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PERFLUOROALKYL CHLOROFORMATES AND CHLOROSULFATES

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We have recently described the synthesis and characterization of a new class of compounds, the perhaloalkyl hypochlorites.(1) These new hypochlorites have been found to react quantitatively with carbon monoxide to produce perfluoroalkyl chloroformates according to equation (I).

$$\text{(I)}\quad R_fOCl + CO \xrightarrow{-20^\circ} R_fOC(O)Cl$$

$$R_f = CF_3,\ C_2F_5,\ i\text{-}C_3F_7,\ SF_5$$

Similarly, the perfluorinated hypochlorites with the exception of SF_5OCl react with sulfur dioxide under conditions identical to those described above to produce perfluoroalkyl chlorosulfates.

$$\text{(II)}\quad R_fOCl + SO_2 \xrightarrow{-20^\circ} R_fOSO_2Cl$$

$$R_f = CF_3,\ i\text{-}C_3F_7$$

This is a simple and unique method for the preparation of perfluoroalkyl chlorosulfates, and the particular examples cited have not been previously described in the literature. However, other investigators have prepared several of the less volatile members of this group from the perfluoroalkyl iodides.(2)

All of the new chloroformates and chlorosulfates were prepared in essentially the same manner. Conventional vacuum techniques (Monel-Kel-F system) were used to condense the appropriate hypochlorite into a 30 ml stainless steel cylinder. This was followed by the addition of excess carbon monoxide or sulfur dioxide at -196°. The mixture was then allowed to warm to -20° and remain at that temperature for several hours. After this time the products were separated by vacuum fractionation or by glc.

The yields of chloroformates were always very nearly quantitative. The yields of the chlorosulfates were about 50%.

The identities of the new chloroformates and chlorosulfates were confirmed by their intense carbonyl or asymmetric sulfuryl absorptions at 1830-1845 or 1463-1466 cm^{-1}, respectively, and by the other supporting data summarized in Table 1 and Table 2..

TABLE 1

ELEMENTAL ANALYSES AND VAPOR PRESSURE DATA

COMPOUND	ELEMENTAL ANALYSES	VAPOR PRESSURE
$CF_3OC(O)Cl$	%C, 16.16; calcd, 16.18	$\log P_{mm} = 7.9385 - \frac{1380.1}{T}$
	%F, 37.78; calcd, 38.40	$H_v = 6324.9$, b.p. = 0°
	%Cl, 24.14; calcd, 23.91	Trouton constant = 23.2
$C_2F_5OC(O)Cl$	%C, 17.92; calcd, 18.15	$\log P_{mm} = 7.8053 - \frac{1483.9}{T}$
	%F, 47.10; calcd, 47.86	$H_v = 6787.7$, b.p. = 28°
	%Cl, 18.08; calcd, 17.86	Trouton constant = 24.0
$(CF_3)_2CFOC(O)Cl$	%C, 19.04; calcd, 19.33	
	%F, 53.52; calcd, 54.00	
	%Cl, 14.10; calcd, 14.27	
$SF_5OC(O)Cl$	%C, 5.71; calcd, 5.81	
	%F, 45.32; calcd, 46.00	
	%Cl, 17.80; calcd, 17.20	
	%S, 15.36; calcd, 15.53	
CF_3OSO_2Cl	%C, 6.27; calcd, 6.50	$\log P_{mm} = 6.7965 - \frac{1270.6}{T}$
	%F, 29.88; calcd, 30.85	$H_v = 5811.9$, b.p. = 50°
	%Cl, 19.80; calcd, 19.21	Trouton constant = 17.9
	%S, 16.85; calcd, 17.34	
$(CF_3)_2CFOSO_2Cl$	%Cl, 13.05; calcd, 12.48	
	%S, 11.50; calcd, 11.25	

TABLE 2

INFRARED AND FLUORINE-19 NMR DATA

COMPOUND	F^{19} NMR	INFRARED (cm^{-1})
$CF_3OC(O)Cl$	ϕ + 63.5 (singlet)	1830(s), 1280(s), 1250(s), 1200(s), 1100(vs), 878(m), 666(m)
$C_2F_5OC(O)Cl$	ϕ + 87.8 (triplet) + 92.2 (quartet)	1840(s), 1242(s), 1210(m), 1178(m), 1110(vs), 1075(vs), 860(w), 800(m), 708(ms)
$(CF_3)_2CFOC(O)Cl$	ϕ + 79.1 (doublet) + 142 (complex) J = 1.9Hz	1845(s), 1335(m, shoulder), 1300(m), 1268(ms), 1192(w), 1170(m), 1118(vs), 1068(ms), 1010(s), 835(m), 725(m), 688(m)
$SF_5OC(O)Cl$	AB_4 ϕ_A -59.2 ϕ_B -67.6 J = 156Hz	1835(s), 1065(s), 938(s), 885(s), 753(broad, w), 705(w), 665(w)
CF_3OSO_2Cl	ϕ + 60.4 (singlet)	1463(s), 1280(s), 1257(s), 1225(s), 1140(vs), 960(ms), 785(m)
$(CF_3)_2CFOSO_2Cl$	ϕ + 82 (doublet) + 146 (complex) J = 2.0Hz	1466(s), 1312(m), 1266(vs), 1221(m), 1175(m), 1092(vs), 1000(s), 836(ms), 765(w), 734(m), 695(m)

The contrast between the fluoroxy compounds (R_fOF) and the hypochlorites (R_fOCl) is marked. While CF_3OF will react with CO under more stringent reaction conditions (ultraviolet irradiation) to form the fluoroformate, $CF_3OC(O)F$ (3), we have found that C_2F_5OF merely fluorinates CO to give COF_2 and $CF_3C(O)F$ as products. Similarly, a much higher temperature (180°) is required to prepare CF_3OSO_2F from CF_3OF and SO_2 (4), and C_2F_5OF only fluorinates SO_2 to give SO_2F_2 and $CF_3C(O)F$.

The new hypochlorites not only differ from the corresponding fluoroxy compounds but from the alkyl hypochlorites as well. We have shown that the only readily available alkyl hypochlorite, $(CH_3)_3COCl$, does not react with CO, even at 80°.

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