An Unusual Reaction of Oxygen Difluoride. The Addition to Carbonyl Fluoride to Produce Bis(trifluoromethyl) Trioxide

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Abstract: Oxygen difluoride has been shown to react with carbonyl fluoride over a cesium fluoride catalyst to give good yields of the unusual compound bis(trifluoromethyl) trioxide, a stable material having a melting point of −138° and a normal boiling point of −16°. Its formulation as a symmetrical trioxide is supported by its infrared spectrum, nuclear magnetic resonance, and other data. A possible mechanism for its formation is given.

In the great majority of its chemical reactions, oxygen difluoride acts as a powerful fluorinating agent with a somewhat higher activation energy than elemental fluorine. With solids and in high-temperature reactions, the usual result is fluorination of the substrate; in aqueous solutions, the formation of HF with concomitant oxidation of the solute predominates.[1] In only two instances, formation of FSO_3OF and FSO_2OSO_2F by photochemical addition of OF_2 to SO_3[2] and SO_2,[3] respectively, have products resulting from simple OF_2 addition to the substrate been obtained. Merritt has proposed that carefully controlled oxidations of amines[4] and certain unsaturated compounds[5-7] by OF_2 may involve intermediate OF_2 adducts, but such intermediates were not isolable and their existence remains unproved.

We have recently found that, under conditions to be described below, 1 mole of oxygen difluoride adds to 2 moles of carbonyl fluoride to produce a high yield of the unusual and stable compound bis(trifluoromethyl) trioxide, CF_3OOOCF_3.

The trioxide was probably first prepared by Thompson[8] through fluorination of sodium trifluoroacetate, but the yield was low (<5%). A material of this composition has also been claimed to result from the photolysis of hexafluoroazomethane and oxygen, but the yield was poor and the product was incompletely characterized.[9] Bis(trifluoromethyl) trioxide is one of only a few compounds known in which an oxygen atom appears to be bonded to two other oxygen atoms.

Benson[10] has predicted on thermochemical grounds that alkyl trioxides would have reasonable thermal stability, and recently two rather unstable trioxides, $(CH_3)_3COOOC(CH_3)_3$ and $C_6H_5C(CH_3)_2OOOC(CH_3)_2C_6H_5$, have been prepared by Bartlett and Günther.[11] These authors refute an earlier claim by Milas and Arzoumanidis[12] to have made $(CH_3)_3COOOC(CH_3)_3$.

Experimental Section

Reagents. Oxygen difluoride (minimum purity 99.0%) was supplied by the Industrial Chemicals Division, Allied Chemical Corp. Carbonyl fluoride (Air Products Co.) was fractionated until the infrared spectrum matched that found in the literature.[13] Cesium and rubidium fluorides (American Potash & Chemical Corp.) and potassium fluoride (Baker & Adamson) were all dried *in vacuo* at 160° and then ground for 5 hr in a Spex Mixer/Mill Model 8000 using a tungsten carbide capsule and ball.

Preparation of CF_3OOOCF_3. In a typical reaction, approximately 2.0 g of CsF was introduced (drybox) into a glass reaction tube of about 30-ml capacity. The reaction vessel was then capped with a 304A Hoke valve *via* a $^3/_8$-in. Swagelok fitting with Teflon ferrules.

Standard vacuum techniques were used to measure and condense equimolar amounts (3.26 mmoles each) of carbonyl fluoride and oxygen difluoride onto the cesium fluoride, after which the reactor was isolated from the remainder of the vacuum line and brought to room temperature. After 16 hr the infrared spectrum of the resultant gases indicated that CF_3OOOCF_3 had been formed and that no COF_2 remained.

The crude CF_3OOOCF_3 was purified by first pumping at −196° to remove excess OF_2 and was then fractionated through a trap maintained at about −140°. The impurities, present in relatively small amounts, consisted of CF_4, SiF_4, CO_2, and CF_3OOCF_3. These passed slowly through the −140° trap, leaving the purified product behind.

The conditions and results of several runs are given in Table I

Table I. The Effect of Catalyst and Reaction Time on CF_3OOOCF_3 Synthesis

Reactants (mmoles)	Catalyst	Reaction time (temp, °C)	Product yield, % (based upon COF_2 introduced)
COF_2 (3.27) OF_2 (3.27)	None	2 days (100)	No reaction
COF_2 (3.30) OF_2 (1.65)	CsF (no previous use)	16 hr (25)	10
COF_2 (3.28) OF_2 (3.28)	CsF (used once previously)	2 days (25)	41
COF_2 (3.26) OF_2 (3.26)	CsF (used twice previously)	4 days (25)	87
COF_2 (3.25) OF_2 (3.25)	RbF (no previous use)	24 hr (25)	~15
COF_2 (3.4) OF_2 (3.4)	KF (no previous use)	6 days (25)	Small amount

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[1] (a) H. R. Leech, "Compounds of Fluorine with Oxygen," in Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Supplement II, Part I, Longmans, Green and Co., New York, N. Y., 1956, p 186; (b) A. G. Streng, *Chem. Rev.*, **63**, 607 (1963); (c) W. B. Fox, "Oxygen Fluorides," in "Encyclopedia of Chemical Technology," Vol. 9, Interscience Publishers, Inc., New York, N. Y., 1966.

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

[3] G. Franz and F. Neumayr, *Inorg. Chem.*, **3**, 921 (1964).

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

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

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

[7] R. F. Merritt, *ibid.*, **30**, 4367 (1965).

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

[9] V. A. Ginsburg, *et al.*, *Dokl. Akad. Nauk SSSR*, **149**, 97 (1963).

[10] S. W. Benson, *J. Am. Chem. Soc.*, **86**, 3922 (1964).

[11] P. D. Bartlett and P. Günther, *ibid.*, **88**, 3288 (1966).

[12] N. A. Milas and G. G. Arzoumanidis, *Chem. Ind.* (London), 66 (1966).

[13] J. H. Simons, Ed., "Fluorine Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1954, p 485.

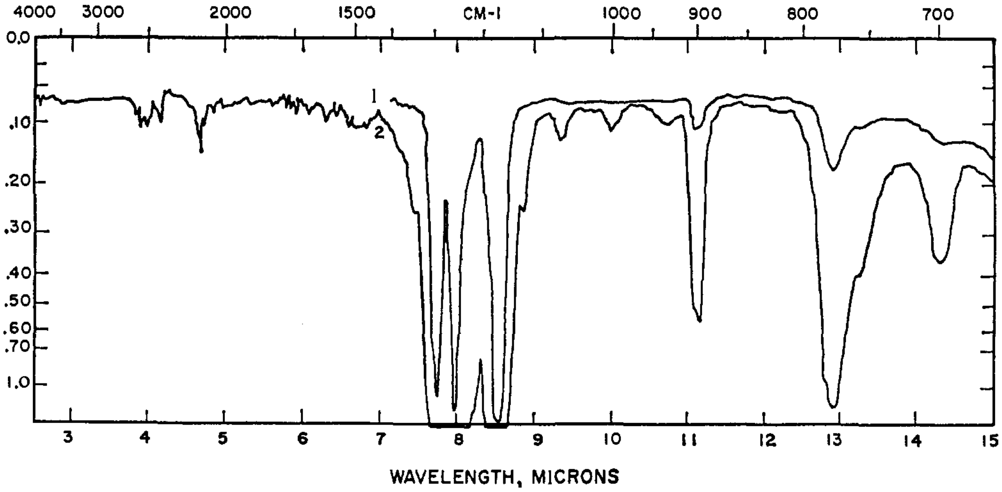

Figure 1. The infrared spectrum of bis(trifluoromethyl) trioxide: curve 1, 3.5 mm; curve 2, 38.8 mm.

Properties of CF_3OOOCF_3. Bis(trifluoromethyl) trioxide is a colorless material which appears to be quite stable at room temperature when stored as a gas in Pyrex or metal vessels. The material begins to decompose slowly at about 70° in glass, yielding CF_3OOCF_3 and O_2 along with trace amounts of COF_2 and SiF_4.

Anal. Calcd for CF_3OOOCF_3: C, 12.9; F, 61.3. Found: C, 13.2; F, 59.4.

Molecular Weight. From the gas density, assuming ideal gas behavior, the molecular weight of CF_3OOOCF_3 was determined to be 183 (calculated 186).

Vapor Pressure and Boiling Point. The vapor pressure of the trioxide over the range −80 to −23° is represented by the equation

$$\log P_{\text{mm}} = 7.705 - \frac{1.241 \times 10^3}{T°\text{K}}$$

which was calculated from the data in Table II. The normal boiling point calculated from the equation is −16°, and the latent heat of vaporization is 5670 cal mole^{-1}, corresponding to a Trouton constant of 22.1 cal deg^{-1} mole^{-1}.

Table II. Vapor Pressure of CF_3OOOCF_3

Temp, °K	*P*, mm	Temp, °K	*P*, mm
249.4	556.8	202.0	36.9
219.3	109.5	196.9	26.0
212.3	72.5	191.7	17.0
206.1	48.2		

Melting Point. The trioxide when frozen was a white solid which melted to a colorless liquid at −138°.

Infrared Spectrum. The infrared spectrum of CF_3OOOCF_3 in the sodium chloride region, as recorded with a Perkin-Elmer 137B Infrarcord spectrophotometer, is shown in Figure 1. The strong bands at 1290, 1252, and 1169 cm^{-1} are probably attributable to the C–F stretching modes of the CF_3O groups,[14-17] and the band at 897 cm^{-1} is probably assignable to the C–O stretching frequency.[14,16] One or more of the bands between 773 and 699 cm^{-1} may be associated with the three expected CF_3 deformation modes.[17] A complete vibrational analysis has been undertaken and will appear in a later paper.[18]

Nmr Spectrum. The F^{19} nmr spectrum of pure CF_3OOOCF_3 at −78°, recorded at 56.4 Mc with a Varian Model V-4302 spectrometer, consisted of a single resonance at +72.4 ppm relative to $CFCl_3$.

Mass Spectrum. A Consolidated Electrodynamics Corp. Model 21-103 spectrometer, with an ionizing potential of 70 v (inlet at room temperature), was used to obtain the fragmentation pattern given below. Only those fragments with a relative intensity of 0.1 (based upon CF_3^+ = 100.0) or greater are recorded.

Table III. Mass Spectrum of CF_3OOOCF_3

m/e	Fragment	Rel intensity
151	$CF_3OOCF_2^+$	0.21
101	CF_3OO^+	0.10
85	CF_3O^+	1.17
82	F_2COO^+	0.30
70	$C^{13}F_3^+$	1.05
69	CF_3^+	100.00
66	F_2CO^+	7.33
50	CF_2^+	3.33
47	COF^+	14.55
44	CO_2^+	2.31
32	O_2^+	2.70
31	CF^+	2.20
28	CO^+	2.04

The mass spectrum of CF_3OOOCF_3 is, as expected, very similar to that of its decomposition product CF_3OOCF_3. However, authentic samples of CF_3OOCF_3 under the same conditions show a parent ion, $CF_3OOCF_3^+$, and a less intense O_2^+ peak. The relative intensities of other fragments are also different.

Discussion

It is evident that the over-all reaction between oxygen difluoride and carbonyl fluoride in the presence of metal fluorides proceeds according to the equation

$$OF_2 + 2COF_2 \xrightarrow{\text{MF}} CF_3OOOCF_3 \tag{1}$$

Although the net result of (1) suggests its analogy to the previously reported OF_2 additions to SO_2[3] and SO_3,[2]

$$OF_2 + 2SO_2 \xrightarrow{\text{ultraviolet}} FSO_2OSO_2F \tag{2}$$

$$OF_2 + SO_3 \xrightarrow{\text{ultraviolet}} FSO_2OOF \tag{3}$$

it appears unlikely that mechanism 1 is similar to mechanisms 2 and 3. In the photochemical reactions 2 and 3, the primary fission of OF_2 to OF· and F· is believed to precede attack by these radicals on the substrate. On the other hand, the dependence of the OF_2–COF_2 reaction on the presence of a metal fluoride (no

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[14] R. T. Lageman, E. A. Jones, and P. J. H. Waltz, *J. Chem. Phys.*, **20**, 1768 (1952).

[15] L. C. Duncan and G. H. Cady, *Inorg. Chem.*, **3**, 850 (1964).

[16] W. H. Hale, Jr., and S. M. Williamson, *ibid.*, **4**, 1342 (1965).

[17] A. J. Arvia and P. J. Aymonino, *Spectrochim. Acta*, **18**, 1299 (1962).

[18] R. Hirschmann, W. B. Fox, and L. R. Anderson, to be published.

reaction occurs without the metal fluoride even at 100°) and the readiness with which the reaction proceeds in the dark suggest a polar mechanism.

The formation of CF_3OOOCF_3 in the OF_2–COF_2–metal fluoride system may involve initial formation of a trifluoromethoxide[19] salt, followed by nucleophilic attack of the CF_3O^- salt on oxygen difluoride to give the intermediate CF_3OOF (eq 4 and 5). This intermediate may then undergo further displacement of fluoride ion by CF_3O^-, or react additively with COF_2 (eq 6 and 7). The intermediate CF_3OOF, if formed,

$$COF_2 + MF \longrightarrow M^+OCF_3^- \qquad (4)$$

$$OF_2 + CF_3O^- \longrightarrow CF_3OOF + F^- \qquad (5)$$

$$CF_3OOF + CF_3O^- \longrightarrow CF_3OOOCF_3 + F^- \qquad (6)$$

$$CF_3OOF + COF_2 \longrightarrow CF_3OOOCF_3 \qquad (7)$$

must react much more rapidly in (6) or (7) than does OF_2 in (5), since only the trioxide product is usually isolated.

In support of the proposed mechanism the following points should be noted. (a) It was observed that the CsF used in these experiments readily absorbed some COF_2 at room temperature even if the pressure was less than 1 atm. (b) It has been shown that CF_3OOOCF_3 is formed if OF_2 is placed in contact with preformed $CsOCF_3$ at room temperature. (c) The proposed intermediate CF_3OOF exists and has been synthesized and characterized by Thompson.[20] (d) Evidence for nucleophilic displacement of F^- from OF_2 has been advanced in other instances.[4] (e) A series of reactions apparently analogous to (5) has recently been reported by Ruff, Pitochelli, and Lustig.[21] (f) Addition of CF_3OOF in (7) would be analogous to the known reaction[22]

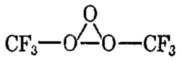
$$COF_2 + CF_3OF \longrightarrow CF_3OOCF_3$$

Evidence that the product of the COF_2–OF_2 reaction should be formulated as the symmetrical trioxide CF_3OOOCF_3 may be summarized as follows. (a) Chemical analysis and molecular weight data support the molecular composition $C_2O_3F_6$. (b) The infrared spectrum shows the existence of CF_3O groupings. (c) The F^{19} nmr spectrum shows the fluorine atoms to be equivalent and in the CF_3 region. (d) Thermal decomposition produces the known CF_3OOCF_3 and O_2 in almost quantitative yields. (e) The mass spectrum is similar to, but not identical with, that of CF_3OOCF_3. (f) The boiling point of the trioxide is somewhat higher than that of the peroxide CF_3OOCF_3, as expected.

Although these considerations alone do not permit a choice between a chain trioxide (*e.g.*, i) and a cyclic trioxide (*e.g.*, ii), the former seems most likely and

$$CF_3—O—O—O—CF_3$$

i



ii

requires no unusual bonding descriptions.

The variation in reaction times (see Table I) was simply a result of waiting until carbonyl fluoride was no longer observed in the infrared spectrum of the product gases. The reaction of CsF and COF_2 to form $CsOCF_3$ is more rapid than the reaction of $CsOCF_3$ with OF_2 to give CF_3OOOCF_3. Because of this rate difference, the product gases will show only CF_3OOOCF_3 and OF_2 after a relatively short period of time over fresh CsF. As the CsF is more nearly converted to $CsOCF_3$ this first process is slowed and the product gases will contain COF_2 for longer periods of time.

Whether or not the increased yield of CF_3OOOCF_3 in the longer runs was a result only of increased reaction time is not known definitely, but it seems qualitatively that a conditioning of the catalyst by previous use is beneficial.

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[19] M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

[20] P. G. Thompson, private communication.

[21] J. K. Ruff, A. R. Pitochelli, and M. Lustig, *J. Am. Chem. Soc.*, **88**, 453 (1966). These authors describe a series of reactions which involve the cesium fluoride catalyzed addition of fluorine across the carbon–oxygen double bond in various perfluorocarbonyl compounds. They find it likely that these fluorinations proceed through an ionic intermediate such as CF_3O^-.

[22] R. S. Porter and G. H. Cady, *ibid.*, **79**, 5628 (1957).