$CF_{3}OOC(O)CF_{3}(0.60) + H_{2}O(0.60) \xrightarrow{1 \text{ day}}$  $CF_{3}CO_{2}H(0.60) + CF_{3}OOH(0.60)$ 

 $[CF_{2}OOC(O)CF_{2}]_{2}CF_{2}(0.37) + H_{2}O(0.76) \xrightarrow{1 \text{ day}}$  $[HOC(O)CF_2]_2CF_2 (0.35) + 2CF_3OOH (0.78)$ 

 $CF_{3}OOC(O)CH_{3}(0.42) + H_{2}O(0.44) \xrightarrow{5 \text{ weeks}}$  $CH_{3}CO_{2}H(0.38) + CF_{3}OOH(0.39)$ 

Traces of  $O_2$  and SiF<sub>4</sub> were observed in each case, and a small amount of unreacted CF3OOC(O)CH3 was present even after 5 weeks.

The cesium fluoride catalyzed reaction of CF<sub>3</sub>OOC-(O)CF<sub>3</sub> with fluorine was carried out to see if the corresponding fluoroxy compound could be obtained.

When the reaction was run for 3 hr from -111 to  $-78^{\circ}$ with stoichiometric quantities of fluorine, a 35% yield of the new fluoroxy compound CF<sub>3</sub>OOCF(OF)CF<sub>3</sub> was obtained. The other product present in significant amounts was  $C_2F_5OF$ . No attempts were made to prepare fluoroxy derivatives of the other RC (O)OOCF<sub>3</sub> compounds, but it is likely that the corresponding  $RCF(OF)OOCF_3$  derivatives can be prepared.

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## Preparation and Properties of Chloroperoxytrifluoromethane<sup>1</sup>

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Abstract: The interaction of chlorine monofluoride with trifluoromethyl hydroperoxide at  $-111^{\circ}$  produces chloroperoxytrifluoromethane, CF<sub>2</sub>OOCl. This material, a stable yellow gas at room temperature, is the first stable compound containing an OOCl linkage. Characterization and physical properties of CF<sub>3</sub>OOCl are consistent with the peroxide structure.

**N**ompounds of the type  $R_fOOX$  (X = halogen) are → very rare, the only previously reported examples being  $CF_3OOF^{2a}$  and a few higher perfluoroalkyl homo-logs,  $R_fOOF^{2b}$  No analogous peroxides containing the OOCl function have hitherto been observed.

The conversion of fluorinated alkoxide salts and fluorinated alcohols to the corresponding hypochlorites by reaction with chlorine momofluoride has recently been noted 3-7

 $R_{f}OM + ClF \longrightarrow R_{f}OCl + MF$ 

$$R_{f}OH + ClF \longrightarrow R_{f}OCl + HF$$

and we have now extended this technique to the preparation of the first stable compound containing an

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OOCl grouping, chloroperoxytrifluoromethane. The

$$CF_{3}OOH + ClF \longrightarrow CF_{3}OOCl + HF$$

existence of a stable OOCI compound is of particular interest in light of recent studies involving detection of the short-lived ClOO · radical.8

Despite the presence of an additional reactive sitethe peroxide linkage-trifluoromethyl hydroperoxide reacts cleanly with chlorine monofluoride at the O-H bond to produce CF<sub>3</sub>OOCl exclusively; no O-O scission to produce CF<sub>3</sub>OCl is discernible. Whether the driving force for this reaction is the production of HF or whether this reflects an unusually strong O-O bond in CF<sub>3</sub>OOH cannot be ascertained from our experiments, though it is likely that the thermodynamic stability of HF is a major factor.

The possibility exists that the new material, with empirical formula CF<sub>3</sub>O<sub>2</sub>Cl, may exist in either of the isomeric forms CF<sub>3</sub>OCl=O or CF<sub>3</sub>OOCl, but only the latter structure is consistent with the observed data. The presence of  $CF_{3}OO^{+}$  and  $CF_{2}OO^{+}$  in the mass spectrum of the material, as well as the similarity between its infrared spectrum and that of CF<sub>8</sub>OOH<sup>9</sup> and CF<sub>8</sub>-

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OOF,<sup>2a</sup> are indicative of the CF<sub>3</sub>OOCl form. Further, no infrared absorption in the Cl=O region (~1100 cm<sup>-1</sup><sup>10</sup>) is observed, though CF<sub>3</sub>Cl=O would be expected to absorb strongly in this region.

Although we have conducted no detailed thermal stability tests, CF<sub>3</sub>OOCl is stable at 25° for prolonged periods, indicating both reasonably strong O-O and O-Cl bonds. There is perhaps a parallel between CF<sub>8</sub>OOCl and CF<sub>3</sub>OOF in that both are reasonably stable molecules (as are CF<sub>3</sub>OCl and CF<sub>3</sub>OF), though the matrix-isolated OOCl<sup>11</sup> and OOF<sup>12</sup> radicals exhibit extremely weak oxygen-halogen bonds.

Although the reaction chemistry of CF<sub>3</sub>OOCl has not been extensively explored as yet, the molecule does not seem to exhibit properties similar to those of the perfluoroalkyl hypochlorites.<sup>13</sup> Thus CF<sub>3</sub>OCl readily adds CO, SO<sub>2</sub>, or C<sub>2</sub>F<sub>4</sub> to yield CF<sub>3</sub>OC(O)Cl, CF<sub>3</sub>-OSO<sub>2</sub>Cl. and CF<sub>8</sub>OC<sub>2</sub>F<sub>4</sub>Cl, respectively, <sup>13,14</sup> while CF<sub>8</sub>-OOCI does not yield the corresponding addition products under similar reaction conditions. This may imply a stronger Cl-O linkage in CF<sub>3</sub>OOCl. The compound may exhibit primarily peroxidic properties inasmuch as it initiates extremely vigorous polymerization of tetrafluoroethylene at relatively low temperatures; further, the products obtained from photolysis of CF<sub>3</sub>OOCl can be readily explained by primary cleavage of the O–O bond.

$$CF_{\$}OOCl \xrightarrow{uv} CF_{\$}O \cdot + \cdot OCl$$
$$2CF_{\$}O \cdot \longrightarrow CF_{\$}OOCF_{\$}$$
$$Clo \cdot \longrightarrow [ClOOCl] \longrightarrow Clo_{2} + Cl \cdot$$

The production of some oxygen in the mixture may indicate the cleavage of the O-Cl bond and subsequent coupling of the resultant  $CF_3OO \cdot$  radicals to yield an unstable tetroxide which could then decompose to  $CF_3OOCF_3 + O_2$ .

The existence of a stable compound containing the OOCI grouping suggests that chemical "trapping" of the OOCl radical in the form of CF<sub>3</sub>OOCl should be explored as a possible alternative to the currently available methods for detecting the OOCl radical by either low-temperature matrix isolation  $(\sim 4^{\circ} K)^{11}$  or elaborate spectroscopic techniques.8

## **Experimental Section**

Preparation of CF<sub>3</sub>OOCI. Chlorine monofluoride was obtained from the Ozark-Mahoning Co. Trifluoromethyl hydroperoxide, CF3OOH, was prepared by oxidation of hexafluoroacetone with hydrogen peroxide<sup>15</sup> and was purified by trap-to-trap fractionation. The product, collected at  $-111^\circ$ , was shown by its infrared spectrum and physical properties to be identical with the CF<sub>3</sub>OOH prepared by Talbott.9

Preparation and characterization procedures were carried out under vacuum conditions in a nickel-Monel line equipped with Kel-F traps. Reaction vessels were fabricated from 3/8-in. Kel-F tubing and attached to metal Hoke valves with Swagelok fittings.

In a typical reaction CF<sub>3</sub>OOH (1.0 mmol) and ClF (1.1 mmol) were condensed at -196° into a 5-ml Kel-F reaction vessel and allowed to warm to  $-111^{\circ}$  for 1 hr. A light yellow product was observed which contained a second clear immiscible layer. Separation of the products was conveniently carried out by condensing the mixture onto dry NaF. The by-product, HF, was effectively removed at room temperature by this technique without decomposing the CF<sub>2</sub>OOCl. Final purification for physical measurements required the removal of trace quantities of  $ClO_2$ . This was accomplished by passing the mixture through a  $-111^{\circ}$  trap, which retained the impurity, and collecting CF<sub>3</sub>OOCl at  $-196^{\circ}$ . Samples were checked for purity by gas chromatography with a 20% Kel-F No. 10 on Teflon 6 column. Yield of the reaction was generally above 95% with 100% conversion of the CF<sub>3</sub>OOH. Anal. Calcd for CF<sub>3</sub>OOC1: C, 8.79; F, 41.76; Cl, 26.00.

C, 8.40; F, 40.00; Cl, 28.30. Found:

Properties of CF<sub>3</sub>OOCI. Chloroperoxytrifluoromethane is a pale yellow liquid which is stable at room temperature and can be stored without decomposition in glass or Kel-F containers. The compound is not readily hydrolyzed by atmospheric moisture and can be easily handled in vacuo after removal of the by-product HF. Thermal decomposition of CF<sub>3</sub>OOCl in a glass tube at 100° was complete in 5 min;  $COF_2$ ,  $SiF_4$ ,  $CO_2$ , and  $ClO_2F$  were the main decomposition products observed by infrared spectroscopy.

Vapor Pressure, Boiling Point, and Melting Point. The vapor pressure of CF<sub>3</sub>OOCl was measured in a Monel vacuum system with a Model F-145 Wallace & Tiernan gauge; temperatures were determined with a chromel-alumel thermocouple attached externally to the sample tube. The vapor pressure over the range -110 to  $23^{\circ}$  is represented by the equation

$$\log P \text{ (mm)} = 7.742 - (1.221 \times 10^3)/T (^{\circ}\text{K})$$

as calculated from the following data [temperature, °K (pressures, mm)]: 253.1 (794.5), 253.0 (770.0), 252.4 (746.5), 251.6 (727.5), 251.0 (705.0), 248.0 (648.0), 247.5 (620.5), 244.8 (568.9), 244.4 (549.0), 241.4 (470.5), 238.6 (417.5), 235.8 (363.5), 233.1 (317.5), 230.5 (275.5), 227.4 (237.0), 225.4 (211.5), 221.8 (175.0), 217.6 (134.0), 212.4 (98.5), 206.1 (64.5), 202.8 (51.7), 197.4 (32.5), 191.5 (22.5), 188.1 (16.7), 186.1 (14.5), 183.1 (11.0).

The boiling point calculated from the above equation is  $-22^{\circ}$ the latent heat of vaporization is 5573 cal/mol, and the Trouton constant is 22.2.

Chloroperoxytrifluoromethane freezes to a yellow solid but tends to form a glass when not totally pure. The melting point was determined to be approximately  $-132^{\circ}$ . Infrared Spectrum. The infrared spectrum of CF<sub>2</sub>OOCl was

recorded on a Perkin-Elmer Model 521 spectrophotometer from 4000 to 450 cm<sup>-1</sup>. The spectrum contained three strong bands at 1275, 1235, and 1207 cm<sup>-1</sup> which can be assigned to C-F asymmetric and symmetric stretching frequencies. The band at 891 (m) can be assigned to C-O stretch while the band at 813 (m) is in the region assigned by others to the O-O stretching mode.<sup>16,17</sup> The three bands at 655 (m), 600 (w), and 570 (m) are in the region expected for OCl stretch as well as CF3 deformation, but cannot definitely be assigned.16,18,19

Nmr and Mass Spectra. The F-19 nmr spectrum was recorded at room temperature on a Varian A56-60 nmr spectrometer. A single resonance was observed at +69.9 ppm relative to CFCl<sub>3</sub> internal standard.

The mass spectrum was determined with a Consolidated Electrodynamics Corp. Model 21-103 spectrometer operating at an ionizing potential of 70 eV. It was necessary to "condition" the inlet chamber with purified samples of CF<sub>3</sub>OOCl before a reproducible cracking pattern could be obtained. Characteristic peaks observed in the cracking pattern are listed below [m/e] (abundance, including isotopic contribution), assignment]: 136(7.2) CF<sub>3</sub>OOCI (m<sup>+</sup>); 104 (1.0) CF<sub>3</sub>Cl<sup>+</sup>; 101 (0.2) CF<sub>3</sub>OO<sup>+</sup>; 82 (5.9) CF<sub>2</sub>OO<sup>+</sup>; 69 (100) CF<sub>3</sub><sup>+</sup>; 66 (39.2) CF<sub>2</sub>O<sup>+</sup>; 53 (36.2) ClO<sup>+</sup>.

Reactions of  $CF_3OOCl$ . With  $C_2F_4$ . The interaction of  $CF_3OOCl$ (2 mmol) with C<sub>2</sub>F<sub>4</sub> (2.2 mmol) was carried out by condensing the two reactants into an evacuated 3-ml Kel-F reactor at  $-196^{\circ}$ .

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As the vessel was warming slowly from  $-196^{\circ}$ , an explosion occurred at about  $-110^{\circ}$ . Products of the reaction were not contained.

With SO<sub>2</sub>. An equimolar mixture of SO<sub>2</sub> and CF<sub>8</sub>OOCl (2 mmol) was observed to react slowly at  $-24^{\circ}$ . The product mixture showed mainly COF<sub>2</sub> and starting materials. Minor products were identified as CF<sub>8</sub>OOH, SiF<sub>4</sub>, and SO<sub>2</sub>ClF.

With CO. A 2-mmol sample of CF<sub>3</sub>OOCl was allowed to react with excess CO in a 75-ml of stainless steel Hoke vessel for 24 hr. The product mixture contained COF<sub>2</sub>, COFCl, CF<sub>3</sub>OOH, and one unidentified product. Spectra of the latter were consistent with spectroscopic data for CF<sub>3</sub>OOC(O)F, but the material was not fully characterized. **Photolysis.** A 2-mmol sample of CF<sub>8</sub>OOCl was condensed into an evacuated 200-ml glass reaction vessel equipped with a concentric quartz well and irradiated at  $-78^{\circ}$  for 30 min with a 20-W uv lamp. After warming to room temperature, the major products were identified as CF<sub>8</sub>OOCF<sub>8</sub>, ClO<sub>2</sub>, and a noncondensable gas (O<sub>2</sub>). No other fluorocarbons were detected in photolysis reactions under the above conditions or at higher temperature. Higher oxygen-containing species may exist as intermediates in the reaction, but were not isolated under these conditions.

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