sublimed at 40° (0.01 mm) to give 0.69 g (96% yield) of colorless crystalline 7,9-$B_9H_{10}CHAsCH_3$, mp 134–134.5°. The infrared spectrum contained absorptions at λ_{max} 3028 (w), 2930 (w), 2580 (s), 1835 (w), 1402 (w), 1252 (w), 1161 (w), 1061 (m), 969 (m), and 739 cm^{-1} (m). The proton nmr spectrum (acetone-d_6) showed a broad singlet at τ 7.5 (1 H) and a sharp singlet at τ 7.8 (3 H).

(C_5H_5)Co(7,8-B_9H_9CHAs).—A mixture of 2.0 g (0.007 mol) of $C_5H_{10}NH_2$(7,8-B_9H_{10}CHAs), 3 ml (0.036 mol) of freshly cracked C_5H_6, 10 ml (0.1 mol) of triethylamine, and 2.7 g (0.02 mol) of anhydrous cobalt(II) chloride in tetrahydrofuran solution was refluxed overnight. The solvent was removed *in vacuo* and the solids were chromatographed on a silica gel column with benzene as eluent. Recrystallization from benzene–heptane gave 0.11 g of yellow crystalline (C_5H_5)Co(7,8-B_9H_9CHAs), mp 250–251°. The mass spectrum of this compound contained a parent ion peak at *m/e* 320.0559 (calcd for $^{11}B_9{}^1H_{15}{}^{12}C_6{}^{75}As^{59}Co$, 320.0559).

1,2-$B_{10}H_{10}$CHSb.—Six grams (0.031 mol) of $B_{10}H_{12}CN(CH_3)_3$ was converted to $Na_3B_{10}H_{10}CH(THF)_2$ by the procedure previously described. The reaction flask was cooled in an ice bath and 17.9 g (0.035 mol) of antimony triiodide, stirred in 200 ml of tetrahydrofuran, was added to the reaction mixture over a 5-hr period. The dark brown solution was allowed to stir at room temperature for an additional 2 hr. The mixture was filtered under nitrogen and the filtrate was evaporated under vacuum. The resulting residues were sublimed at 120–150° at 10^{-2} mm to give a red-yellow sublimate. The crude product was crystallized three times from benzene to give 3.4 g (41% yield) of white crystalline 1,2-$B_{10}H_{10}$CHSb. The compound decomposed above 240° without melting. The infrared spectrum contained absorptions at λ_{max} 3020 (m), 2530 (s), 1095 (w), 1010 (m), 960 (m), 895 (m), 750 (w), 720 (m), 660 (w), 630 (w), and 240 cm^{-1} (w). The molecular weight was determined osmometrically in benzene: calcd, 253; found, 252.

1,7-$B_{10}H_{10}$CHSb.—1,2-$B_{10}H_{10}$CHSb (0.20 g) was sealed into an evacuated thick-wall glass tube and maintained at 450° for 13 hr. The pyrolysate was sublimed at 60° at 10^{-2} mm pressure to give 0.04 g (20% yield) of colorless 1,7-$B_{10}H_{10}$CHSb, mp 403.5–404.5°. Gas chromatographic analysis indicated the product was 99.9% the 1,7 isomer. The infrared spectrum contained absorptions at λ_{max} 3038 (m), 2550 (s), 1100 (m), 1025 (m), 960 (m), 890 (m), 870 (w), 700 (m), 640 (w), 620 (w), and 235 cm^{-1} (m).

$(CH_3)_4N$[7,8-B_9H_{10}CHSb].—A solution of 0.211 g (0.0008 mol) of 1,2-$B_{10}H_{10}$CHSb in 50 ml of benzene was brought to reflux, and 0.28 g (0.0033 mol) of piperidine in 50 ml of benzene was added dropwise over 2 hr. The solvent was removed under vacuum and methanol was slowly added to the residue until gas evolution ceased. A saturated solution of tetramethylammonium chloride was added until precipitation was complete. The solids were crystallized from acetone–methanol to give 0.209 g (74% yield) of colorless crystalline $(CH_3)_4N$[7,8-B_9H_{10}CHSb]. The infrared spectrum contained absorptions at λ_{max} 3001 (m), 2960 (m), 2510 (s), 1485 (s), 1475 (m), 1450 (m), 1434 (m), 1413 (w), 1392 (m), 1290 (w), 1190 (w), 1171 (s), 1055 (m), 997 (s), 900 (w), 873 (w), 858 (w), 784 (s), 755 (w), 734 (w), 685 (w), and 488 cm^{-1}.

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The Reaction of Bis(fluoroxy)difluoromethane with Cesium Trifluoromethoxide[1]

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The reaction of bis(fluoroxy)difluoromethane, $CF_2(OF)_2$, with cesium trifluoromethoxide, $CsOCF_3$, in the presence of cesium fluoride forms CF_3OF, CF_3OOOCF_3, and the new compound $CF_3OOOCF_2OOCF_3$. When excess carbonyl fluoride is added, CF_3OF and $CF_3OOC(O)F$ are the products. The characterization of $CF_3OOOCF_2OOCF_3$ is discussed along with a possible mechanism for the reaction.

Introduction

The reaction of carbonyl fluoride with strong oxidizing agents in the presence of metal fluorides forms a variety of interesting compounds in high yields. For example the following reactions are known[2-7]

$$COF_2 + F_2 \xrightarrow{CsF} CF_3OF$$

$$COF_2 + OF_2 \xrightarrow{CsF} CF_3OOOCF_3$$

$$COF_2 + ClF \xrightarrow{CsF} CF_3OCl$$

$$COF_2 + S_2O_6F_2 \xrightarrow{KF} CF_3OOSO_2F$$

The reactive species in these reactions appears to be trifluoromethoxide salt which can be preformed from metal fluoride and carbonyl fluoride or formed *in situ* in the presence of the oxidizing agent. While CF_3OF does not react with $CsOCF_3$ at 22° to form the peroxide, CF_3OOCF_3,[7-9] the reaction of OF_2 suggests that other

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[1] During the course of this work it was learned that similar studies had been carried out: L. R. Anderson and W. B. Fox, *Inorg. Chem.*, **9**, 2182 (1970).

[2] J. K. Ruff, A. R. Pitochelli, and M. Lustig, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

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[5] D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *ibid.*, **91**, 1310 (1969).

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

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

[8] D. D. DesMarteau, unpublished results.

[9] Bis(trifluoromethyl) peroxide is readily obtained by reaction of CF_3OF with COF_2 at 250°: R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 5638 (1957).

fluoroxy compounds might react to form new peroxides or trioxides. In particular previous work with $CF_2(OF)_2$ indicated that the compound was considerably more reactive than CF_3OF.[10] It was therefore of interest to investigate the reaction of $CF_2(OF)_2$ with $CsOCF_3$.

Experimental Section

General Data.—All manipulations of volatile compounds were conducted in a Pyrex or 316 stainless steel vacuum system. 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. All reactions were carried out in a 71-ml Monel reactor with a working pressure of 10,000 psi at 22°.

Infrared spectra were recorded on a Beckman IR 10 using a 10-cm Pyrex cell fitted with silver chloride windows. Identification of volatile products by infrared analyses was made by comparison with known samples run under similar conditions. Nuclear magnetic resonance spectra were taken on a Varian A-56-60 instrument using trichlorofluoromethane as an internal reference. Relative areas of different peaks were obtained by integration. Molecular weights were determined by vapor density measurements using a calibrated Pyrex bulb fitted with a glass Teflon valve. Values determined on pure known samples were accurate to 0.5%. Vapor pressures were measured using the method of Kellogg and Cady.[11]

Caution! The peroxides, trioxides, and fluoroxy compounds described in this work are all potentially hazardous. Explosive mixtures are readily formed with other oxidizable materials and spontaneous explosive decomposition is possible for some. Inexperienced workers should not attempt to handle these materials without adequate supervision by experienced personnel.

Reagents.—Carbonyl fluoride was obtained from the Matheson Co. and used without further purification. Cesium fluoride was 99.99% pure from Research Inorganic Chemical Corp. Bis(fluoroxy)difluoromethane was prepared by allowing CO_2 to react with excess F_2 in the presence of CsF.[12,13]

Cesium trifluoromethoxide was prepared by adding 5 g (33 mmol) of CsF to a 71-ml reactor containing ten 0.25-in and ten 0.375-in. stainless steel ball bearings. The reactor was then placed in a Red Devil paint shaker and shaken for several minutes to pulverize the CsF. Several atmospheres of COF_2 was then added and allowed to stand for 12 hr at 22°. The excess COF_2 was then removed and excess F_2 was added to the reactor. After a few hours at 22° the unreacted F_2 was removed at −195° and the pure CF_3OF formed by reaction of F_2 with $CsOCF_3$ was collected. The reactor was shaken again for several minutes and excess COF_2 was again added. After standing for 12 hr the CsF absorbed 20 mmol of COF_2 or 60% of the theoretical amount for the formation of pure $CsOCF_3$. Subsequent preparations were carried out similarly with about the same yield.

Reaction of $CsOCF_3$ with $CF_2(OF)_2$ in the Presence of CsF.—This reaction was carried out under a variety of conditions in attempting to obtain optimum yields. A typical run which resulted in good yields will be described.

Bis(fluoroxy)difluoromethane (15 mmol) was condensed onto a mixture of $CsOCF_3$ (20 mmol) and CsF (13 mmol) held at −195°. The reactor was then placed in a −78° bath and allowed to warm to −5° over a 10-hr period. The reactor was then cooled to −195° and the O_2 (2.4 mmol) was pumped out. The material remaining in the reactor was then fractionated through traps held at −78, −131, and −195°.

The −195° trap contained 13 mmol of volatile liquid having a molecular weight of 106. The infrared spectrum showed the presence of large amounts of CF_3OF (mol wt 104) with small amounts of $CF_2(OF)_2$ and CF_3OOCF_3. The −131° trap contained 1.1 mmol of colorless liquid having a molecular weight of 185. The infrared spectrum showed large amounts of CF_3OOOCF_3 (mol wt 186) with small amounts of $CF_2(OF)_2$ and CF_3OOCF_3. The ^{19}F nmr showed a single absorption at φ 69.3.[9,14] The −78° trap contained 0.4 mmol of $CF_3OOOCF_2OOCF_3$ with a molecular weight of 270 (calcd 268).

The infrared spectrum showed absorptions at (cm^{-1}): 1285 (s), 1250 (vs), 1215 (m), 1180 (s), 1125 (vs), 960 (w), 920 (w), 885 (m), 763 (s), 715 (w), 690 (w), 640 (w), 610 (m), 580 (m), 550 (w). The ^{19}F nmr contained three absorptions at φ 69.5 (singlet), 69.8 (triplet), and 79.2 (quartet) with $J = 4.0$ Hz. The relative areas were 3.1:3.1:2.0. The per cent fluorine in the compound was also determined from the nmr spectrum using weighed amounts of $CFCl_3$ and compound. *Anal.* Calcd for $C_3F_8O_5$: F, 56.7. Found: F, 56.0. The vapor pressure followed the equation: $\log P\ (\text{mm}) = -(1440.0/T) + 7.141$. The extrapolated boiling point was 65° with a heat of vaporization of 6.58 kcal/mol and a Trouton constant of 21.5 cal/mol deg.

The compound was strongly oxidizing toward aqueous potassium iodide and was thermally stable at 22°. However, while measuring the vapor pressure at *ca.* 40° a sharp explosion occurred. The decomposition products contained oxygen with COF_2 and CF_3OOCF_3 as shown by infrared analysis.

Reaction of $CsOCF_3$ with $CF_2(OF)_2$ and COF_2 in the Presence of CsF.—Bis(fluoroxy)difluoromethane (6.0 mmol) and COF_2 (12.0 mmol) were condensed onto a mixture of CsF (10 mmol) and $CsOCF_3$ (23 mmol) held at −195°. The reaction was then warmed to −22° and held at this temperature for 16 hr. Oxygen (0.13 mmol) was then removed at −195° and the remaining volatile substances were fractionated through traps held at −111 and −195°. The −195° trap contained 10 mmol of material having a molecular weight of 95. The infrared spectrum showed large amounts of CF_3OF (mol wt 104) and COF_2 (mol wt 66). The −111° trap contained pure $CF_3OOC(O)F$[15,16] (3.9 mmol) as shown by infrared and vapor density molecular weight of 149.0 (calcd 148.0).

The ^{19}F nmr showed two absorptions at φ 70.7 (doublet) and 33.4 (quartet) with $J = 2.0$ Hz. The vapor pressure is given by the equation $\log P\ (\text{mm}) = -(1353.0/T) + 8.112$. The extrapolated boiling point is −14.2° with a heat of vaporization of 6.19 kcal/mol and a Trouton constant of 23.9 cal/mol deg.

Discussion

The reaction of $CF_2(OF)_2$ with $CsOCF_3$ in the presence CsF forms CF_3OF in high yield along with smaller amounts of O_2, CF_3OOOCF_3, and $CF_3OOOCF_2OOCF_3$. The reaction offers a convenient alternate method for the preparation of CF_3OOOCF_3. The maximum yields obtained approach 20% and these compare favorably with higher yields employing the less readily available OF_2.[4]

The new compound $CF_3OOOCF_2OOCF_3$ is the only reported example of a molecule containing both trioxide and peroxide linkages. The infrared and nmr spectra are consistent with the proposed molecular structure and the compound shows a strong resemblance to other known peroxides and trioxides.[17]

The infrared absorptions from 1285 to 1125 cm^{-1} can readily be assigned to CF stretches and those at 960, 920, and 885 cm^{-1} can probably be assigned to CO stretches. The bands at 763 cm^{-1} along with some other lower energy absorptions can be assigned to CF_3 deformation modes.

The ^{19}F nmr is particularly unequivocal in that three

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[10] F. A. Hohorst and J. M. Shreeve, *Inorg. Chem.*, **7**, 624 (1968).

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

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

[13] R. Cauble and G. H. Cady, *ibid.*, **89**, 1962 (1967).

[14] P. G. Thompson, *ibid.*, **89**, 4316 (1967).

[15] R. Cauble and G. H. Cady, *J. Org. Chem.*, **33**, 2099 (1968).

[16] R. L. Talbott, *ibid.*, **33**, 2095 (1968).

[17] See ref 4, 9, and 14–16, and references therein.

distinct fluorine environments are present in the molecule, yet only two show spin–spin coupling. The coupling constant through three oxygens is less than 1 Hz and would not be observed under normal resolution. The coupling constant for peroxides is 3–5 Hz and would be easily observed. In addition the chemical shifts are very consistent with the presence of CF_3OOO, CF_3OO, and OCF_2O groups. Table I summarizes the ^{19}F nmr data for $CF_3OOOCF_2OOCF_3$ and several related compounds.

Table I
^{19}F Nuclear Magnetic Resonance Data for Peroxides and Trioxides

Compound	CF_3O^a	OCF_2O^a	$J_{F-F}{}^b$	Ref
CF_3OOCF_3	69.0	...	...	14
$CF_3OOC_2F_5$	68.7	...	4.3	14
CF_3OOOCF_3	68.7	...	...	4, 14
$CF_3OOOC_2F_5$	68.7	...	<1	14
CF_3OOCF_2OF	69.0	80.6	3.4	16
$(CF_3OO)_2CFOF$	68.7	...	3.5	16
$CF_3OOOCF_2OOCF_3$	69.5, 69.8	79.2	< 1, 4.0	...

[a] φ values. [b] J in Hz for $CF_3O_nCF_2-$ and $CF_3O_nCF<$.

The thermal stability of $CF_3OOOCF_2OOCF_3$ is considerably lower than that of the two other known trioxides CF_3OOOCF_3 and $CF_3OOOC_2F_5$.[4,14] Bis(trifluoromethyl) trioxide begins to decompose slowly at 70° whereas $CF_3OOOCF_2OOCF_3$ undergoes explosive decomposition at about 40°. The decomposition appears to follow the equation

$$CF_3OOOCF_2OOCF_3 = CF_3OOCF_3 + COF_2 + O_2$$

The extrapolated boiling point of 65° is very close to that which would be predicted based on comparison with the boiling points of C_2F_6 (−78°),[18] CF_3OCF_3 (−59°),[18] CF_3OOCF_3 (−37°)[9], and CF_3OOOCF_3 (−16°).[4] The average increase for this series of related compounds is 20.7° for each added oxygen. Assuming a similar trend starting with C_3F_8 (−38°),[18] the predicted boiling point of $CF_3OOOCF_2OOCF_3$ would be about 65°.

The influence of COF_2 on the reaction of $CF_2(OF)_2$ with $CsOCF_3$ is very striking. When a 2:1 molar excess of COF_2 to $CF_2(OF)_2$ is added, CF_3OF and $CF_3OOC(O)F$ are the only fluorocarbon products observed and the formation of O_2 is markedly less. The yields of $CF_3OOC(O)F$ approach 80% and thus the reaction is far superior to existing methods for the preparation of the peroxide. With or without added COF_2 the major product under all conditions is always CF_3OF.

While the mechanism for the reaction is obviously complex, a scheme based on the initial reaction

$$CF_2(OF)_2 + CsOCF_3 = CF_3OF + CsOOCF_3$$

is reasonable. The $CsOOCF_3$[7] could then decompose to O_2 and $CsOCF_3$ or undergo subsequent reaction with $CF_2(OF)_2$ and CF_3OF leading to CF_3OOOCF_3 and $CF_3OOOCF_2OOCF_3$. In the presence of excess COF_2 the reaction

$$CsOOCF_3 + 2COF_2 = CF_3OOC(O)F + CsOCF_3$$

could occur. If the latter reaction was fast compared to the decomposition of $CsOOCF_3$ and its subsequent reactions with $CF_2(OF)_2$ and CF_3OF, the observed high yields of $CF_3OOC(O)F$ with only small amounts of oxygen would be reasonable.

In support of this reaction scheme the following observations should be noted. (a) CF_3OF is always formed in approximately equimolar amounts based on $CF_2(OF)_2$. (b) The amount of O_2 formed is strongly dependent on the reaction temperature. If the reaction is warmed rapidly to 22° and allowed to stand for several hours, CF_3OF and O_2 are the only significant products. (c) No $CF_3OOC(O)F$ is observed in the absence of gaseous COF_2 whereas no trioxides are observed with excess gaseous COF_2.[19]

Acknowledgment.—The author thanks D. T. Dix and the Dow Chemical Co. for the use of the nmr spectrometer. The financial support of the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

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(18) J. H. Simons, Ed., "Fluorine Chemistry," Vol. 1, Academic Press, New York, N. Y., 1950, pp 452, 500.

(19) Note Added in Proof. When the reaction of $CsOCF_3$ with $CF_2(OF)_2$ and COF_2 is run on a 30-mmol scale at −22 to −5° for 2 days, small amounts of $(CF_3OO)_2CO^{15}$ are obtained in addition to $CF_3OOC(O)F$. This product could be formed by the reaction $CF_3OOC(O)F + CsOOCF_3 \rightarrow (CF_3OO)_2CO + CsF$. The appearance of $(CF_3OO)_2CO$ when the reaction is run on a large scale is consistent with the proposed mechanism.