π-bonding ligand than is $[(C_6H_5)_2PCH_2CH_2P^+(C_6H_5)_2CH_2C_6H_5][PF_6^-]$ or $(C_6H_5)_2PCH_2P(C_6H_5)_2$ but since the $A_1^{(1)}$ mode is not resolvable in complexes of the latter ligands, the interpretation is speculative. Attempts to put a positive charge in a position α to the bonding phosphorus atom by quaternizing such precursors as $(CO)_5WP(C_6H_5)_2N(C_6H_5)_2$ and $(CO)_5WP(C_6H_5)_2P(C_6H_5)_2$ were unsuccessful.

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Fluoroperoxytrifluoromethane, CF_3OOF. Preparation from Trifluoromethyl Hydroperoxide and Fluorine in the Presence of Cesium Fluoride

BY DARRYL D. DESMARTEAU*

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Fluoroperoxytrifluoromethane, CF_3OOF, was first reported as a product in the fluorination of sodium trifluoroacetate.[1] It was later postulated to be an intermediate in the preparation of CF_3OOOCF_3 by the reaction of OF_2 and COF_2 in the presence of CsF[2] and has subsequently been prepared by this method.[3]

Recently we have obtained a number of new compounds containing the CF_3OO group by reactions involving CF_3OOH.[4] In this paper a convenient preparation of CF_3OOF from the reaction of CF_3OOH and F_2 in the presence of CsF is described and its physical properties are reported. The chemical properties of CF_3OOF are under investigation and will be the subject of a future paper.

Experimental Section

General Information.—All volatile compounds were handled in a stainless steel[5] or Pyrex glass vacuum system fitted with stainless steel and glass–Teflon valves. Connections to the vacuum system were made by means of Swagelok fittings or glass joints lubricated with Kel-F90 grease. Pressures were measured using a precision Heise Bourdon tube gauge in the metal system and Wallace and Tiernan differential pressure gauge in the glass line. Amounts of volatile materials were determined by *PVT* measurements assuming ideal gas behavior.

Infrared spectra were taken on a Beckman IR-10 using a 10-cm glass cell with silver chloride windows. Fluorine nmr spectra were recorded on a Varian A-56/60 at 15° using 80 mol % $CFCl_3$ as an internal reference. In order to observe the large negative chemical shifts of the OOF group, a Krohn–Hite oscillator operated at 72.5 kc was substituted for the frequency offset oscillator normally used for fluorine operation.

Molecular weights were determined by vapor density measurements and were accurate to 0.5% when taken on pure CF_3OF. The vapor pressure as a function of temperature was obtained in the usual way[6] and a least-squares fit of the data was used to obtain the vapor pressure equation. Liquid density was obtained using a calibrated dilatometer.

Reagents.—Fluorine was passed through a NaF scrubber before using. Cesium fluoride was pretreated with several atmospheres of F_2 at 250° and was pulverized in the usual way.[7] Trifluoromethyl hydroperoxide was prepared by a modification of the procedure reported by Talbott[4,8] and was checked for purity by means of its infrared spectrum and molecular weight.

Reaction of CF_3OOH with F_2.—The reaction of CF_3OOH with fluorine was carried out under a variety of conditions in attempting to optimize the yield of CF_3OOF. The procedure used involved condensing CF_3OOH into a 75-ml stainless steel reactor onto 10 g of CsF at −196° and adding the desired amount of F_2. The vessel was then warmed to the desired reaction temperature by placing it in a $CFCl_3$ or CF_2Cl_2 cold bath. After reaction had proceeded for the appropriate time, the vessel was cooled to −196° and the F_2 and O_2 were removed. The remaining material was then transferred to a glass sample tube and separated by pumping through traps at −111, −140, −160, and −196° as the sample tube warmed from −196° in an empty 1-pt dewar at 22°. The −111° trap retained CF_3OOCF_2OF and $(CF_3OO)_2CFOF$;[8] the CF_3OOOCF_3[2,9] and CF_3OOCF_3[10] were retained in the −140° trap; CF_3OOF collected at −160° and CF_3OF[6] at −196°. Small amounts of CF_3OOF passed through the −160° trap and a small amount of CF_3OOCF_3 was often observed in the −160° trap. This was removed by a second fractionation through the −140° trap. Known compounds were identified by ^{19}F nmr, infrared spectra, and molecular weight (molecular weights found were within 2% of the calculated values). The CsF was replaced every third run and was treated with several atmospheres of F_2 at 22° after each run. Essentially no volatile products were observed on treating with F_2. The data for the reactions are summarized in Table I and the physical

TABLE I

REACTIONS OF CF_3OOH WITH F_2

Amt of reactants,[a] mmol CF_3OOH	F_2	Conditions Time, hr	Temp, °C	Products (mmol)[b]
1.8	1.8[c]	3	−111 to −100	CF_3OOH (1.8), F_2 (1.8), trace of COF_2–HF
0.43	0.43[d]	20	−78	CF_3OF (0.14), $CF_3O_3CF_3$ (0.14), O_2, F_2
6.0	6.0	6	−196 to −15	CF_3OF (1.0), CF_3OOF (1.0), $CF_3O_2CF_3$ (1.0), CF_3OOCF_2OF–$(CF_3OO)_2CFOF$ (0.7), O_2, F_2
6.0	6.0	1	−15	CF_3OF (1.0), CF_3OOF (0.7), $CF_3O_2CF_3$ (0.7), CF_3OOCF_2OF–$(CF_3OO)_2CFOF$ (1.4), O_2, F_2
4.6	4.6	18	−78	CF_3OF (1.8), CF_3OOF (0.6), $CF_3O_2CF_3$ (0.6), CF_3OOCF_2OF–$(CF_3OO)_2CFOF$ (0.3), O_2, F_2
6.0	6.0	14	−111 to −78	CF_3OF (0.5), CF_3OOF (1.8), COF_2 (0.6), $CF_3O_2CF_3$ (1.2), CF_3OOCF_2OF–$(CF_3OO)_2CFOF$ (0.1), O_2, F_2
6.0	18.0	2 5	−196 to −78 −78	CF_3OF (1.5), CF_3OOF (1.5), $CF_3O_2CF_3$ (0.6), CF_3OOCF_2OF–$(CF_3OO)_2CFOF$ (0.9), O_2, F_2
6.0	3.0	19	−78	CF_3OOF (2.0), COF_2 (0.17), CF_3OOH–$(CF_3OO)_2CO$ (1.8), O_2 (1.2)

[a] Reactor contained 10 g of CsF except where noted. [b] O_2 and F_2 were not measured quantitatively. Small amounts of CF_4 may also have been present. [c] No alkali metal fluoride. [d] Ten grams of dried NaF.

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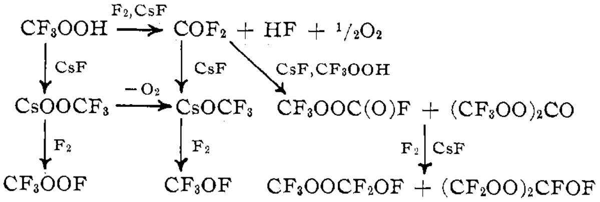
properties of CF_3OOF are as follows: bp −69.4°; mp $<-196°$; mol wt: calcd, 120.00; found, 120.0; $\Delta H_{vap} = 4.36$ kcal/mol; $\Delta S_{vap} = 21.4$ eu; nmr: ϕ^* 68.9 (d, CF_3OO), −292 (q, OOF), $J_{FF} = 5.0$ Hz; ir: 2605 (vw), 2570 (vw), 2490 (vw), 2140 (w), 2060 (w), 2000 (vw), 1960 (vw), 1932 (vw), 1855 (vw), 1820 (w), 1775 (vw), 1705 (w), 1630 (vw), 1565 (vw), 1500 (w), 1460 (w), 1380 (w), 1300 (vs), 1270 (vs), 1190 (vs), 950 (s), 870 (w, br), 755 (s), 685 (w), 620 (m), 585 (m), 510 (m) cm^{-1}. Values of the vapor pressure measured over a range of temperatures are as follows [P (mm), T (°C)]: 24.7, −116.9; 60.7, −106.5; 84.6, −104.2; 115.4, −99.5; 193.0, −91.8; 237.0, −89.4; 250.7, −87.9; 307.2, −85.3; 349.0, −83.3; 410.0, −80.3; 451.6, −78.4; 498.0, −76.7; 542.2, −75.9; 611.3, −73.6; 687.0, −71.8; 701.0, −71.2; 757.3, −69.6.

$$\log P(\text{mm}) = 6.8764 - \frac{673.90}{T} - \frac{28442}{T^2}$$

Values of the liquid density measured over a range of temperatures are as follows [ρ (g/cm³), T (°C)]: 1.869, −131.6; 1.721, −92.9; 1.655, −72.4. $\rho(T) = 1.3875 - 0.00365T$.

Results and Discussion

Fluoroperoxytrifluoromethane can be obtained in yields as high as 35% from the reaction of CF_3OOH with F_2 in the presence of CsF. The data summarized in Table I clearly show that CsF is necessary for the formation of CF_3OOF. Substitution of NaF for CsF yields CF_3OF whereas the absence of alkali metal fluorides results in essentially no reaction at low temperature. All of the observed products except CF_3OOCF_3 can be explained by the following reaction scheme, based on the known chemistry of CF_3OOH[4] and the behavior of carbonyl compounds in the presence of CsF and F_2[11]



The formation of CF_3OOCF_3 in large amounts is difficult to explain. It is not formed from the reaction of CF_3OOF or CF_3OF with CF_3OOH. When these were allowed to react at −78° in the presence of CsF, the fluoroxy compounds were quantitatively recovered and only minor decomposition products of CF_3OOH were observed in the unreacted material. The CF_3OOCF_3 could be formed from the decomposition of $CF_3OOOOCF_3$ which might be formed as an unstable product. However, no tetraoxide has been isolated from the reaction products, in spite of considerable efforts to do so.

The thermal stability of CF_3OOF is quite good and the compound has shown no tendency to undergo explosive decomposition in the vapor or condensed state. At 22° in glass, CF_3OOF (100 mm) showed no change after 4 days. In prefluorinated stainless steel at 22°, CF_3OOF undergoes rapid initial decomposition to CF_4 and O_2 until the vessel becomes passivated. Further decomposition is then very slow. A 0.42-mmol sample of CF_3OOF (100 mm) was 10% converted to CF_4 and O_2 after 1 hr but only a trace more of O_2 was observed after 24 hr. The remaining CF_3OOF had to be heated at 95° for 4 hr for complete conversion to CF_4 and O_2. The decomposition follows the equation $CF_3OOF \rightarrow CF_4 + O_2$. The stability of CF_3OOF probably approaches that of $CF_2(OF)_2$[12−14] in a properly conditioned vessel. However, CF_3OOF is obviously more sensitive than the isomeric $CF_2(OF)_2$.

The infrared spectrum of CF_3OOF shows a number of combination and overtone bands in addition to several fundamental stretching and deformation absorptions. The observed spectrum shows considerable similarity to that of CF_3OOH[4] and based on the recent vibrational assignments for CF_3OF,[15] CF_3OOCF_3,[16,17] CF_3OOOCF_3,[18] and FOOF[19] some tentative assignments can be made. The very strong absorptions at 1300, 1270, and 1190 cm^{-1} are assigned to the three expected CF stretches. Three of the bands at 685, 620, 585, and 510 cm^{-1} can be assigned to CF_3 deformations. The remaining bands at 950, 870, and 755 cm^{-1} can probably be assigned to CO, OO, and OF stretches. The 950-cm^{-1} band is assigned to the CO stretch because it is observed in CF_3OOH and other CF_3OO derivatives. The OO stretch in CF_3OOCF_3, CF_3OOOCF_3 (average of symmetric and asymmetric), and H_2O_2[20] occurs between 800–900 cm^{-1} and a band is observed in CF_3OOH at 860 cm^{-1}. The 870-cm^{-1} band is thus assigned to the OO stretch. The most striking difference in the ir of CF_3OOF and CF_3OOH is the strong band at 755 cm^{-1} in CF_3OOF and the absence of any observable absorption in CF_3OOH between 700 and 800 cm^{-1}. The 755-cm^{-1} band is therefore assigned to the OF stretch. This represents a low value compared to other R_fOF compounds but is not unreasonable when compared to FOOF (average symmetric and asymmetric OF stretch, 618 cm^{-1}). This is especially true if a simple comparison of FOF[21,22] *vs.* FOOF and CF_3OF *vs.* CF_3OOF is valid.

The ^{19}F nmr of CF_3OOF shows a high-field doublet assigned to the CF_3OO group (ϕ^* 68.9) and a low-field quartet assigned to the OOF group (ϕ^* −292) with $J_{FF} = 5.0$ Hz. The chemical shift of the CF_3OO group is very close to that of other similar compounds[4,8,9] and that of the OOF group is identical with that of C_3F_7OOF and FO_2SOOF (ϕ^* −291 and −292).[23−25] Since the chemical shift of OOF in FOOF occurs below −800 ppm,[26] the OF bonds in CF_3OOF and FO_2SOOF must be of considerably different character. The chemical shift of an OF attached to carbon occurs over a narrow range at about −150 ppm[27,28] and CF_3OOF shows a large shift

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compared to these compounds. One can conclude that CF_3OOF will resemble CF_3OF in the types of chemical reactions it will undergo but it should show much greater reactivity under similar conditions.

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The Preparation of Fluoroperoxytrifluoromethane. The Mechanism of the Reaction of Oxygen Difluoride and Carbonyl Fluoride

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Fluoroperoxysulfuryl fluoride, FSO_2OOF, was the first compound reported to contain the fluoroperoxy, OOF, group. This compound was prepared[1] by the photolytic reaction of sulfur trioxide, SO_3, and oxygen difluoride, OF_2, and by the reaction of sulfur dioxide, SO_2, and dioxygen difluoride.[2] Thompson[3] reported that the direct fluorination of salts of trifluoroacetic acid, CF_3CO_2H, produced a number of products including very small amount of fluoroperoxytrifluoromethane, CF_3OOF, and fluoroperoxypentafluoroethane, CF_3CF_2OOF. 1- and 2-fluoroperoxyperfluoropropanes have also been reported[4] to result from the reaction of perfluoropropene, C_3F_6, and O_2F_2. At the time this research was initiated a convenient method for the preparation of a fluoroperoxyperfluoroalkane was not available.

Anderson and Fox[5] reported that oxygen difluoride, OF_2, and carbonyl fluoride, COF_2, react in the presence of cesium fluoride, CsF, catalyst to give good yields of bis(trifluoromethyl) trioxide, CF_3OOOCF_3, and have suggested that the formation of CF_3OOOCF_3 proceeds by the mechanism

$$COF_2 + CsF \longrightarrow Cs^+OCF_3^- \quad (1)$$

$$OF_2 + CF_3O^- \longrightarrow CF_3OOF + F^- \quad (2)$$

$$CF_3OOF + CF_3O^- \longrightarrow CF_3OOOCF_3 + F^- \quad (3)$$

$$CF_3OOF + COF_2 \longrightarrow CF_3OOOCF_3 \quad (4)$$

They, however, did not detect CF_3OOF in their experiments.

We have additional proof of the validity of this mechanism and also wish to report the first convenient method for the preparation of fluoroperoxytrifluoromethane, CF_3OOF.

In the majority of its reactions, OF_2 acts as a powerful fluorinating agent, but in a few cases simple addition of OF_2 to a substrate has been observed. The photochemical addition of OF_2 to SO_3[6,7] has been shown to proceed *via* an ·OF intermediate. Also, Merritt has proposed that carefully controlled oxidations of amines[8] and certain unsaturated compounds[9-11] by OF_2 may involve intermediate OF_2 adducts.

Results and Discussion

A. Mechanism.—The mechanism of the reaction of COF_2 and OF_2 was elucidated by using ^{17}O-tracer techniques and ^{17}O nmr analysis. According to the proposed mechanism, if $C^{17}OF_2$ is allowed to react with ordinary OF_2, the ^{17}O should be in the positions

$$C^{17}OF_2 + CsF \longrightarrow Cs^{+17}OCF_3^- \quad (1a)$$

$$^{16}OF_2 + {}^{17}OCF_3^- \longrightarrow CF_3{}^{17}O^{16}OF + F^- \quad (2a)$$

$$CF_3{}^{17}O^{16}OF + {}^{17}OCF_3^- \longrightarrow CF_3{}^{17}O^{16}O^{17}OCF_3 + F^- \quad (3a)$$

$$CF_3{}^{17}O^{16}OF + C^{17}OF_2 \longrightarrow CF_3{}^{17}O^{16}O^{17}OCF_3 \quad (4a)$$

Thus, the product should contain ^{16}O in the center position and ^{17}O in other positions. Alternatively, if ordinary COF_2 is allowed to react with $^{17}OF_2$, the labels should be reversed.

In order to determine the chemical shifts of the various oxygen atoms in CF_3OOOCF_3, $C^{17}OF_2$ was allowed to react with $^{17}OF_2$, and a randomly labeled $CF_3{}^{17}O^{17}O^{17}OCF_3$ was obtained. A two-line ^{17}O nmr spectrum was obtained. Since the −321-ppm line had approximately twice the intensity of the −479 ppm line, lines were assigned as shown in Table I. Ordinary OF_2 was then treated with $C^{17}OF_2$ and only the −321-ppm line appeared; alternatively the reaction of $^{17}OF_2$ with ordinary COF_2 resulted in a product that showed only the −479-ppm line.

TABLE I

CHEMICAL SHIFTS FOR ^{17}O-LABELED BIS(TRIFLUOROMETHYL) TRIOXIDE

Source of sample	Chem shift, ppm relative to $H_2{}^{17}O$ $CF_3{}^{17}OO^{17}OCF_3$	$CF_3O^{17}OOCF_3$
$^{17}OF_2 + C^{17}OF_2$	−321	−479
$OF_2 + C^{17}OF_2$	−321	. . .
$^{17}OF_2 + COF_2$	. . .	−479

In considering the mechanism shown by eq 1a–4a, an excess of OF_2 or the removal of free COF_2 should favor the isolation of CF_3OOF. As will be seen in the next section, CF_3OOF was prepared using these types of experiments. It was found, however, that CF_3OOF does not react with COF_2 as shown in eq 4.

It was concluded that the proposed mechanism is supported by the ^{17}O nmr results and by the isolation of CF_3OOF in the reaction of COF_2 and OF_2.

B. Preparation of Fluoroperoxytrifluoromethane.—Fluoroperoxytrifluoromethane was prepared as follows.

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