compared to these compounds. One can conclude that CF_3OOF will resemble CF_3OF in the types of chemical reactions it will undergo but it should show much greater reactivity under similar conditions.

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The Preparation of Fluoroperoxytrifluoromethane. The Mechanism of the Reaction of Oxygen Difluoride and Carbonyl Fluoride

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Fluoroperoxysulfuryl fluoride, FSO_2OOF, was the first compound reported to contain the fluoroperoxy, OOF, group. This compound was prepared[1] by the photolytic reaction of sulfur trioxide, SO_3, and oxygen difluoride, OF_2, and by the reaction of sulfur dioxide, SO_2, and dioxygen difluoride.[2] Thompson[3] reported that the direct fluorination of salts of trifluoroacetic acid, CF_3CO_2H, produced a number of products including very small amount of fluoroperoxytrifluoromethane, CF_3OOF, and fluoroperoxypentafluoroethane, CF_3CF_2OOF. 1- and 2-fluoroperoxyperfluoropropanes have also been reported[4] to result from the reaction of perfluoropropene, C_3F_6, and O_2F_2. At the time this research was initiated a convenient method for the preparation of a fluoroperoxyperfluoroalkane was not available.

Anderson and Fox[5] reported that oxygen difluoride, OF_2, and carbonyl fluoride, COF_2, react in the presence of cesium fluoride, CsF, catalyst to give good yields of bis(trifluoromethyl) trioxide, CF_3OOOCF_3, and have suggested that the formation of CF_3OOOCF_3 proceeds by the mechanism

$$COF_2 + CsF \longrightarrow Cs^+OCF_3^- \qquad (1)$$

$$OF_2 + CF_3O^- \longrightarrow CF_3OOF + F^- \qquad (2)$$

$$CF_3OOF + CF_3O^- \longrightarrow CF_3OOOCF_3 + F^- \qquad (3)$$

$$CF_3OOF + COF_2 \longrightarrow CF_3OOOCF_3 \qquad (4)$$

They, however, did not detect CF_3OOF in their experiments.

We have additional proof of the validity of this mechanism and also wish to report the first convenient method for the preparation of fluoroperoxytrifluoromethane, CF_3OOF.

In the majority of its reactions, OF_2 acts as a powerful fluorinating agent, but in a few cases simple addition of OF_2 to a substrate has been observed. The photochemical addition of OF_2 to SO_3[6,7] has been shown to proceed *via* an ·OF intermediate. Also, Merritt has proposed that carefully controlled oxidations of amines[8] and certain unsaturated compounds[9–11] by OF_2 may involve intermediate OF_2 adducts.

Results and Discussion

A. Mechanism.—The mechanism of the reaction of COF_2 and OF_2 was elucidated by using ^{17}O-tracer techniques and ^{17}O nmr analysis. According to the proposed mechanism, if $C^{17}OF_2$ is allowed to react with ordinary OF_2, the ^{17}O should be in the positions

$$C^{17}OF_2 + CsF \longrightarrow Cs^{+17}OCF_3^- \qquad (1a)$$

$$^{16}OF_2 + {}^{17}OCF_3^- \longrightarrow CF_3{}^{17}O^{16}OF + F^- \qquad (2a)$$

$$CF_3{}^{17}O^{16}OF + {}^{17}OCF_3^- \longrightarrow CF_3{}^{17}O^{16}O^{17}OCF_3 + F^- \qquad (3a)$$

$$CF_3{}^{17}O^{16}OF + C^{17}OF_2 \longrightarrow CF_3{}^{17}O^{16}O^{17}OCF_3 \qquad (4a)$$

Thus, the product should contain ^{16}O in the center position and ^{17}O in other positions. Alternatively, if ordinary COF_2 is allowed to react with $^{17}OF_2$, the labels should be reversed.

In order to determine the chemical shifts of the various oxygen atoms in CF_3OOOCF_3, $C^{17}OF_2$ was allowed to react with $^{17}OF_2$, and a randomly labeled $CF_3{}^{17}O^{17}O^{17}OCF_3$ was obtained. A two-line ^{17}O nmr spectrum was obtained. Since the −321-ppm line had approximately twice the intensity of the −479 ppm line, lines were assigned as shown in Table I. Ordinary OF_2 was then treated with $C^{17}OF_2$ and only the −321-ppm line appeared; alternatively the reaction of $^{17}OF_2$ with ordinary COF_2 resulted in a product that showed only the −479-ppm line.

TABLE I

CHEMICAL SHIFTS FOR ^{17}O-LABELED BIS(TRIFLUOROMETHYL) TRIOXIDE

Source of sample	Chem shift, ppm relative to $H_2{}^{17}O$	
	$CF_3{}^{17}OO^{17}OCF_3$	$CF_3O^{17}OOCF_3$
$^{17}OF_2 + C^{17}OF_2$	−321	−479
$OF_2 + C^{17}OF_2$	−321	. . .
$^{17}OF_2 + COF_2$	. . .	−479

In considering the mechanism shown by eq 1a–4a, an excess of OF_2 or the removal of free COF_2 should favor the isolation of CF_3OOF. As will be seen in the next section, CF_3OOF was prepared using these types of experiments. It was found, however, that CF_3OOF does not react with COF_2 as shown in eq 4.

It was concluded that the proposed mechanism is supported by the ^{17}O nmr results and by the isolation of CF_3OOF in the reaction of COF_2 and OF_2.

B. Preparation of Fluoroperoxytrifluoromethane.—Fluoroperoxytrifluoromethane was prepared as follows.

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[1] R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, *Z. Phys. Chem.* (*Frankfurt am Main*), **35**, 343 (1962).

[2] I. J. Solomon, A. J. Kacmarek, and J. K. Raney, *Inorg. Chem.*, **7**, 1221 (1968).

[3] P. G. Thompson, *J. Amer. Chem. Soc.*, **89**, 4316 (1967).

[4] I. J. Solomon, A. J. Kacmarek, and J. K. Raney, *ibid.*, **90**, 6557 (1968).

[5] L. R. Anderson and W. B. Fox, *ibid.*, **89**, 4313 (1967).

[6] R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, *Angew. Chem.*, **75**, 137 (1963).

[7] I. J. Solomon, A. J. Kacmarek, and J. K. Raney, *J. Phys. Chem.*, **72**, 2262 (1968).

[8] R. F. Merritt and J. K. Ruff, *J. Amer. Chem. Soc.*, **86**, 1392 (1964).

[9] R. F. Merritt and J. K. Ruff, *J. Org. Chem.*, **30**, 328 (1965).

[10] R. F. Merritt and J. K. Ruff, *ibid.*, **30**, 3968 (1965).

[11] R. F. Merritt and J. K. Ruff, *ibid.*, **30**, 4367 (1965).

Carbonyl fluoride was condensed into a stainless steel reactor that contained CsF and thawed. Any unreacted COF_2 was then pumped off, and a fourfold excess of OF_2 was condensed into the reactor. The reactor was maintained at room temperature for 72 hr. The reaction mixture was then passed through a −160° bath (to trap the CF_3OOOCF_3) and a −183° bath (to trap the CF_3OOF), and then the excess OF_2 was condensed in a −196° trap. The products CF_3OOF and CF_3OOOCF_3 were found in approximately 75 and 25% yields, respectively, based on the stoichiometry given in eq 1–3.

C. Properties of Fluoroperoxytrifluoromethane.—The CF_3OOF was characterized by ^{19}F nmr spectral analysis and molecular weight determinations. The ^{19}F nmr spectrum agrees with that of Thompson[12] and contains the characteristic line (−291.5 ppm) due to the $OO^{19}F$ as well as the $C^{19}F_3$ line (69.2 ppm). The molecular weight was determined by gas density measurements (calcd, 120; obsd, 118, 121).

Fluoroperoxytrifluoromethane is a colorless liquid with a melting point below −196°. Room-temperature stability studies were made by confining a sample in an ir cell and monitoring spectral changes as a function of time. At 5 mm pressure, it required some 138 hr before most of the CF_3OOF decomposed; it has not been ascertained whether the decomposition is due to instability or reaction with its surroundings.

The infrared spectrum consisted of strong bands at 7.75 μ (1290 cm^{-1}), 7.90 μ (1266 cm^{-1}), and 8.55 μ (1170 cm^{-1}) which correspond closely to the infrared spectrum of bis(trifluoromethyl) trioxide. The difference appears to be the 10.5-μ (952-cm^{-1}) band for the CF_3OOF and the 11.15-μ (897-cm^{-1}) band for the CF_3OOOCF_3.

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[12] P. J. Thompson, personal communication, 1967.

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Solvent-Exchange Rates from Manganese(III) Protoporphyrin IX Dimethyl Ester Studied by Nuclear Magnetic Resonance Line Broadening

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It has been found previously that a knowledge of the solvent-exchange rates from the first coordination sphere of a metal ion is useful in establishing the general lability and mechanism of complexation to the metal.[1,2] The exchange rates of the solvents methanol and *N,N*-dimethylformamide from manganese(III) protoporphyrin IX dimethyl ester ($Mn(DMPrpor)^+$) are reported here. The general reaction being studied is

$$Mn(DMPrpor)(S)_2^+ + S^* \rightleftharpoons Mn(DMPrpor)(S)(S^*)^+ + S$$

where S^* and S are initially free and coordinated solvent molecules, respectively. In a previous study[3] Fleischer did not observe any complexing with manganese(III) hematoporphyrin; therefore there is no information on the reaction rates of these high-spin d^4 systems. It was also of interest to extend earlier studies on iron(III) protoporphyrin IX[4] and cobalt(III) and iron(III) hematoprophyrin.[3]

Experimental Section

The chloride salt of manganese(III) protoporphyrin IX dimethyl ester $Mn(DMPrpor)^+$ was prepared and purified as described by Boucher.[5] *Anal.* Calcd for $C_{36}H_{36}O_4N_4MnCl\cdot H_2O$: C, 62.02; H, 5.49; N, 8.04. Found: C, 62.88; H, 5.45; N, 7.53.

The visible spectrum of $Mn(DMPrpor)Cl\cdot H_2O$ in methanol shows maxima (with molar extinction coefficients in parentheses) at 27,000 cm^{-1} (7.73×10^{-4} M^{-1} cm^{-1}), 21,600 cm^{-1} (5.90×10^4 M^{-1} cm^{-1}), and 18,200 cm^{-1} (1.1×10^4 M^{-1} cm^{-1}), with a further weak band at ~17,200 cm^{-1}. The band positions agree with those given by Boucher,[5] but the extinction coefficients seem to be slightly higher than those which can be read from Figure 5 of ref 5. It has also been found, in agreement with Boucher, that removal of chloride ion with silver perchlorate has no effect on the spectrum in methanol.

The effective magnetic moment of $Mn(DMPrpor)^+$ in methanol has been determined between −60 and +40°, using the nmr shift method suggested by Evans.[6] The sample was prepared under vacuum by treating $Mn(DMPrpor)Cl\cdot H_2O$ with $AgClO_4$ and molecular sieves. Cyclopentane was used as an internal standard. A Curie law temperature dependence, with an effective magnetic moment of 5.01 (after correction for diamagnetism of the porphyrin), was found. This result is in agreement with values of 4.86–4.97 determined by Boucher[5] on various solid salts.

All solutions for nmr analysis were prepared on a vacuum line using standard techniques. All samples were treated with $AgClO_4$ and molecular sieves to remove chloride and water, respectively, from $Mn(DMPrpor)Cl\cdot H_2O$. The metal complex concentration was determined from the weight of solvent and complex used. In several cases this concentration was checked spectrophotometrically, and agreement with the expected value was always better than 5%.

In methanol the $Mn(DMPrpor)^+$ concentrations used were 9.65×10^{-2}, 9.81×10^{-3}, and 2.38×10^{-2} *m*, in order to obtain line broadenings in the range of 5–50 Hz and shifts of 1–12 Hz. The shifts and broadenings were found to be directly dependent on the $Mn(DMPrpor)^+$ concentration and in a separate study this dependence was confirmed, at 40°, up to 8.25×10^{-2} *m*, the maximum concentration studied.

In DMF, complex concentrations of 6.88×10^{-3}, 1.23×10^{-2}, and 2.39×10^{-2} *m* were used to give broadenings and shifts in the same range as those observed in methanol. The methyl proton broadenings were determined by a least-squares fit of the two overlapping methyl resonances to the sum of two Lorentzian curves. Only the data for the higher field methyl resonance are given here, since the other methyl resonance shows essentially the same behavior.

The solvents were purified by double vacuum distillation from molecular sieves, the middle fraction of each distillation being used. Solvents were stored under vacuum over molecular sieves.

The nmr measurements were made on a Varian Associates A-56/60 spectrometer equipped with a Varian Model V-4343 temperature controller. Temperatures were determined from the peak separation in pure methanol or ethylene glycol.

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[1] M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965).

[2] D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1970).

[3] E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Amer. Chem. Soc.*, **90**, 2527 (1968).

[4] N. S. Angerman, B. B. Hasinoff, H. B. Dunford, and R. B. Jordan, *Can. J. Chem.*, **47**, 3217 (1969).

[5] L. J. Boucher, *J. Amer. Chem. Soc.*, **90**, 6640 (1968).

[6] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).