

Table VI. Intermolecular Distances and Angles in the Crystal

A. Interatomic Distances Involving the Sodium Ions ^a			
Bond	Length, Å	Bond	Length, Å
Na ₁ -O ₅	2.313 (2)	Na ₂ -O ₆	2.486 (2)
Na ₁ -O ₅ '	2.347 (2)	Na ₂ -O ₄	2.532 (2)
Na ₁ -O ₄	2.458 (2)	Na ₂ -W ₄	2.536 (3)
Na ₁ -W ₂	2.456 (2)	Na ₃ -W ₃	2.367 (2)
Na ₁ -O ₂	2.504 (2)	Na ₃ -O ₁	2.304 (2)
Na ₁ -O ₈	2.652 (2)	Na ₃ -O ₇	2.329 (2)
Na ₂ -O ₉	2.300 (2)	Na ₃ -W ₄	2.506 (2)
Na ₂ -O ₇	2.327 (2)	Na ₃ -O ₃	2.545 (2)
Na ₂ -O ₆	2.339 (2)	Na ₃ -W ₁	2.646 (3)

B. Hydrogen-Bonding Parameters ^a			
Bond	Length, Å	Bond angle	Value, deg
W ₁ -O ₁₀	2.728 (3)	O ₁₀ -W ₁ -O ₆	108.72 (9)
W ₁ -O ₆	2.802 (3)	O ₁₀ -W ₁ -W ₄	98.91 (9)
W ₂ -O ₃	2.928 (3)	O ₆ -W ₁ -W ₄	92.27 (9)
W ₂ -W ₃	2.930 (3)	O ₃ -W ₂ -W ₃	96.51 (9)
W ₂ -W ₄	2.963 (3)	O ₃ -W ₂ -W ₄	102.82 (10)
W ₃ -O ₁₀	2.693 (3)	W ₃ -W ₂ -W ₄	123.53 (10)
W ₃ -O ₂	3.006 (3)	O ₁₀ -W ₃ -W ₂	117.96 (9)
W ₃ -O ₁	3.009 (2)	O ₁₀ -W ₃ -O ₂	125.37 (9)
W ₄ -O ₇	2.948 (3)	O ₁₀ -W ₃ -O ₁	141.26 (10)
W ₄ -W ₁	2.988 (3)	W ₂ -W ₃ -O ₂	80.58 (8)
		W ₂ -W ₃ -O ₁	100.32 (9)
		O ₂ -W ₃ -O ₁	52.25 (5)
		O ₇ -W ₄ -W ₂	157.91 (10)
		O ₇ -W ₄ -W ₁	85.48 (8)
		W ₂ -W ₄ -W ₁	141.09 (9)

^a The figures in parentheses are the estimated standard deviations.
^b W_i is the symbol employed for the *i*th water molecule.

the near identity of all corresponding bond parameters in the coordination groups of the unconstrained [O₂-VAH₂]⁻ and [O₂VA]³⁻ species is highly probable.

It is perhaps surprising to find that substitution of charged carboxylate oxygen for neutral amino nitrogen in the trans positions of the coordination group has no significant effect on the averaged V-O bond length in the VO₂ entity. That this parameter should have nearly or exactly the same value in the [O₂V(ox)₂]³⁻ species as in the EDTA complexes lends strong support to the conclusion that the latter pair utilize the same quantitative pattern of complexing bond parameters. As pointed out in paper I,² the substitution of oxide oxygen for carboxylate oxygen atoms does have a significant, if not large, effect on the bond distances in the VO₂ entity.

We note further that the deviations of the V-O₁ and V-O₂ bond lengths from their averaged values as given by least-squares refinements of the three structures tend generally (with one minor exception) to decrease with increasing range of the X-ray data in (sin θ)/λ. This observation together with the fact that the mean deviation has dropped to just 0.004 Å for the values derived from Fourier synthesis¹⁴ of the most nearly complete set of structure amplitudes strongly support chemical and structural equivalence of the V-O₁ and V-O₂ bonds in the unconstrained complexes.

Interatomic distances involving the sodium ions and the parameters describing the hydrogen bonding are listed in Table VI. All three structural types of sodium ions are in six-coordination with bond distances to carboxylate oxygen atoms and water molecules lying in the range 2.300 (2)-2.652 (2) Å.

(14) See ref 8b and references cited therein for a discussion of the advantages accruing from the use of very nearly convergent Fourier synthesis for the precise determination of atomic positions.

Trifluoromethyl Hydroperoxide. Properties and Reactions with Some Acid Fluorides

Peter A. Bernstein, Frederick A. Hohorst, and Darryl D. DesMarteau*

Contribution from the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115. Received October 19, 1970

Abstract: A convenient preparation of trifluoromethyl hydroperoxide, CF₃OOH, is described and its physical and chemical properties are reported. Trifluoromethyl hydroperoxide behaves as a weak protic acid and readily forms trifluoromethyl peroxides with a variety of reactants. With acid fluorides trifluoromethylperoxy esters are formed in high yield. The synthesis and properties of the new compounds CF₃C(O)OOCF₃, CH₃C(O)OOCF₃, CF₃OOC(O)CF₂CF₂CF₂C(O)OOCF₃, CF₃OOC(O)CF₂CF₂CF₂C(O)F, and CF₃CF(O)OOCF₃ are discussed.

Trifluoromethyl hydroperoxide, CF₃OOH, was first prepared by Talbott,¹ who obtained the compound in small amounts by hydrolysis of trifluoromethyl fluoroformyl peroxide, CF₃OOC(O)F.^{1,2} The synthesis of CF₃OOC(O)F was difficult and there have been no reports on the chemistry of CF₃OOH. Recently an improved method for the preparation of the formyl

peroxide was found,^{3,4} which permits us to undertake an investigation of its properties and reactions.

Trifluoromethyl hydroperoxide is a weak acid in water and reacts with a variety of compounds forming trifluoromethyl peroxides. For example, it reacts with N₂O₅ forming CF₃OONO₂ and HONO₂,⁵ cleaves P₂O₃F₄

(1) R. L. Talbott, *J. Org. Chem.*, **33**, 2095 (1968).

(2) R. L. Cauble and G. H. Cady, *ibid.*, **33**, 2099 (1968).

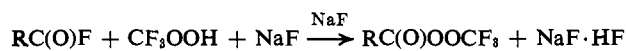
(3) D. D. DesMarteau, *Inorg. Chem.*, **9**, 2179 (1970).

(4) L. R. Anderson and W. B. Fox, *ibid.*, **9**, 2182 (1970).

(5) F. A. Hohorst and D. D. DesMarteau, manuscript in preparation.

forming $F_2P(O)OOCF_3$ and $HOPOF_2$,⁶ and reacts with COF_2 in the presence of NaF forming $CF_3OOC(O)F$ and $(CF_3OO)_2CO$.

In this paper we report the reactions of CF_3OOH with COF_2 , $COFCl$, $[FC(O)]_2$, $[FC(O)O]_2$, $CF_3OC(O)F$, $CF_3C(O)F$, $CH_3C(O)F$, and $[FC(O)CF_2]_2CF_2$. In all cases the reactions can be explained as fluoride displacement by CF_3OO according to the general equation



With $COClF$, $[FC(O)]_2$, $[FC(O)O]_2$, and $CF_3OC(O)F$ the intended peroxide could not be isolated, but in all other cases the trifluoromethyl peroxide is obtained in high yield.

Experimental Section

General. All compounds were handled in Pyrex or stainless steel vacuum systems equipped with glass-Teflon or stainless steel valves. (Note: The term stainless steel refers to either Type 316 or Type 304 as defined in "Properties of Some Metals and Alloys," The International Nickel Co., Inc., New York, N. Y.) Pressures were measured with a precision Heise Bourdon tube gauge in the metal system and a Wallace and Tiernan differential pressure gauge in the glass system. Amounts of volatile compounds were determined by PVT measurements assuming ideal gas behavior.

Molecular weights were determined by vapor density measurements. Infrared spectra were recorded on a Beckman IR10 using a 10-cm glass cell fitted with silver chloride windows. Nmr spectra were taken on a Varian A56-60 using internal trichlorofluoromethane and external tetramethylsilane as references.⁷

Vapor pressures were obtained by the method of Kellogg and Cady.⁸ Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data. Melting points were determined using a calibrated thermometer on samples sealed in glass capillaries.

Caution! All of the peroxides and fluoroxy compounds in this work are strong oxidizers and must be handled with care. Although CF_3OF , $CF_2(O)F$, $CF_3OOC(O)F$, and CF_3OOH have been handled on a scale of a few grams without incident, compounds of the type $RC(O)OOCF_3$ appear to be quite explosive. We recommend a maximum sample size of 0.5 g for the latter and adequate shielding at all times.

Reagents. Carbonyl fluoride was prepared by the reaction of phosgene with an excess of a mixture consisting of antimony trifluoride plus 10 mol % chlorine. A 1-l. stainless steel bomb heated to 250° was the reaction vessel. Large-scale preparations (1 mol) always showed the presence of some carbonyl chlorofluoride. This was removed by heating with excess sodium fluoride at 250° and collecting the product at -160°.

Carbonyl chlorofluoride was obtained by the reaction at 150° of phosgene with a small excess of the mixture consisting of antimony trifluoride and 10 mol % chlorine in a 95-ml bomb. After 24 hr the products were fractionated through traps at -111, -135, and -196°. Pure carbonyl chlorofluoride was retained in the -135° trap.

Oxalyl fluoride was obtained by heating oxalyl chloride with excess potassium fluoride in a 95-ml bomb for 18 hr at 125°. The products were fractionated through traps at -50, -111, and -196°. Pure oxalyl fluoride collected in the -111° trap. Perfluoroglutaryl fluoride was prepared by the reaction of perfluoroglutaryl chloride with an excess of a mixture composed of antimony trifluoride and 10 mol % chlorine. A 95-ml bomb was used at 140° for 18 hr. The products were passed through a -40° trap and pure perfluoroglutaryl fluoride was collected at -78°. Bis-(fluoroformyl) peroxide, $CF_3OOC(O)F$, CF_3OF , and $CF_2(O)F_2$ were prepared using literature methods.^{4,9-12} Perfluoroglutaryl chlo-

ride, perfluoroacetyl fluoride, and acetyl fluoride were obtained from Penninsular ChemResearch and used without further purification. All other reagents were of reagent grade quality and were used without further purification.

Preparation of Trifluoromethyl Hydroperoxide. Trifluoromethyl hydroperoxide was prepared using a modification of the procedure reported by Talbott.¹ The highest yields were obtained when $CF_3OOC(O)F$ was hydrolyzed in the condensed phase. The vapor phase hydrolysis commonly gave lower yields and the product was always contaminated with $(CF_3OO)_2CO$ which was difficult to separate from the CF_3OOH . The preparation of $CF_3OOC(O)F$ was carried out using the method of DesMarteau.^{3,13}

Trifluoromethyl hydroperoxide was obtained from the reaction between the somewhat impure $CF_3OOC(O)F$ from the -111° trap and a 4:1 molar excess of water in a 100-ml glass bulb fitted with a glass-Teflon valve. The peroxides were condensed into the bulb containing the water and the mixture was warmed rapidly to 22° and allowed to remain at this temperature for 18 hr. The contents were then passed through traps at -55 and -111°. Pure CF_3OOH collected in the -111° trap. In a typical run $CF_3OOC(O)F$ (about 7.0 mmol) gave 5.5 mmol of CF_3OOH for ~80% yield; bp 11.3°; mp -75.0 to -74.0°; ρ_{20} 1.460; mol wt 102.4, calcd 102.0; ir 3580 (m, OH), 1382 (m), 1268 (s, CF), 1238 (vs, CF), 1140 (w), 945 (m), 675 (m), 613 (w); nmr ϕ^* 72.3 s, δ -9.20 (s); ΔH_{vap} 7.34 kcal/mol; ΔS_{vap} 26.0 eu. Values of the vapor pressure, measured over a range of temperatures are (temperature, °C; pressure, mm): -47.2, 16.5; -42.1, 30.9; -39.6, 39.5; -35.9, 51.2; -33.7, 61.5; -31.4, 71.5; -29.6, 81.5; -27.4, 93.0; -25.8, 106.0; -20.2, 150.0; -15.0, 200.3; -7.9, 300.0; -6.5, 313.5; -3.6, 376.4; -0.8, 430.0; -0.3, 443.4; 2.9, 499.7; 5.3, 571.3; 7.6, 634.2; 9.2, 696.2; 11.5, 759.0. The vapor pressure of CF_3OOH as a function of temperature is given by the equations

$$\log P \text{ (mm)} = 8.5568 - 1614.5/T \text{ (-25 to } 11.5^\circ)$$

$$\log P \text{ (mm)} = -9.4176 + 7303.9/T - 1106340/T^2 \text{ (-47 to } -25^\circ)$$

Reaction of Trifluoromethyl Hydroperoxide with Acid Fluorides.

All reactions were carried out in a 95-ml Monel bomb containing 15 g of dry sodium fluoride and several stainless steel ball bearings. The stoichiometric amounts of CF_3OOH and the acid fluoride were condensed into the bomb at -196° and the mixture was allowed to warm to 22°. After reaction was complete the bomb was cooled to -196°. The contents were then allowed to vaporize into a known volume, and the total moles of volatile materials determined. The products were separated where possible by trap to trap distillation. Known products were identified by their molecular weights and infrared spectra. Oxygen was identified by its volatility at -196° and by its molecular weight. The reactions are summarized in Table I and the data characterizing the compounds are given below.

$(CF_3OO)_2CO$. Bp 41°; mp -85.8 to -84.5°; mol wt 230.0, calcd 229.0; ir 1896 (s, C=O), 1431 (w), 1296 (vs, CF), 1242 (vs, CF), 1222 (vs, CF), 1162 (w), 1135 (w), 1115 (vs), 1014 (w), 939 (w), 735 (m), 607 (w); nmr ϕ^* 69.6, s; ΔH_{vap} 7.34 kcal/mol; ΔS_{vap} 26.0 eu; $\log P$ (mm) = 8.2045 - 1672.4/T.

$CF_3OOC(O)CF_3$. Bp 8.9°; mp (glassed at low temperature); mol wt 198.0, calcd 198.0; ir 1859 (vs, C=O), 1298 (vs, CF), 1244 (vs, CF), 1212 (vs, CF), 1110 (sh), 1068 (vs), 939 (m), 890 (w), 847 (w), 741 (s), 680 (w), 610 (w), 568 (w), 520 (w), 474 (w); nmr ϕ^* 74.0 (s, CF_3O-), 77.2 (s, CF_3-C); ΔH_{vap} 7.34 kcal/mol; ΔS_{vap} 26.0 eu; $\log P$ (mm) = 8.5664 - 1603.4/T.

$CF_3OOC(O)CH_3$. Bp 64.2°; mp -83.0 to -81.5°; mol wt 144.7, calcd 144.0; ir 1850 (s, C=O), 1424 (w), 1366 (w), 1288 (s, CF), 1224 (vs, CF), 1158 (s, CF), 1114 (s), 1066 (w), 1007 (w), 997 (w), 985 (w), 940 (w), 832 (m), 738 (w), 662 (w), 608 (w), 599

(9) P. J. Aymonino, *Chem. Commun.*, 241 (1965).

(10) M. Lustig, A. R. Pitochelli, and J. K. Ruff, *J. Amer. Chem. Soc.*, **89**, 2841 (1967).

(11) F. A. Hohorst and J. M. Shreeve, *ibid.*, **89**, 1809 (1967).

(12) R. L. Cauble and G. H. Cady, *ibid.*, **89**, 1962 (1967).

(13) Careful control of the temperature is very important in obtaining high yields of $CF_3OOC(O)F$. If the cold bath warms too rapidly and rises too much above 0°, the yields of $CF_3OOC(O)F$ are low. On the other hand, if the bath does not warm to at least -5°, there may be unreacted $CF_2(O)F_2$.

(6) P. A. Bernstein and D. D. DesMarteau, manuscript in preparation.

(7) ¹⁹F chemical shifts are ϕ^* values obtained in ~80 mol % $CFCl_3$: G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(8) K. B. Kellogg and G. H. Cady, *J. Amer. Chem. Soc.*, **70**, 3986 (1948).

(w), 580 (w), 567 (w); nmr ϕ^* 65.6 s, δ -2.3 s; ΔH_{vap} 7.77 kcal/mol; ΔS_{vap} 23.0 eu; $\log P$ (mm) = 7.9163 - 1698.8/T.

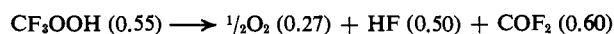
$\text{CF}_3\text{OOC}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{F}$. Bp 100.2°; mp (glassed at low temperature); mol wt 326.0, calcd 326.0; ir 1882 (s, C=O), 1854 (s, C=O), 1295 (vs, CF), 1203 (vs, CF), 1132 (s, CF), 1099 (s), 1014 (m), 891 (m), 809 (w), 760 (w), 732 (w), 703 (w), 679 (w), 645 (w), 585 (w); nmr ($\text{CF}_3\text{OOC}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{F}^{\text{D}}$) ϕ^* 68.6 (s, $\text{CF}_3\text{-O}$), 116.0 (t, d, CF_2^{A}), 123.0 (d, CF_2^{B}), 117.5 (d, t, CF_2^{C}), -23.3 (t, t, t, $\text{C}(\text{O})\text{F}^{\text{D}}$), $J_{\text{AD}} = 2$, $J_{\text{AC}} = 10$, $J_{\text{BD}} = J_{\text{CD}} = 7$ Hz; ΔH_{vap} 10.5 kcal/mol; ΔS_{vap} 28.0 eu; $\log P$ (mm) = 9.0086 - 2287.7/T.

$[\text{CF}_3\text{OOC}(\text{O})\text{CF}_2]_2\text{CF}_2$. Bp 116.2°; mp -77.0 to -76.0°; mol wt 408.0, calcd 408.0; ir 1896 (s, C=O), 1431 (w), 1296 (vs, CF), 1242 (vs, CF), 1162 (w), 1135 (w), 1115 (vs), 1014 (w), 939 (w), 735 (m), 607 (w); nmr ($\text{CF}_3\text{OOC}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{F}^{\text{D}}$) ϕ^* 68.6 (s, $\text{CF}_3\text{-O}$), 116.0 (s, $\text{C}(\text{O})\text{CF}_2$), 122.5 (s, $\text{CF}_2\text{CF}_2\text{CF}_2$); ΔH_{vap} 11.3 kcal/mol; ΔS_{vap} 29.1 eu; $\log P$ (mm) = 9.2322 - 2472.7/T.

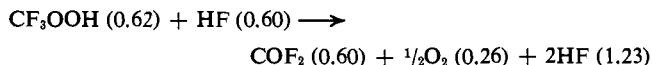
Preparation of $\text{CF}_3\text{OOCF}(\text{O})\text{CF}_3$. Fluorine (1.5 mmol) and $\text{CF}_3\text{OOC}(\text{O})\text{CF}_3$ (1.5 mmol) were placed in a 75-ml stainless steel reactor with 5 g of CsF. The vessel was allowed to warm from -111 to -78° over a 3-hr period. The products were then fractionated through traps at -111 and -196°. The -196° trap contained $\text{C}_2\text{F}_5\text{OF}$ and CF_3OF as shown by infrared analysis. The -111° trap contained 0.52 mmol of $\text{CF}_3\text{OOCF}(\text{O})\text{CF}_3$: mol wt 237.0, calcd 236.0; ir 1345 (m), 1295 (s, CF), 1240 (vs, CF), 1190 (s, CF), 1085 (s, CF), 1020 (w), 930 (w, OF), 895 (w), 743 (m), 690 (w), 613 (w), 570 (w), 540 (w); nmr ($\text{CF}_3^{\text{A}}\text{OOCF}^{\text{B}}(\text{O})\text{CF}_3^{\text{D}}$) ϕ^* 69.0 (d, d, CF_3^{A}), 110.0 (d, q, CF^{B}), -139.0 (d, q, q, OF^{C}), 78.8 (d, CF_3^{D}), $J_{\text{AB}} = 5.3$, $J_{\text{AC}} = 1.7$, $J_{\text{BC}} = 37.0$, $J_{\text{CD}} = 12.5$ Hz.

Results and Discussion

Trifluoromethyl Hydroperoxide. Trifluoromethyl hydroperoxide is a stable, water-like liquid. Samples stored as liquids in glass containers showed no appreciable decomposition after several weeks at 22°. When heated to 150° in glass the compound was rapidly decomposed to CO_2 , SiF_4 , and O_2 . In a pre-fluorinated 75-ml stainless steel cylinder, CF_3OOH was 12% decomposed after 18 hr at 22°. At 135° in the same vessel decomposition was complete after 18 hr according to the equation (mmol).



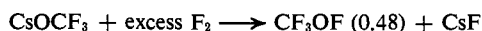
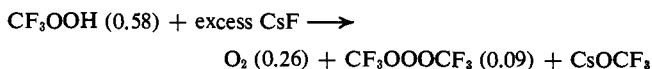
The decomposition of CF_3OOH is apparently catalyzed by HF. When the sample was allowed to stand at 22° in a 75-ml stainless steel vessel with an equimolar amount of anhydrous HF, decomposition was complete after 20 hr, forming COF_2 , O_2 , and HF as shown (mmol).



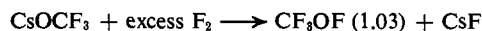
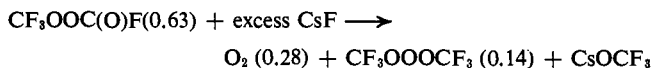
The instability of CF_3OOH in the presence of HF and metal may be related to the reaction of CF_3OOH with certain metal fluorides. With excess sodium fluoride in glass no reaction was observed after 2 days at 22°. However, in a prefluorinated stainless steel vessel under the same conditions, reaction was complete to form O_2 , COF_2 , $\text{CF}_3\text{OOC}(\text{O})\text{F}$, and presumably $\text{NaF} \cdot \text{HF}$. Since no reaction was observed in glass and since CF_3OOH was partially decomposed in a stainless steel vessel without added sodium fluoride, the observed decomposition was probably caused by transition metal fluorides on the walls of the container. The sodium fluoride served to promote the reaction by the formation of $\text{NaF} \cdot \text{HF}$. The $\text{CF}_3\text{OOC}(\text{O})\text{F}$ formed only in the presence of sodium fluoride probably results from the

reaction of COF_2 with CF_3OOH (see section on reaction of CF_3OOH with COF_2 in the presence of sodium fluoride).

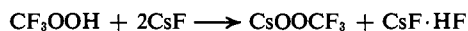
The effect of active metal fluorides was further demonstrated by the reaction of CF_3OOH with excess cesium fluoride. At 22° in a stainless steel vessel, reaction was complete after 16 hr, forming O_2 and a small amount of $\text{CF}_3\text{OOOCF}_3$ ^{14,15} plus a solid residue of CsOOCF_3 .¹⁶ Fluorination of the residue gave CF_3OF .¹⁰ The overall reaction can be summarized by the equations (mmol)



In contrast to the decomposition of CF_3OOH in the presence of sodium fluoride no $\text{CF}_3\text{OOC}(\text{O})\text{F}$ was observed with CsF since $\text{CF}_3\text{OOC}(\text{O})\text{F}$ reacts with CsF at 22° as indicated by the following equation (mmol).¹⁷



It seems reasonable that the trioxide probably arises from the same mechanism in both reactions. The stoichiometry in both cases suggests that an unstable intermediate CsOOCF_3 ^{3,18} is formed and undergoes subsequent reaction to form $\text{CF}_3\text{OOOCF}_3$ or decomposes to CsOOCF_3 and O_2 according to the equations



Further reactions involving the intermediate CsOOCF_3 are under study, and experiments using ¹⁸O-labeled compounds are being conducted to confirm the proposed mechanism.

Trifluoromethyl hydroperoxide is soluble in water without decomposition. The solutions have a pungent irritating odor and are strongly oxidizing toward aqueous potassium iodide. The pH of a freshly prepared 0.5 M solution was about 4 and when titrated with 0.0125 M sodium hydroxide, a typical weak acid-strong base titration curve was observed similar to that of acetic acid. From the pH at the equivalence point K_a was found to be 4.0×10^{-7} M at 22°. After neutralization most of the oxidizing power remained, indicating that CF_3OO^- is reasonably stable in dilute aqueous solution.

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

(15) P. G. Thompson, *ibid.*, **89**, 4316 (1967).

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

(17) This observation accounts for the critical temperatures required in order to obtain significant yields of $\text{CF}_3\text{OOC}(\text{O})\text{F}$ from reactions described in ref 3 and 4. If the reaction is run at 22° in the absence of excess COF_2 , only small amounts of $\text{CF}_3\text{OOOCF}_3$ are observed along with CF_3OF and O_2 . Apparently some $\text{CF}_3\text{OOC}(\text{O})\text{F}$ is obtained but it is consumed at 22° by the CsF.

(18) J. K. Ruff and R. F. Merritt, *Inorg. Chem.*, **7**, 1219 (1968).

Table I. Reaction of CF₃OOH with Acid Fluorides

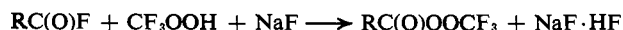
Fluoride (mmol)	CF ₃ OOH ^a	Time ^b	Products ^{a,c,d}
COF ₂ (0.60)	1.20	2	(CF ₃ OO) ₂ CO (0.60) ^e
COFCl (3.00)	3.00	2	CF ₃ OOC(O)F (1.45), ^e Cl ₂ (1.5), CO ₂ (1.5), COF ₂ (1.5)
[FC(O)] ₂ (0.30)	0.60	3	CF ₃ OOC(O)F (0.1), ^e CO ₂ -COF ₂ (0.8)
[FC(O)O] ₂ (2.40)	2.40	1	CF ₃ OOC(O)F (1.9), ^e CO ₂ -COF ₂ (3.2), O ₂ (1.2)
CF ₃ OC(O)F (3.00)	3.00	1	CF ₃ OOC(O)F (2.90), ^e COF ₂ (3.10)
CF ₃ C(O)F (2.23)	2.23	18	CF ₃ OOC(O)CF ₃ (2.12), ^e O ₂ -COF ₂ -CO ₂ -CF ₃ C(O)F (0.11)
CH ₃ C(O)F (3.58)	3.58	17	CF ₃ OOC(O)CH ₃ (3.40), ^f CO ₂ -O ₂ (0.13)
[FC(O)CF ₂] ₂ CF ₂ (3.58)	7.16	22	[CF ₃ OOC(O)CF ₂] ₂ CF ₂ (3.4), ^g (CF ₃ OO) ₂ CO-[FC(O)CF ₂] ₂ CF ₂ (0.2)
[FC(O)CF ₂] ₂ CF ₂ (3.58)	3.58	18	CF ₃ OOC(O)CF ₂ CF ₂ CF ₂ C(O)F (3.4) ^h (CF ₃ OO) ₂ CO-[FC(O)CF ₂] ₂ CF ₂ (0.2)

^a Millimoles. ^b Reaction time at 22° in hours. ^c HF was assumed to be quantitatively absorbed by NaF (see Experimental Section).
^d Temperature referenced for trap used to collect peroxide. Other products were collected at -196°. ^e -111°. ^f -78°. ^g -42°. ^h -22°.

Several of the observed infrared absorptions in CF₃OOH¹⁹ can be assigned by comparison with assignments made for H₂O₂,²⁰ CF₃OOCF₃,^{21,22} and CF₃-OOOCF₃.²³ The sharp band at 3580 cm⁻¹ can be assigned to the OH stretch and the band at 1383 cm⁻¹ is probably assignable to an OOH bending mode. The very strong bands at 1270 and 1230 cm⁻¹ can be assigned to CF stretches, and medium absorptions at 676, 615, and 590 cm⁻¹ result from CF₃ deformation modes. The strong absorption at 946 cm⁻¹ is assigned to the CO stretch, and the weaker band at 862 cm⁻¹ to the OO stretch. The ¹⁹F nmr showed a single absorption at ϕ^* 72.3 and the proton resonance was observed at δ -9.20.²⁴

Reaction of Trifluoromethyl Hydroperoxide with Acid Fluorides. The decomposition of CF₃OOH in the presence of metal fluorides and the formation of CF₃OOC(O)F in the presence of sodium fluoride suggested that CF₃OOH might react with acid fluorides in the presence of sodium fluoride to form trifluoromethyl peroxides. The effect of sodium fluoride in these reactions other than the formation of NaF·HF is unclear, but COF₂ and CF₃OOH do not react readily in the absence of NaF.

Reactions with COF₂, COFCl, [FC(O)]₂, [FC(O)O]₂, CF₃OC(O)F, CF₃C(O)F, CH₃C(O)F, and [FC(O)-CF₂]₂CF₂ were carried out, and in all cases reaction occurred readily under the experimental conditions used. The expected products were not obtained in all cases because of secondary reactions, but the products can be explained by the initial reaction



(19) The ir spectrum of CF₃OOH has been deposited as document No. NAPS-01319 with ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$2.00 for microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC-NAPS.

(20) O. Bain and P. A. Giguere, *Can. J. Chem.*, **23**, 527 (1955).

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

(22) J. R. Durig and D. W. Wertz, *J. Mol. Spectrosc.*, **25**, 467 (1968).

(23) R. P. Hirschmann, W. B. Fox, and L. R. Anderson, *Spectrochim. Acta, Part A*, **25**, 811 (1969).

(24) Talbott¹ reported a value of ϕ^* = 70.5, but did not report the ¹H nmr.

With COFCl, [FC(O)O]₂, and CF₃OC(O)F the desired RC(O)OOCF₃ could not be isolated, but CF₃OOC(O)F and other products were observed instead. The data are not sufficient to rule out the formation of CF₃OOC(O)F by reaction of COF₂ and CF₃OOH, but we feel the products are best explained by initial formation of an unstable RC(O)OOCF₃ which then decomposes to give the observed products. Data for all the reactions are summarized in Table I. The yields of the new peroxides are greater than 90% and this method offers a convenient preparation of the previously reported (CF₃OO)₂CO.¹

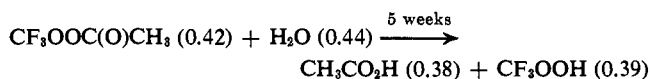
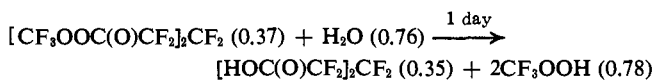
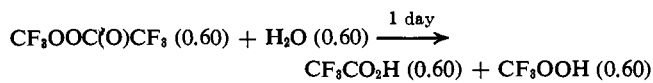
All the compounds were stable at 22° in glass both in the gas and liquid phases. No decomposition was observed during routine handling in glass or stainless steel vacuum lines. However, a 1-g sample of CF₃OOC(O)-CH₃ exploded violently when a sample at -196° was transferred into a water bath at 22°. Similarly, a 0.5-g sample of CF₃OOC(O)CF₂CF₂CF₂C(O)F exploded while measuring its vapor pressure at ca. 70°. In view of these observations, the stability of compounds of the type RC(O)OOCF₃ when R is not fluorine must be considered limited, and they should be treated as both thermally and mechanically shock sensitive. The infrared spectra of the compounds show a characteristic carbonyl stretch as well as absorptions characteristic of the CF₃O- group and the parent acid fluoride.^{25,26} The ¹⁹F nmr spectra of the compounds show a resonance assignable to the CF₃OO groups at about ϕ^* 70 in all compounds, which is consistent with previously reported spectra of related compounds.²⁷

The hydrolysis of the compounds produces CF₃OOH and the carboxylic acid in nearly quantitative yield. Of the three compounds investigated, CF₃OOC(O)CF₃ and [CF₃OOC(O)CF₂]₂CF₂ reacted rapidly at 22° while CF₃OOC(O)CH₃ required several weeks for complete reaction as indicated (mmol).

(25) See ref 1, 3, 21-23, and references therein.

(26) For CF₃C(O)F, D. G. Weiblen, *Fluorine Chem.*, **2**, 485 (1950), gives 1848 (s), 1425 (w), 1376 (w), 1365 (w), 1168 (vs), 1052 (w), 989 (w), 830 (sh), 814 (m), 606 (w), 597 (w), 584 (w), 566 (w); [FC(O)CF₂]₂CF₂ 1880 (s), 1282 (sh), 1202 (vs), 1133 (s), 1108 (m), 1021 (m), 924 (w), 896 (m), 757 (w), 697 (w), 677 (sh), 630 (w), 555 (w).

(27) See ref 1, 3, and 15.



Traces of O_2 and SiF_4 were observed in each case, and a small amount of unreacted $\text{CF}_3\text{OOC}(\text{O})\text{CH}_3$ was present even after 5 weeks.

The cesium fluoride catalyzed reaction of $\text{CF}_3\text{OOC}(\text{O})\text{CF}_3$ 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° with stoichiometric quantities of fluorine, a 35% yield of the new fluoroxy compound $\text{CF}_3\text{OOCF}(\text{O})\text{CF}_3$ was obtained. The other product present in significant amounts was $\text{C}_2\text{F}_5\text{OF}$. No attempts were made to prepare fluoroxy derivatives of the other $\text{RC}(\text{O})\text{OOCF}_3$ compounds, but it is likely that the corresponding $\text{RCF}(\text{O})\text{OOCF}_3$ derivatives can be prepared.

Acknowledgment. This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society, under Grant No. PRF-4563, and the National Science Foundation, under Grant No. NSF-GP23098. The nmr spectrometer was made available through the courtesy of D. T. Dix and the Dow Chemical Co. F. A. H. thanks Goodyear Atomic Corp. for a leave of absence.

Preparation and Properties of Chloroperoxytrifluoromethane¹

C. T. Ratcliffe,* C. V. Hardin, L. R. Anderson, and W. B. Fox

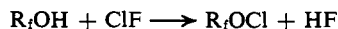
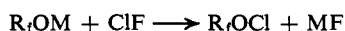
Contribution from the Corporate Chemical Research Laboratory, Allied Chemical Corporation, Morristown, New Jersey 07960.

Received July 28, 1970

Abstract: The interaction of chlorine monofluoride with trifluoromethyl hydroperoxide at -111° produces chloroperoxytrifluoromethane, CF_3OOCl . This material, a stable yellow gas at room temperature, is the first stable compound containing an OOCl linkage. Characterization and physical properties of CF_3OOCl are consistent with the peroxide structure.

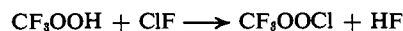
Compounds of the type R_fOOX ($X = \text{halogen}$) are very rare, the only previously reported examples being $\text{CF}_3\text{OOF}^{2a}$ and a few higher perfluoroalkyl homologs, R_fOOF .^{2b} No analogous peroxides containing the OOCl function have hitherto been observed.

The conversion of fluorinated alkoxide salts and fluorinated alcohols to the corresponding hypochlorites by reaction with chlorine monofluoride has recently been noted³⁻⁷



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

OOCl grouping, chloroperoxytrifluoromethane. The



existence of a stable OOCl compound is of particular interest in light of recent studies involving detection of the short-lived $\text{ClOO}\cdot$ radical.⁸

Despite the presence of an additional reactive site—the peroxide linkage—trifluoromethyl hydroperoxide reacts cleanly with chlorine monofluoride at the $\text{O}-\text{H}$ bond to produce CF_3OOCl exclusively; no $\text{O}-\text{O}$ scission to produce CF_3OCl is discernible. Whether the driving force for this reaction is the production of HF or whether this reflects an unusually strong $\text{O}-\text{O}$ bond in CF_3OOH 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 $\text{CF}_3\text{O}_2\text{Cl}$, may exist in either of the isomeric forms $\text{CF}_3\text{OCl}=\text{O}$ or CF_3OOCl , but only the latter structure is consistent with the observed data. The presence of CF_3OO^+ and CF_2OO^+ in the mass spectrum of the material, as well as the similarity between its infrared spectrum and that of CF_3OOH ⁹ and CF_3-

(1) Presented in part at the Summer Fluorine Symposium honoring Professor G. H. Cady, June 15-17, 1970, Milwaukee, Wis.

(2) (a) P. G. Thompson, *J. Amer. Chem. Soc.*, **89**, 4316 (1967); (b) I. J. Solomon, A. J. Kacmarek, J. N. Keith, and J. K. Raney, *ibid.*, **90**, 6557 (1968).

(3) D. E. Gould, L. R. Anderson, D. E. Young, and B. W. Fox, *Chem. Commun.*, 1564 (1968).

(4) D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *J. Amer. Chem. Soc.*, **91**, 1310 (1969).

(5) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *ibid.*, **92**, 2313 (1970).

(6) C. J. Schack and W. Maya, *ibid.*, **91**, 2902 (1969).

(7) C. J. Schack, R. D. Wilson, J. S. Muirhead, and S. N. Cohn, *ibid.*, **91**, 2907 (1969).

(8) H. S. Johnston, E. D. Morris, Jr., and I. Van den Bogaerde, *ibid.*, **91**, 7712 (1969).

(9) R. L. Talbott, *J. Org. Chem.*, **33**, 2095 (1968).