1300, vs, CF stretch; 1247, vs, CF stretch; 1172, vs, CF stretch; 1007, m, CO stretch; 932, m, CO stretch; 753, m; 691, w, $CF_3$ symmetrical deformation; and 615, m. All assignments should be considered tentative.

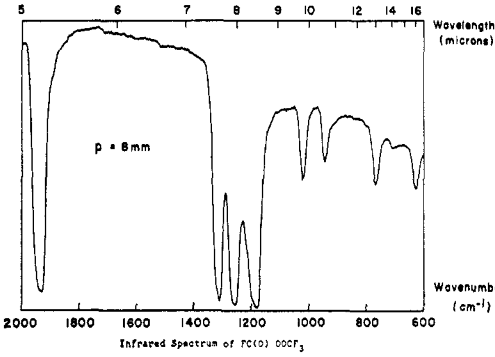

Figure 1.—Infrared spectrum of $FC(O)OOCF_3$.

**Nuclear Magnetic Resonance Spectrum.**—The $^{19}F$ nmr spectrum was taken at 40 Mc with a Varian Model No. V4311 spectrometer using 76 mol % $CCl_3F$ as an internal standard. The resultant spectrum consisted of a sharply defined doublet with a chemical shift of 68.8 ppm for the $CF_3$ group and a quadruplet with a chemical shift of 32.3 ppm for the FC=O group. The coupling constant, $J$, was 1.7 cps.

For comparison, the chemical shift of the FC=O group, with respect to external $CCl_3F$, of $(FCO)_2O_2$,[3] and of internal $CCl_3F$ of $FC(O)OOSF_5$,[4] was +34.4 ppm. The chemical shift of the $OCF_3$ group with respect to internal $CCl_3F$ of $CF_3OOCF_3$ was +69.0 ppm.[5]

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