

ions,<sup>33</sup> a result which contrasts with observations in the present study.

Another question which remains unsettled is the following. Do the pathways for solvolysis of *trans*-(H<sub>2</sub>O)<sub>4</sub>Cr(OS(CH<sub>3</sub>)<sub>2</sub>)I<sup>2+</sup> with transition states of net charge 2+ and 1+ yield intermediates which are in rapid equilibrium with one another? Regrettably the form of the equation giving the hydrogen ion dependence of the ratio of the isomeric (H<sub>2</sub>O)<sub>4</sub>Cr(OS(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub><sup>3+</sup> products is the same whether independent intermediates are produced or a rapidly established proton dissociation-association equilibrium of the intermediates exists, giving a common pool of intermediates which go on to yield bis(dimethyl sulfoxide)chromium(III) products regardless of the pathway by which the intermediates are formed. The equation relating  $[cis-Cr(OS(CH_3)_2)_2^{3+}]/[trans-Cr(OS(CH_3)_2)_2^{3+}]$  to  $[H^+]$  has the form

$$\frac{[cis-Cr(OS(CH_3)_2)_2^{3+}]}{[trans-Cr(OS(CH_3)_2)_2^{3+}]} = \frac{A[H^+] + B}{C[H^+] + 1}$$

The uncorrected data presented in Table II are correlated with this equation with the parameters  $A = 10.1 \text{ l. mol}^{-1}$ ,  $B = 2.0$ , and  $C = 48 \text{ l. mol}^{-1}$ . The

(33) D. W. Hoppenjans, G. Gordon, and J. R. Hunt, *Inorg. Chem.*, **10**, 754 (1971).

parameter  $B$  (2.0) can be compared with  $A/C$  (0.21). Each of these is the ratio of rate constants for formation of the *cis* isomer compared to the *trans* isomer;  $B$  is the ratio for the case where the precursor contains hydroxide ion, and  $A/C$  is the ratio for the case where the precursor does not contain hydroxide ion. The *cis* product is formed more readily from the precursor containing hydroxide. (This qualitative conclusion would not be altered by use of corrected values of the product ratio.)

The limited data (Table II) showing an appreciable dependence of the relative yields of the isomeric bis(dimethyl sulfoxide)chromium(III) products upon the ionic strength reveal additional complexity in this system. Perchlorate ion appears to play a role in the reaction. Presumably this is due to an intermediate containing perchlorate ion, either iodoperchloratochromium(III) or perchlorato(dimethyl sulfoxide)chromium(III) ion,<sup>34</sup> which produces relatively more *trans* bis product.

**Acknowledgment.** The authors acknowledge preliminary experiments on some aspects of this study by Dr. S. P. Ferraris in 1969–1970.

(34) D. M. Jones and J. Bjerrum, *Acta Chem. Scand.*, **19**, 974 (1965), have shown the existence of an inner-sphere perchloratochromium(III) in concentrated perchloric acid.

## Reactions of Bis(trifluoromethyl) Trioxide<sup>1</sup>

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**Abstract:** Reactions of bis(trifluoromethyl) trioxide, CF<sub>3</sub>OOOCF<sub>3</sub>, with a variety of inorganic compounds are described. The trioxide is shown to be a convenient source of compounds containing CF<sub>3</sub>O- and CF<sub>3</sub>OO- groups. Improved syntheses of the previously reported CF<sub>3</sub>ONF<sub>2</sub>, CF<sub>3</sub>OOSO<sub>2</sub>F, and (CF<sub>3</sub>O)<sub>2</sub>SF<sub>4</sub> are described, and the new compounds CF<sub>3</sub>OOSO<sub>2</sub>OCF<sub>3</sub>, *cis*-CF<sub>3</sub>OOSF<sub>4</sub>OCF<sub>3</sub>, and CF<sub>3</sub>OOC(O)OCF<sub>3</sub> are reported.

Perfluoroalkyl trioxides are the only catenated oxygen compounds of the type sufficiently stable for isolation and study in the pure state under ambient conditions. The four known examples are CF<sub>3</sub>OOOCF<sub>3</sub>,<sup>2,3</sup> CF<sub>3</sub>OOOC<sub>2</sub>F<sub>5</sub>,<sup>3</sup> C<sub>2</sub>F<sub>5</sub>OOOC<sub>2</sub>F<sub>5</sub>,<sup>4</sup> and CF<sub>3</sub>OOOCF<sub>2</sub>OOOCF<sub>3</sub>.<sup>5</sup> Based on the chemistry of peroxides, trioxides are expected to behave similarly with facile cleavage of the O-O bonds forming R<sub>1</sub>O· and R<sub>1</sub>OO· radicals. Because of its symmetry, availability, and the decreasing stability of higher perfluoroalkoxy radicals, CF<sub>3</sub>OOOCF<sub>3</sub> is the most suitable trioxide for study in order to provide information on the chemistry of these novel

materials. In this paper reactions of CF<sub>3</sub>OOOCF<sub>3</sub> with a variety of inorganic substrates are reported. Convenient syntheses of the previously known CF<sub>3</sub>ONF<sub>2</sub>,<sup>6,7</sup> CF<sub>3</sub>OOSO<sub>2</sub>F,<sup>8</sup> and (CF<sub>3</sub>O)<sub>2</sub>SF<sub>4</sub><sup>9,10</sup> are given and the new compounds CF<sub>3</sub>OOSO<sub>2</sub>OCF<sub>3</sub>, CF<sub>3</sub>OOSF<sub>4</sub>OCF<sub>3</sub>, and CF<sub>3</sub>OOC(O)OCF<sub>3</sub> are reported.

### Results and Discussion

Bis(trifluoromethyl) trioxide is a convenient chemical source of both CF<sub>3</sub>O- and CF<sub>3</sub>OO- moieties; its reactions with S<sub>2</sub>O<sub>2</sub>F<sub>2</sub>, N<sub>2</sub>F<sub>4</sub>, and SO<sub>3</sub> yield CF<sub>3</sub>O- derivatives exclusively, while reactions with SF<sub>4</sub>, SO<sub>2</sub>,

(1) Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 27–Sept 1, 1972.

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

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

(4) I. J. Solomon, *U. S. Gov. Res. Develop. Rep.*, **70**, 71 (1970).

(5) D. D. DesMarteau, *Inorg. Chem.*, **9**, 2179 (1970).

(6) J. M. Shreeve, L. C. Duncan, and G. H. Cady, *Inorg. Chem.*, **4**, 1516 (1965).

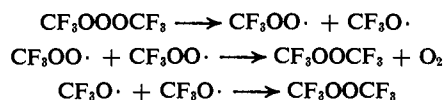
(7) W. H. Hale and S. M. Williamson, *Inorg. Chem.*, **4**, 1342 (1965).

(8) W. P. Van Meter and G. H. Cady, *J. Amer. Chem. Soc.*, **82**, 6005 (1960).

(9) C. I. Merrill and G. H. Cady, *J. Amer. Chem. Soc.*, **85**, 909 (1963).

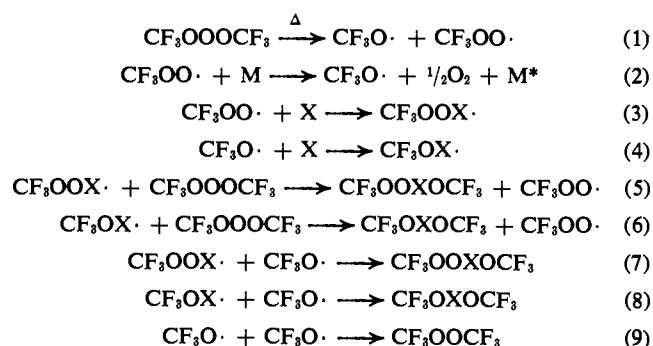
(10) L. C. Duncan and G. H. Cady, *Inorg. Chem.*, **3**, 850 (1964).

and CO give products incorporating both  $\text{CF}_3\text{O}\cdot$  and  $\text{CF}_3\text{OO}\cdot$  groups. Reactions of the trioxide occur readily at  $70^\circ$  where the decomposition also occurs to  $\text{CF}_3\text{OOCF}_3$  and  $\text{O}_2$ . The decomposition of the trioxide is readily explained by the simple mechanism<sup>11</sup>



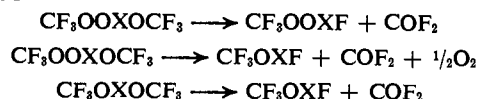
and the reaction chemistry of  $\text{CF}_3\text{OOOCF}_3$  is that of  $\text{CF}_3\text{O}\cdot$  and  $\text{CF}_3\text{OO}\cdot$  radicals. The relatively inert peroxide,  $\text{CF}_3\text{OOCF}_3$ , formed in decomposition has little importance in the chemistry of the trioxide as it has previously been shown not to react with most of the substrates under these conditions. The high yield of the known compounds  $\text{CF}_3\text{ONF}_2$ <sup>6,7</sup> and  $\text{CF}_3\text{OOSO}_2\text{F}$ <sup>8</sup> derived from reactions of the trioxide with  $\text{N}_2\text{F}_4$  and  $\text{S}_2\text{O}_6\text{F}_2$  probably involve  $\text{CF}_3\text{O}\cdot$  radicals combining with the  $\text{NF}_2\cdot$  and  $\text{FSO}_3\cdot$  radicals known to arise from the symmetrical homolytic scission of these reactants. No evidence could be found for the compounds  $\text{CF}_3\text{OONF}_2$  and  $\text{CF}_3\text{OOOSO}_2\text{F}$  that would result from simple combination of  $\text{CF}_3\text{OO}\cdot$  with  $\text{NF}_2\cdot$  and  $\text{FSO}_3\cdot$ . This implies that either  $\text{CF}_3\text{OO}\cdot$  has a short lifetime under the conditions of the experiments or that the peroxy products are unstable.

With  $\text{SF}_4$ , both  $(\text{CF}_3\text{O})_2\text{SF}_4$ <sup>6,10</sup> and  $\text{CF}_3\text{OOSF}_4\text{OCF}_3$  are formed, but no  $(\text{CF}_3\text{OO})_2\text{SF}_4$  is observed. Similarly,  $(\text{CF}_3\text{O})_2\text{CO}$  and  $\text{CF}_3\text{OOC}(\text{O})\text{OCF}_3$  are formed with CO as are  $(\text{CF}_3\text{O})_2\text{SO}_2$  and  $\text{CF}_3\text{OOSO}_2\text{OCF}_3$  with  $\text{SO}_2$ . The following reaction scheme is proposed to explain the products ( $\text{X} = \text{SO}_2, \text{SF}_4, \text{or CO}$ ).



We visualize  $[\text{CF}_3\text{OO}\cdot] < [\text{CF}_3\text{O}\cdot] \ll [\text{X}]$  such that most product formation occurs through steps 2-6. This sequence is in accord with (a) the observed production of the new  $\text{CF}_3\text{OOXOCF}_3$  compounds, (b) the failure to observe compounds of the type  $(\text{CF}_3\text{OO})_2\text{X}$ , and (c) the apparent stability of the  $\text{CF}_3\text{OOXOCF}_3$  compounds which makes it doubtful that  $(\text{CF}_3\text{O})_2\text{X}$  is formed from them by simple loss of oxygen.

Products of the type  $\text{CF}_3\text{OXF}$  and  $\text{CF}_3\text{OOXF}$  may result from carbonyl fluoride elimination reactions of the type



This type of decomposition has been shown for  $\text{CF}_3\cdot$

(11) This mode of decomposition has been suggested for  $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$  and  $\text{CF}_3\text{OOOCF}_3$ : S. W. Benson and R. Shaw, "Organic Peroxides," D. F. Swern, Ed., Wiley, New York, N. Y., 1970, pp 124-125. Consistent with this, we have found that the decomposition of  $\text{CF}_3\text{OOOCF}_3$  obeys first-order kinetics with an activation energy close to that predicted.

$\text{OONO}_2$ ,<sup>12</sup>  $\text{CF}_3\text{OOPOF}_2$ , and  $\text{CF}_3\text{OPOF}_2$ <sup>13</sup> and may be common for other  $\text{CF}_3\text{O}\cdot$  and  $\text{CF}_3\text{OO}\cdot$  derivatives. In nearly all cases  $\text{CF}_3\text{OOXF}$  is formed in greater amounts than  $\text{CF}_3\text{OXF}$ , which is consistent with the fact that  $\text{CF}_3\text{ONO}_2$  is unknown and that  $\text{CF}_3\text{OOPOF}_2$  has greater thermal stability than  $\text{CF}_3\text{OPOF}_2$ . However,  $\text{CF}_3\text{OOX}\cdot$  and  $\text{CF}_3\text{OX}\cdot$  may also react with  $\text{F}\cdot$  donors present among the intermediates of these reactions and thus could be formed directly.

The identities of the new compounds  $\text{CF}_3\text{OOSO}_2\text{OCF}_3$ ,  $\text{CF}_3\text{OOSF}_4\text{OCF}_3$ , and  $\text{CF}_3\text{OOC}(\text{O})\text{OCF}_3$  are convincingly established by the data given in the Experimental Section. Their ir spectra, though unique, are in all cases sufficiently similar to those of the corresponding  $(\text{CF}_3\text{O})_2\text{X}$  compounds so that assignments for the majority of the bands may be made by simple comparisons. The nmr spectra of these new peroxy compounds are particularly revealing in that all show two distinct  $\text{CF}_3$  peaks of equal area which can be assigned unambiguously to  $\text{OCF}_3$  ( $\phi^* \approx 58$ ) and  $\text{OOCF}_3$  ( $\phi^* \approx 68$ ).<sup>3,5,14</sup>

The nmr spectrum of *cis*- $\text{CF}_3\text{OOSF}_4\text{OCF}_3$  is of special interest because there appear to be three types of fluorines attached to sulfur. We therefore postulate the structure  $\text{CF}_3^{\text{E}}\text{OOSF}_2^{\text{B}}(\text{F})^{\text{A}}(\text{F})^{\text{C}}\text{OCF}_3^{\text{D}}$  where fluorines E and D are *cis* to each other and *trans* to A and C, respectively. The fluorines within each  $\text{CF}_3$  group are equivalent and do not couple with that sulfur fluorine which is *trans* to the group or with the other  $\text{CF}_3$  group. Coupling to the remaining three fluorines on sulfur is identical and results in splitting of each  $\text{CF}_3$  peak into 1:3:3:1 quartets. Limitations on storage prevented complete computer analysis of the system; however, the calculated splitting for the  $\text{SF}_4$  group, as plotted by the computer, is shown in Figure 1C. Each peak shown there is subsequently split by one or both  $\text{CF}_3$  groups to give the experimental spectrum shown in Figure 1B. The similarity of the nmr spectrum of this compound to that of *cis*- $\text{CF}_3\text{OSF}_4\text{NF}_2$  is readily apparent, even though the latter could not be analyzed completely because the chemical shift of  $\text{F}^{\text{C}}$  and  $\text{F}^{\text{B}}$ 's were nearly identical.<sup>15</sup>

In conclusion,  $\text{CF}_3\text{OOOCF}_3$  is perhaps the best single source of compounds containing  $\text{CF}_3\text{O}\cdot$  and  $\text{CF}_3\text{OO}\cdot$  groups. When reaction does occur, products containing  $\text{CF}_3\text{O}\cdot$  or  $\text{CF}_3\text{OO}\cdot$  and  $\text{CF}_3\text{OO}\cdot$  are obtained in good yield. A limitation of  $\text{CF}_3\text{OOOCF}_3$  as a reagent is the requirement that all reactions required heating at  $70^\circ$  or higher. Many compounds that could possibly be derived from  $\text{CF}_3\text{OOOCF}_3$  will likely be unstable under these conditions. However, the extension of this work to the addition of  $\text{CF}_3\text{OOOCF}_3$  across multiple bonds is indicated and work is in progress.

## Experimental Section<sup>16</sup>

**General Procedures.** Unless otherwise noted, vacuum equipment and procedures were the same as those described elsewhere. Al-

(12) F. A. Hohorst and D. D. DesMarteau, submitted for publication.

(13) P. A. Bernstein and D. D. DesMarteau, *J. Fluorine Chem.*, **2**, 315 (1972).

(14) R. L. Talbott, *J. Org. Chem.*, **33**, 2095 (1968); R. L. Cauble and G. H. Cady, *ibid.*, **33**, 2099 (1968); L. R. Anderson and W. B. Fox, *Inorg. Chem.*, **9**, 2182 (1970).

(15) L. C. Duncan and G. H. Cady, *Inorg. Chem.*, **3**, 1045 (1964).

(16) Further details regarding vapor pressure, liquid density, mass spectra, etc., can be found in the Ph.D. dissertation of Frederick A. Hohorst, Northeastern University, Boston, Massachusetts, 1973.

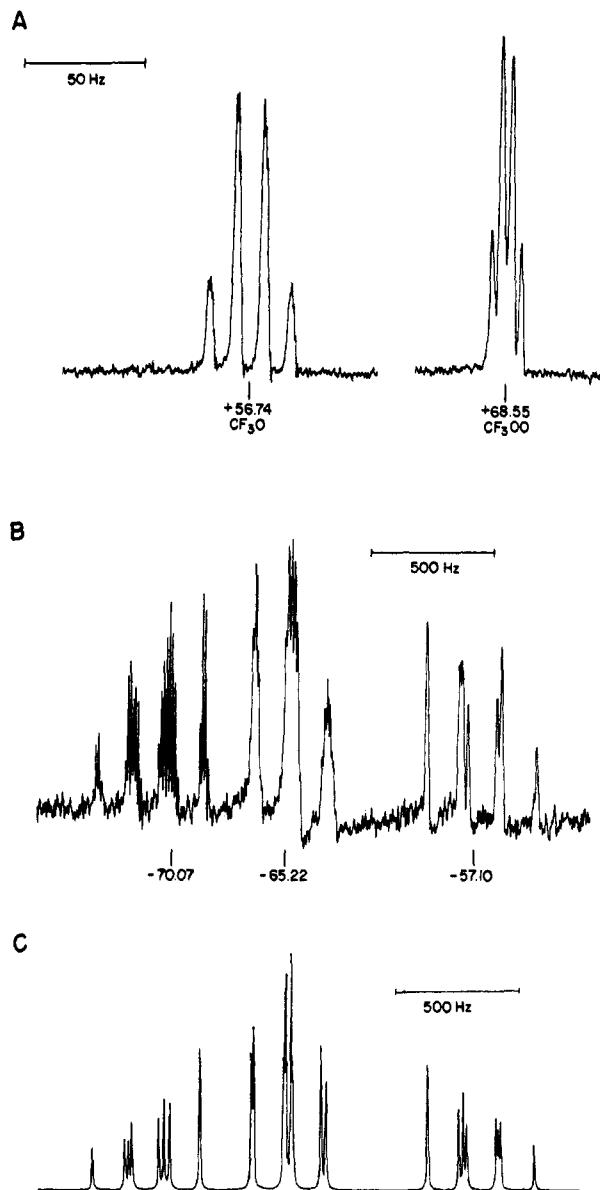


Figure 1.  $^{19}\text{F}$  nmr spectrum of *cis*- $\text{CF}_3\text{OOSF}_4\text{OCF}_3$ : (A)  $\text{CF}_3$  region, (B)  $\text{SF}_4$  region, (C) computer plot of calculated  $\text{SF}_4$  region (the  $\text{CF}_3$ - $\text{SF}$  couplings are not shown).

though the peroxy materials involved in this study appeared to be well behaved and relatively stable, such materials must be regarded as potentially hazardous, and the same precautions invoked in earlier work with  $\text{CF}_3\text{OO}$ -compounds (*i.e.*, adequate shielding and sample limit of 0.5 g) were followed.<sup>17</sup> Nmr spectra were obtained with a Varian XL-100 spectrometer using 10 mol % solutions in  $\text{CFCl}_3$ . Ir spectra were recorded on a Perkin-Elmer 337 in 10-cm glass or Monel cells with  $\text{AgCl}$  windows. Mass spectra were observed on an AEI MS9 at 50 eV.

Gas chromatographic separations were carried out on a Victoreen 4000 Series gas chromatograph equipped for gas sampling and collection, thermal conductivity detection, and subambient operation. A  $\frac{3}{8}$  in.  $\times$  10 ft SS-304 column packed with 49% Halocarbon 11-21 on acid-washed 60-80 Chromosorb P was used.

**Reagents.** Sulfur trioxide was obtained by vacuum distillation of Sulfan B (Baker and Adamson). Tetrafluorohydrazine was obtained from Air Products and Chemicals. Chlorine, carbon monoxide, sulfur dioxide, and sulfur tetrafluoride were obtained from Matheson Gas Products. The latter was purified *via* its boron trifluoride complex.<sup>18</sup>

(17) P. A. Bernstein, F. A. Hohorst, and D. D. DesMarteau, *J. Amer. Chem. Soc.*, **93**, 3882 (1971).

(18) F. A. Cotton and J. W. George, *J. Inorg. Nucl. Chem.*, **7**, 397 (1958).

Peroxydisulfuryl difluoride,  $\text{S}_2\text{O}_6\text{F}_2$ , was prepared from  $\text{SO}_2$  and  $\text{F}_2$  according to literature method.<sup>19</sup> Bis(trifluoromethyl) trioxide  $\text{CF}_3\text{OOOCF}_3$ , was prepared by either the method of DesMarteau<sup>4</sup> or that of Anderson and Fox.<sup>2</sup> Its purity was checked by comparison of ir spectra with those reported and by molecular weight determination.

**Reactions.** Numbers in parentheses represent typical quantities in millimoles, as determined either by direct weighing or by the usual PVT gas measurements.

**Reaction of  $\text{S}_2\text{O}_6\text{F}_2$  with  $\text{CF}_3\text{OOOCF}_3$ .** With  $\text{CF}_3\text{OOOCF}_3$  in slight excess,  $\text{S}_2\text{O}_6\text{F}_2$  (2.28) and  $\text{CF}_3\text{OOOCF}_3$  (2.99) were condensed into a 62-ml Pyrex reaction vessel having a glass-Teflon valve. After heating at  $75^\circ$  for 4.5 hr, the vessel was degassed at  $-196^\circ$  and the oxygen was measured (1.3). The condensables, separated by glc at  $30^\circ$ , were found to be  $\text{COF}_2$  (0.02),  $\text{CF}_3\text{OOCF}_3$  (0.43),  $\text{CF}_3\text{OOOCF}_3$  (0.31),  $\text{CF}_3\text{OOSO}_2\text{F}$  (3.97), and  $\text{S}_2\text{O}_6\text{F}_2$  (0.02). This represents an 87% yield of the previously known trifluoromethyl peroxyfluorosulfate,  $\text{CF}_3\text{OOSO}_2\text{F}$ .<sup>8</sup>

**Reaction of  $\text{N}_2\text{F}_4$  with  $\text{CF}_3\text{OOOCF}_3$ .**  $\text{CF}_3\text{OOOCF}_3$  (2.4) was condensed into a 30-ml stainless steel cylinder followed by  $\text{N}_2\text{F}_4$  (2.5). The reactor was heated to  $84^\circ$  for 25 hr and the product gases separated and identified. Oxygen (0.7) was determined by comparison of the amount of condensables with that of the total gas. It was pumped away at  $-196^\circ$ . Repeated fractionation of the remaining material through  $-111$ ,  $-140$ ,  $-158$ , and  $-196^\circ$  traps resulted in separation of the other products:  $\text{NF}_3$  (1.5),  $\text{CF}_3\text{ONF}_2$  (2.4),  $\text{CF}_3\text{OOCF}_3$  (0.6), and  $\text{NO}_2$  (0.4). With  $\text{CF}_3\text{OOCF}_3$  in slight excess, reaction at  $76^\circ$  for 3 hr gives the same products as above plus some unreacted  $\text{CF}_3\text{OOOCF}_3$  upon separation by glc at  $0^\circ$ . This represents a 50% yield of difluoroaminoxyperfluoromethane.<sup>6,7</sup>

**Reaction of  $\text{SO}_2$  with  $\text{CF}_3\text{OOOCF}_3$ .**  $\text{SO}_2$  (2.01) and  $\text{CF}_3\text{OOOCF}_3$  (2.99) were sequentially condensed into a 15-ml reaction tube equipped with a glass-Teflon valve, allowed to warm to  $22^\circ$ , and then placed in an oven at  $70^\circ$  for 24 hr. Upon cooling, the reactor contents were degassed at  $-196^\circ$  and the oxygen measured (0.86). Condensables were then separated *via* glc at  $40^\circ$ , yielding  $\text{CF}_3\text{OOCF}_3$ - $\text{SO}_2\text{F}_2$  (1.61),  $\text{CF}_3\text{OSO}_2\text{F}$  (0.20),  $\text{CF}_3\text{OOSO}_2\text{F}$  (0.06),  $\text{CF}_3\text{OOSO}_2\text{OCF}_3$  (0.14), and  $\text{CF}_3\text{OOSO}_2\text{OCF}_3$  (0.66). This represents a 31% yield of bis(trifluoromethyl) peroxymonosulfate.

$\text{CF}_3\text{OOSO}_2\text{OCF}_3$ . Bp  $46.2^\circ$ ; mp, glasses; mol wt 247.0, calcd 250.1; ir (in  $\text{cm}^{-1}$ ) 2100 (vw), 1492 (s), 1294 (sh), 1282 (vs), 1263 (vs), 1248 (vs), 1190 (vvs), 1142 (vvs), 962 (s), 922 (vw), 845 (vw), 802 (s), 782 (sh), 669 (vw), 615 (sh), 581 (m), 543 (w); nmr  $\phi^*$  (relative area, assignment) 56.36 (3.04,  $\text{CF}_3\text{O}$ ), 68.20 (3.00,  $\text{CF}_3\text{OO}$ );  $\log P(\text{mm}) = 6.8958 - 1001.8/T - 89500/T^2$ .  $\Delta H(\text{vap}) = 7.15$  kcal/mol;  $\Delta S(\text{vap}) = 22.4$  eu.  $\rho(t) = 1.684 - 0.002891t$ . The mass spectrum was as expected for  $\text{CF}_3\text{OOSO}_2\text{OCF}_3$ .<sup>16</sup> In a test of the stability of this compound, a sample (0.99) previously purified *via* glc was heated at  $87^\circ$  for 18 hr in the reaction vessel and was recovered unchanged.

**Reaction of  $\text{SO}_2$  with  $\text{CF}_3\text{OOOCF}_3$ .** Reactions of  $\text{SO}_2$  with  $\text{CF}_3\text{OOOCF}_3$  were carried out at either  $\sim 70$  or  $\sim 100^\circ$ . Typically,  $\text{SO}_2$  (1.32) and excess  $\text{CF}_3\text{OOOCF}_3$  (1.98) were condensed into a reaction tube like that used for the  $\text{SO}_2$  reaction. After 18 hr at  $70$ - $72^\circ$ , the products were subjected to glc at  $40^\circ$ , yielding  $\text{O}_2$  (0.4),  $\text{COF}_2$  (0.04),  $\text{CF}_3\text{OOCF}_3$  (0.78),  $\text{CF}_3\text{OOSO}_2\text{F}$  (0.04), and  $\text{CF}_3\text{OOSO}_2\text{OCF}_3$  (1.21). The latter, identical with the material formed in the  $\text{SO}_2$ -trioxide reaction, represents a 92% yield of bis(trifluoromethyl) peroxymonosulfate.

In experiments conducted at  $90$  to  $100^\circ$ , the yield of  $\text{CF}_3\text{OOSO}_2\text{OCF}_3$  fell to 15-25%. At these temperatures, traces of  $\text{CF}_3\text{OOSO}_2\text{F}$  along with considerable  $\text{CF}_3\text{OOSO}_2\text{F}$  and  $\text{COF}_2$  were observed. In all runs, small quantities of substances that were non-volatile at  $-78^\circ$  were observed. Nmr spectra of these materials showed resonance at  $\phi^* \approx -50$  and  $+50$ , suggesting a mixture containing the polysulfuryl compounds  $\text{CF}_3(\text{OSO}_2)_n\text{F}$  and  $\text{CF}_3(\text{OSO}_2)_n\text{OCF}_3$  previously reported by Van Meter and Cady.<sup>8</sup>

**Reaction of  $\text{SF}_4$  with  $\text{CF}_3\text{OOOCF}_3$ .** Reaction was carried out by condensing  $\text{SF}_4$  (5.47) and  $\text{CF}_3\text{OOOCF}_3$  (5.48) into a passivated 75-ml Hoke 304 stainless steel sampling cylinder and heating the mixture at  $70$ - $72^\circ$  for 12 hr. As in the case of  $\text{SO}_2$ ,  $\text{O}_2$  (1.10) was measured by degassing at  $-196^\circ$ , and remaining condensables subjected to glc at  $41^\circ$ , yielding  $\text{SOF}_2$ - $\text{SF}_6$ - $\text{SiF}_4$ - $\text{COF}_2$ - $\text{CF}_3\text{OOCF}_3$  (2.05),  $\text{CF}_3\text{OSF}_2$  (0.20),  $\text{CF}_3\text{OOSF}_2$  (0.03),  $(\text{CF}_3\text{O})_2\text{SF}_4$  (1.15), and  $\text{CF}_3\text{OOSF}_4\text{OCF}_3$  (2.54). This represents a 21% yield of the previously reported *cis*-tetrafluorobis(trifluoromethanolato)sulfur.<sup>9,10</sup>

(19) J. M. Shreeve and G. H. Cady, *Inorg. Syn.*, **7**, 124 (1963).

and a 46% yield of the new compound, *cis*-tetrafluoro(trifluoromethanolato)(trifluoromethylhydroperoxidato)sulfur.

$\text{CF}_3\text{OOSF}_4\text{OCF}_3$ . Bp 43.9°; mp, glasses; mol wt 297.4, calcd 294.1; ir (in  $\text{cm}^{-1}$ ) 1291 (s), 1276 (s), 1246 (vs), 1217 (s), 1172 (vs), 980 (m), 948 (vw), 919 (m), 862 (vs), 840 (vs), 740 (w), 702 (vw), 670 (w), 627 (w), 592 (m), 568 (m), 520 (vw); nmr  $\text{CF}_3^{\text{E}}\text{OOSF}_2^{\text{B}}(\text{F})^{\text{A}}(\text{F})^{\text{C}}\text{OCF}_3^{\text{D}}$   $\phi^*$  (relative area, assignment) -70.07 (0.91,  $\text{SF}^{\text{A}}$ ), -65.22 (2.10,  $\text{SF}_2^{\text{B}}$ ) -57.10 (1.00,  $\text{SF}^{\text{C}}$ ) 56.74 (3.03,  $\text{CF}_3^{\text{D}}$ ) 68.55 (2.97,  $\text{CF}_3^{\text{E}}$ ).  $J_{\text{AB}} = 147.4$ ,  $J_{\text{AC}} = 151.4$ ,  $J_{\text{BC}} = 149.2$ ,  $J_{\text{AD}} = 10.8$ ,  $J_{\text{BD}} = 10.8$ ,  $J_{\text{BE}} = 3.9$ ,  $J_{\text{CE}} = 3.9$ . The preceding represent the best fit *via* computer-assisted analysis of the experimental spectrum shown in Figure 1;  $\log P(\text{mm}) = 7.0939 - 1066.8/T - 85260/T^2$ ;  $\Delta H(\text{vap}) = 7.34$  kcal/mol;  $\Delta S(\text{vap}) = 23.3$  eu.  $\rho(t) = 1.856 - 0.003026t$ . The mass spectrum was as expected for  $\text{CF}_3\text{OOSF}_4\text{O}-\text{CF}_3$ .<sup>16</sup> In a test of the stability of this compound, a mixture of  $(\text{CF}_3\text{O})_2\text{SF}_4$  and  $\text{CF}_3\text{OOSF}_4\text{OCF}_3$  was placed in 3.6 M NaOH. After 8 weeks at ambient temperature, appreciable quantities of both were recovered.

**Reaction of CO with  $\text{CF}_3\text{OOOCF}_3$ .** Reaction of CO with  $\text{CF}_3\text{OOOCF}_3$  was carried out in a 75-ml vessel like that in the case of  $\text{SF}_4$ .  $\text{CF}_3\text{OOOCF}_3$  (3.25) was condensed into the vessel. CO (3.15) was added and the vessel heated for 3 hr at 74°. After cooling the vessel to -196°, the noncondensables (0.63), presumably oxygen, were pumped off. The mixture of condensables was then subjected to glc at 31°. We found  $\text{COF}_2-\text{CO}_2$  (1.64),  $\text{CF}_3\text{OOOCF}_3$  (1.52),  $\text{CF}_3\text{OOOCF}_3$  (0.30),  $\text{CF}_3\text{OC}(\text{O})\text{F}^{20}$  (0.05),  $\text{CF}_3\text{OOC}(\text{O})\text{F}^{5,14}$  (0.33),  $(\text{CF}_3\text{O})_2\text{CO}^{21}$  (0.02), and  $\text{CF}_3\text{OOC}(\text{O})\text{OCF}_3$  (0.93). A trace of a slightly volatile solid was also observed in the mixture described above. Subsequent runs at higher pressures increased its yield and

we were able to identify it as  $[\text{CF}_3\text{OC}(\text{O})]_2$ .<sup>22</sup> The reaction gave a 29% yield of the new compound, bis(trifluoromethyl) peroxy-carbonate.

$\text{CF}_3\text{OOC}(\text{O})\text{OCF}_3$ . Bp 25.0°; mp -80.0 to -81.3°; mol wt 213.0, calcd 214.0; ir (in  $\text{cm}^{-1}$ ) 1878 (s), 1412 (vw), 1300 (s), 1250 (s), 1146 (vs), 1024 (s), 933 (m), 900 (m), 746 (m), 702 (m), 657 (vw), 607 (w), 580 (m), 471 (w); nmr  $\phi^*$  (relative area, assignment) 59.31 (3.00,  $\text{CF}_3\text{O}$ ), 69.50 (3.08,  $\text{CF}_3\text{OO}$ );  $\log P(\text{mm}) = 6.8141 - 822.30/T = 104546/T^2$ ;  $\Delta H(\text{vap}) = 6.97$  kcal/mol;  $\Delta S(\text{vap}) = 23.4$  eu;  $\rho(t) = 1.571 - 0.002747t$ . The mass spectrum was as expected for  $\text{CF}_3\text{OOC}(\text{O})\text{OCF}_3$ .<sup>16</sup>

**Other Reactions of  $\text{CF}_3\text{OOOCF}_3$ .** Reaction of  $\text{CF}_3\text{OOOCF}_3$  with  $\text{H}_2\text{O}$  and Hg for 6 hr at 22° was negligible and the trioxide was recovered unchanged. With  $\text{Cl}_2$  at 70° quantitative decomposition of the trioxide to  $\text{CF}_3\text{OOCF}_3$  and  $\text{O}_2$  was observed after 18 hr and the  $\text{Cl}_2$  was recovered unchanged.

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## Crystal and Molecular Structure of a Salt of the (*o*-Benzoquinone diimine)tetracyanoiron(II) Ion

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**Abstract:** The two-electron oxidation product of *o*-phenylenediamine has been stabilized by coordination to low-spin iron(II) in the complex anion  $[\text{Fe}(\text{CN})_4(\text{C}_6\text{H}_4(\text{NH})_2)]^{2-}$ . The chemical and structural evidence conclusively demonstrates that the oxidation product contains stabilized *o*-benzoquinone diimine. We report here the three-dimensional single-crystal X-ray structure determination of the (*o*-benzoquinone diimine)tetracyanoiron(II) anion as the *N,N'*-dimethyl-1,4-diazabicyclo[2.2.2]octonium salt. The complex crystallizes with the orthorhombic space group  $P2_12_12_1$  ( $D_2^8$ , No. 19) with cell dimensions  $a = 14.526$  (10),  $b = 11.239$  (8),  $c = 12.724$  (7) Å. There are four molecules of the complex per unit cell ( $\rho_{\text{obsd}} = 1.40 \pm 0.01$  g  $\text{cm}^{-3}$ ,  $\rho_{\text{calcd}} = 1.423 \pm 0.002$  g  $\text{cm}^{-3}$  for  $Z = 4$ ). All atoms including the hydrogen atoms have been located and their positional and thermal parameters refined by Fourier and least-squares techniques to a conventional *R* factor of 5.6% for 4317 reflections. The average C-N distance in the *o*-benzoquinone ligand is 1.321 Å while the C-C distance of the  $\alpha$ -diimine linkage is 1.443 Å. This result is consistent only with the  $\alpha$ -diimine character expected of coordinated *o*-benzoquinone diimine.

Transition metal ions play an important role in the activation of coordinated ligands, enabling them to undergo various types of reactions and also stabilizing otherwise reactive species. Examples of this type of metal-assisted reaction are oxidative deamination and oxidative dehydrogenation of amine ligands; the course of the reaction is dependent on the nature of the metal ion involved. In oxidative deamination, an amine ligand in the presence of a labile transition metal ion and an appropriate oxidizing agent undergoes catalytic oxida-

tion presumably facilitated by a higher unstable oxidation state of the metal ion. Deamination occurs during subsequent ligand dissociation and reaction with the solvent media.<sup>2-4</sup>

Oxidative dehydrogenation, on the other hand, occurs when an amine ligand is part of a complex that is stable to dissociation but which has an accessible higher oxidation state. The metal atom is oxidized to this

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