

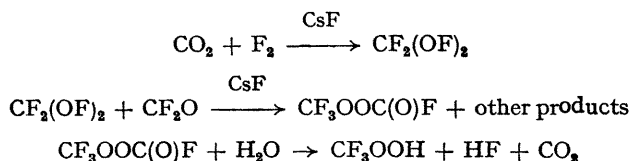
A Convenient Synthesis of Trifluoromethyl Hydroperoxide¹

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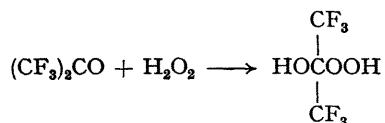
Summary The novel compound trifluoromethyl hydroperoxide, CF₃OOH, can be conveniently prepared by decomposition of the "perhydrate" of hexafluoroacetone, HOC(CF₃)₂OOH, which is produced by the 1:1 addition of hydrogen peroxide and hexafluoroacetone.

TRIFLUOROMETHYL HYDROPEROXIDE, CF₃OOH, was first described by Talbott, who obtained small amounts of this novel material by hydrolysis of the relatively inaccessible trifluoromethyl fluoroformyl peroxide, CF₃OOC(O)F.² Although the accessibility of this key intermediate has been somewhat improved by the recent discovery of superior techniques for its preparation^{3,4} and a more efficient hydrolysis procedure for the conversion into CF₃OOH,⁵ this pathway to CF₃OOH is still relatively complex and requires the manipulation of fluorine and highly reactive intermediates.^{3,4}



In the light of recent interest in CF₃OOH as a versatile intermediate for the synthesis of novel trifluoromethylperoxy-compounds,^{5,6} we report a convenient, straightforward preparation of CF₃OOH from the simple raw materials hexafluoroacetone and hydrogen peroxide.

We¹ and others⁷ have recently found that hexafluoroacetone and 90% hydrogen peroxide readily form the 1:1 adduct 2-hydroperoxyhexafluoropropan-2-ol, which may



be regarded as a "perhydrate" analogous to the hexafluoroacetone "monohydrate" produced by addition of

water to the ketone.⁸ Although the viscous liquid "perhydrate" appears to be relatively stable for short periods of time, careful examination of the material shows that slow decomposition at 25° produces a number of volatile products. Approximately 90% of the volatile mixture consists of CF₃OOH, CO₂, and O₂ (1:1:1 ratio). Minor amounts of COF₂, C₂F₆, CF₃OOCF₃, SiF₄, and CF₃OC(O)CF₃ are also detectable by g.l.c. analysis, but the total of these generally contributes less than 10% to the volatile product mixture.

Although the yield of CF₃OOH is reasonably high, the rate of production at 25° is slow and the conversion of "perhydrate" is somewhat variable from one experiment to another. After a variety of unsuccessful attempts to accelerate the production of CF₃OOH (*i.e.*, heat, u.v. light, addition of various metal ions, acids, or bases were all ineffective or even deleterious), the following procedure was found to be reasonably effective for obtaining useful amounts of product: approximately 20 mmol quantities of "perhydrate" (prepared by condensing 20 mmol of hexafluoroacetone on to 20 mmol of 90% H₂O₂) were formed in 100 ml Pyrex flasks fitted with Kontes glass-Teflon valves and maintained at 25°. Volatile products were removed at 24 h intervals, and the CF₃OOH was recovered by fractionation through traps at -78°, -111°, and -196° in a conventional glass vacuum system. Pure CF₃OOH (2-5 mmols per reactor per week) was collected at -111° and identified by elemental analysis as well as i.r. and n.m.r. spectroscopy.² A variation of this method in which 20 mmols of reactants were placed in a 3 l bulb yielded 8-10 mmols of CF₃OOH in 4 days. This apparent volume-dependence, coupled with the observation that CF₃OOH yields are drastically reduced if the products are not removed at frequent (24 h) intervals, suggests that the reaction proceeds in the vapour phase (possibly involving dissociated hexafluoroacetone and H₂O₂ vapours) and involves some equilibrium process. A mechanistic study of the reaction involving ¹⁸O-labelled hexafluoroacetone is in progress.

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¹ C. T. Ratcliffe, C. V. Hardin, L. R. Anderson, and W. B. Fox, presented at the Summer Symposium on Fluorine Chemistry, Milwaukee, Wisconsin, June 1970.

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⁵ D. DesMarteau, personal communication.

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⁷ R. D. Chambers and M. Clark, *Tetrahedron Letters*, 1970, 2741.

⁸ W. J. Middleton and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1964, **86**, 4948; C. B. Miller and C. Woolf, *U.S.P.*, 2,870,211 (1959); W. J. Cunningham and C. Woolf, *Fr.P.*, 1,385,110 (1965).