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The Reaction of Peroxydisulfuryl Difluoride with Anhydrides of Certain Perhalocarboxylic Acids to Form Perhaloacyl Fluorosulfates

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Peroxydisulfuryl difluoride reacts almost quantitatively with the anhydride of a perfluorocarboxylic acid at 100° under autogenous pressure according to the equation $(R_fCO)_2O + S_2O_6F_2 = CO_2 + R_fOSO_2F + R_fC(O)OSO_2F$. New compounds obtained in this manner are: $CF_3C(O)OSO_2F$, $ClCF_2OSO_2F$, $ClCF_2C(O)OSO_2F$, $C_2F_5C(O)OSO_2F$, $C_3F_7C(O)OSO_2F$, and $FO_2SOCF_2CF_2C(O)OSO_2F$.

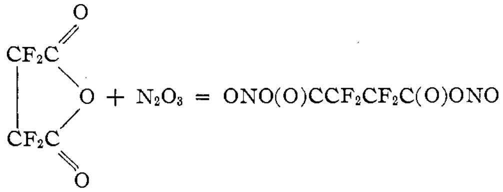
The reaction of perfluoroacetic anhydride with iodine[1]

$$(CF_3CO)_2O + I_2 = CF_3COI + CF_3C(O)OI$$

$$CF_3C(O)OI \overset{I_2}{=} CF_3I + CO_2$$

and of perfluoro acid anhydrides with dinitrogen trioxide[2]

$$(R_fCO)_2O + N_2O_3 = 2R_fC(O)ONO$$

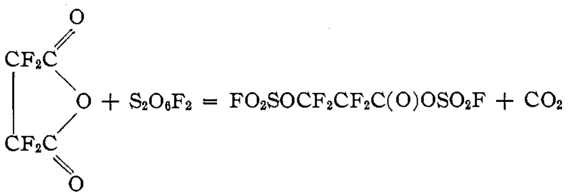


$$+ N_2O_3 = ONO(O)CCF_2CF_2C(O)ONO$$

suggest that peroxydisulfuryl difluoride may react similarly.

This has been found to be true. The following reactions occur

$$(R_fCO)_2O + S_2O_6F_2 = R_fOSO_2F + R_fC(O)OSO_2F + CO_2$$



$$+ S_2O_6F_2 = FO_2SOCF_2CF_2C(O)OSO_2F + CO_2$$

These reactions are negligible at 25° but occur readily at 100°. Since $S_2O_6F_2$ undergoes appreciable dissociation into fluorosulfate free radicals[3,4] at 100° it is likely that the radicals play a part in the mechanism of the reaction.

The new perhaloacyl fluorosulfates are stable volatile liquids at room temperature. They are moisture sensitive but do not react readily with glass. Perfluoroacetyl fluorosulfate decomposes to perfluoroacetyl fluoride and sulfur trioxide at 200°, and it is probable that the other perhaloacyl fluorosulfates behave similarly. The decomposition of fluorosulfates to the corresponding fluoride and SO_3 is well known.[5]

Nuclear magnetic resonance data for the compounds are given in Table I. The δ values in p.p.m. relative to $CF_3C(O)OH$, coupling constants, measured relative areas, and type of peaks observed are shown. The spectrum observed for $C_3F_7C(O)OSO_2F$ is consistent with those for other compounds containing the C_3F_7 group.[6-8]

No spin-spin coupling was observed between the fluorine of the fluorosulfate attached to $-C(=O)-$ and fluorine atoms of the R_f group. Infrared spectra of the new compounds are given in Table II. All show characteristic $-S(=O)_2$ stretching frequencies at 1485–1495 cm.$^{-1}$ (asymmetric) and 1240–1257 cm.$^{-1}$ (symmetric). The perhaloacyl fluorosulfates have $-C(=O)-$ stretching frequencies at 1845–1850 cm.$^{-1}$. The more abundant positive ions in the mass spectra of the compounds are, in order of decreasing intensity: $[ClCF_2OSO_2F]$: $^{35}ClCF_2^+$, SO_2F^+, FCO^+, $^{37}ClCF_2^+$, SO^+, $^{35}Cl^+$, CF_2^+, SOF^+, CF^+, CO^+, $^{35}ClCO^+$, SO_2^+, S^+, $^{37}Cl^+$, CO_2^+; $[ClCF_2C(O)OSO_2F]$: $^{35}ClCF_2^+$, $^{37}ClCF_2^+$, SO_2F^+, FCO^+, CO^+, CF_2^+, CF^+, $^{35}Cl^+$,

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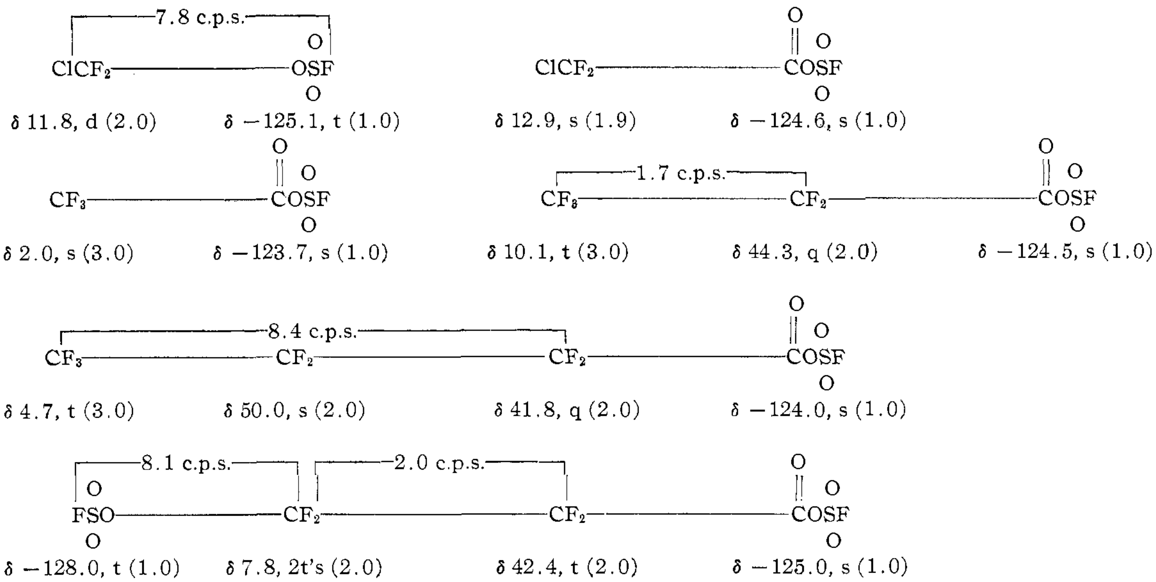
TABLE I

NUCLEAR MAGNETIC RESONANCE DATA[a]



7.8 c.p.s.

$ClCF_2$—OSO_2F

δ 11.8, d (2.0) δ −125.1, t (1.0)

$ClCF_2$—$C(O)OSO_2F$

δ 12.9, s (1.9) δ −124.6, s (1.0)

CF_3—$C(O)OSO_2F$

δ 2.0, s (3.0) δ −123.7, s (1.0)

1.7 c.p.s.

CF_3—CF_2—$C(O)OSO_2F$

δ 10.1, t (3.0) δ 44.3, q (2.0) δ −124.5, s (1.0)

8.4 c.p.s.

CF_3—CF_2—CF_2—$C(O)OSO_2F$

δ 4.7, t (3.0) δ 50.0, s (2.0) δ 41.8, q (2.0) δ −124.0, s (1.0)

8.1 c.p.s. 2.0 c.p.s.

FSO_2O—CF_2—CF_2—$C(O)OSO_2F$

δ −128.0, t (1.0) δ 7.8, 2t's (2.0) δ 42.4, t (2.0) δ −125.0, s (1.0)

[a] s, singlet; d, doublet; t, triplet; q, quartet; δ, chemical shift with respect to $CF_3C(O)OH$; relative peak area in parentheses.

TABLE II

MAJOR INFRARED ABSORPTION BANDS (VALUES IN WAVE NUMBERS, CM.$^{-1}$)[a]

$ClCF_2$-OSO_2F	$ClCF_2C(O)$-OSO_2F	$CF_3C(O)$-OSO_2F	$C_2F_5C(O)$-OSO_2F	$C_3F_7C(O)$-OSO_2F	FO_2SOCF_2-$CF_2C(O)$-OSO_2F
	1850 s	1850 s	1850 s	1847 s	1845 s
1486 s	1487 s	1485 s	1490 s	1490 s	1495 s
1257 s	1255 s	1250 s	1240 s	1250 s	1255 s
1217 s	1238 s	1305 m	1340 m	1355 m	1220 s
1195 s	1190 s	1200 s	1110 s	1220 s	1150 s
1135 s	1075 s	1130 m	990 s	1200 s	1102 s
1050 s	1030 m	1040 s	865 s	1135 s	1025 m
1030 s	950 s	860 s	845 s	948 m	980 s
920 s	860 s	830 s	820 s	914 s	840 s
878 m	843 s	780 s	782 s	862 m	810 m
835 s	826 s	595 m	560 m	843 s	765 m
765 m	785 s	545 s		818 m	550 m
705 m	710 m			780 m	
650 m	628 m			750 m	
580 s	565 s			645 m	
				560 m	

[a] s, strong; m, medium.

TABLE III

ANALYTICAL DATA

	Sulfur, wt. %		Fluorine, wt. %		Moles of OH$^-$ consumed	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
$ClCF_2OSO_2F$[d]	17.0	17.4	30.0[a]	30.9[a]		
$ClCF_2O(O)OSO_2F$	14.1	15.1	10.0[b]	9.0[b]	4.0	4.0
$CF_3O(O)OSO_2F$	15.0	16.3	9.6[b]	9.7[b]	3.9	4.0
$C_2F_5O(O)OSO_2F$	13.5	13.0	7.9[b]	7.7[b]	4.1	4.0
$C_3F_7O(O)OSO_2F$	10.6	10.8	6.5[b]	6.4[b]	4.0	4.0
$FO_2SOCF_2CF_2O(O)OSO_2F$	19.7	20.0	22.5[c]	23.3[c]	9.8	10.0

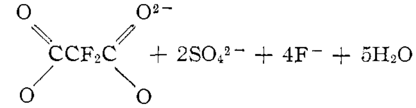
[a] Total fluorine. [b] Fluorine in SO_3F group only. [c] Four of the six fluorine atoms in the molecule. [d] Chlorine wt. %: found 19.0; calcd. 19.2.

CO_2^+, SO^+, $^{35}ClCO^+$, SO_2^+, SOF^+, $CF_2OSO_2F^+$, S^+, $^{37}Cl^+$; [$CF_3C(O)OSO_2F$]: CF_3^+, CO_2^+, CO^+, CF^+, SO_2F^+, SO^+, CO_2^+, CF_2^+, S^+, SOF^+, SO_2^+; [$C_2F_5C(O)OSO_2F$]: CF^+, $C_2F_3^+$, CO_2^+, CF_3^+, SO_3^+, CF_2^+, SO^+, SO_2^+, $C_2F_4^+$, $C_2F_5^+$, CO^+, S^+, FCO^+, CF_2CO^+, SO_2F^+; [$C_3F_7C(O)OSO_2F$]: CF_3^+, CF^+, CO_2^+, $C_3F_5^+$, SO^+, SO_3^+, $C_2F_4^+$, $C_3F_6^+$, SO_2^+, $C_3F_7^+$, $C_2F_5^+$, S^+, CF_2^+, FCO^+, CO^+, $C_2F_3^+$; [$FOSO_2CF_2CF_2C(O)OSO_2F$]: SO^+, CF^+, SO_3^+, CO^+, SO_2^+, CO_2^+, CF_2^+, CF_3^+, $C_2F_4^+$, FCO^+, S^+, SO_2F^+, CF_2CO^+, $C_2F_3^+$, $C_2F_5^+$, $C_2F_3O^+$, $CF_2OSO_2F^+$, $C_2F_4OSO_2F^+$. No parent peaks were observed and $FO_2SOCF_2CF_2C(O)OSO_2F$ gives an unusual number of high-intensity peaks, relative to the other compounds. The reaction of $CF_3C(O)OSO_2F$, $ClCF_2C(O)OSO_2F$, $C_2F_5C(O)OSO_2F$, and $C_3F_7C(O)OSO_2F$ with aqueous sodium hydroxide can be represented by the general equation

$$R_fC(O)OSO_2F + 4OH^- = R_fCOO^- + SO_4^{2-} + F^- + 2H_2O$$

For $FO_2SOCF_2CF_2C(O)OSO_2F$ the following reaction appears to occur

$FO_2SOCF_2CF_2C(O)OSO_2F + 10OH^- =$



$$[O_2CCF_2CO_2]^{2-} + 2SO_4^{2-} + 4F^- + 5H_2O$$

In each case the stoichiometric amounts of reactants and products (other than water and R_fCOO^- and $[OOCCF_2COO]^{2-}$) were observed. No attempts were made to identify or measure R_fCOO^- and $[OOCCF_2COO]^{2-}$. $ClCF_2OSO_2F$ reacts with aqueous sodium hydroxide, but a good measurement of OH^- consumed was not obtained because buffer-type behavior of the products caused a vague end point in the titration. Table III gives analytical data for the compounds. The fluorine value obtained for $ClCF_2C(O)OSO_2F$ is unusually high due to partial hydrolysis of the $ClCF_2$ group.

Physical properties of the compounds are given in Table IV. The Trouton constants are high but reasonable for the perhaloacyl fluorosulfates. The temperatures at which the compounds have vapor pressures of 10, 20, 40, 60, 100, 200, 400, and 760 mm., respectively, are as follows. [$ClCF_2OSO_2F$]: −45.8°, −36.7°, −26.3°, −19.5°, −10.0°, 4.3°, 14.2°, 36.6°; [$ClCF_2C(O)OSO_2F$]: −8.1°, 1.5°, 12.7°, 19.7°, 29.8°,

TABLE IV

PHYSICAL PROPERTIES[a]

	ΔH_{vap}, kcal./mole	Trouton constant	Vapor density, g./g.m.v. Calcd.	Found
$ClCF_2OSO_2F$	7.13	23.0	184.5	186
$ClCF_2C(O)OSO_2F$	8.89	25.3	212.5	211
$C_2F_5C(O)OSO_2F$	8.29	24.8	246.0	245
$C_3F_7C(O)OSO_2F$	8.67	24.6	296.0	299
$FO_2SOCF_2CF_2C(O)OSO_2F$	10.57	26.2	326.0	324

[a] Vapor density of $CF_3C(O)OSO_2F$: 196 calcd.; 196 found. Other physical properties of this compound have been determined by J. J. Delfino and J. M. Shreeve, *Inorg. Chem.*, **5**, 308 (1966).

44.7°, 61.2°, 78.3°; [$C_2F_5C(O)OSO_2F$]: −21.0°, −11.6°, −0.9°, 5.8°, 13.5°, 28.9°, 45.0°, 61.2°; [$C_3F_7C(O)OSO_2F$]: −5.0°, 4.3°, 16.5°, 23.2°, 33.4°, 48.3°, 54.9°, 78.9°; [$FO_2SOCF_2CF_2C(O)OSO_2F$]: 34.7°, 45.7°, 57.9°, 65.8°, 76.7°, 93.1°, 111.4°, 130.0°.

Experimental Section

Reagents.—$S_2O_6F_2$ was prepared and purified according to the method described by Shreeve and Cady.[9]

The anhydrides were obtained from commercial sources and were purified by distillation.

Infrared spectra were studied using a Beckman I.R.-10 spectrometer. Gaseous samples were contained in a 10-cm. Pyrex glass cell fitted with silver chloride windows.

Nuclear magnetic resonance spectra were obtained by use of a Varian Model 4311B high-resolution spectrometer with a 40- or 54.6-Mc. oscillator. Perfluoroacetic acid was used as an external reference. Areas of the absorption peaks were measured using a Keuffel and Esser Co. compensating polar planimeter.

Mass spectra were recorded at 70 v. using a Consolidated Engineering Corp. Type 21-103 mass spectrometer.

Vapor pressures were determined using the method commonly employed in this laboratory.[10] A smooth curve was fitted to the points and values given were taken from these curves. Heats of vaporization and Trouton constants were calculated from the Clausius–Clapeyron equation using the slopes of the vapor pressure curves at the normal boiling point.

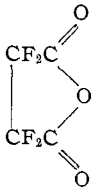
Melting points were not determined, because all the compounds formed glasses at low temperatures under all conditions tried.

Vapor densities were determined using a calibrated Pyrex glass bulb with stopcock, and values were determined on successive fractions of each compound.

Separation of reaction products was accomplished by fractional codistillation[11] for all compounds except $FO_2SOCF_2CF_2C(O)OSO_2F$, which because of its low volatility was separated by trap-to-trap distillation. Identification of separated carbon dioxide and the known perfluoroalkyl fluorosulfates was made by comparison of their infrared spectra with known infrared spectra of the compounds.[12–15] The comparisons showed identical spectra in each case. In addition carbon dioxide was easily recognizable from its physical properties.

Chemical analyses were obtained for all new compounds by hydrolyzing weighed amounts (at least 1 g.) with excess standard aqueous sodium hydroxide (1.885 *N*) at 100° for 35 hr. Samples were contained in sealed evacuated Pyrex glass tubes. Aliquots of the resulting solutions were taken for sulfur and fluorine determinations. Sulfur was determined gravimetrically as barium sulfate. Fluorine was determined by steam distillation of fluorosilicic acid from sulfuric acid followed by titration with standard thorium nitrate solution using sodium alizarin sulfonate as the indicator. Aliquots for sulfur determination were first titrated with standard hydrochloric acid to the phenophthalein end point to determine the amount of base consumed in hydrolysis. For $ClCF_2OSO_2F$ chlorine was determined volumetrically by the Volhard method.

All reactions of $S_2O_6F_2$ were run in the same manner. (The molar amounts of starting materials varied slightly.) In a typical reaction, equimolar amounts of $S_2O_6F_2$ (0.018 mole) and $(CF_3CO)_2O$ (0.018 mole) were condensed into a 100-ml. Pyrex glass reaction tube (35 mm. o.d.). The tube was fitted with a break-seal at one end and a ground joint at the other. After condensing in the reactants, the tube was sealed under vacuum and heated in a steam bath. The course of the reaction was followed by the color. When the characteristic yellow of SO_3F radical was no longer visible (approximately 3 hr.) heating was stopped and the products were separated. The product consisted almost completely of $R_fC(O)OSO_2F$, R_fOSO_2F, and CO_2. Trace amounts of carbonyl fluoride and silicon tetrafluoride were observed. In addition, a small amount of a liquid residue of low volatility and high oxidizing strength remained in the reaction tube after distilling away the principal products. The time for complete reaction for equal amounts of starting materials was approximately the same for $(CF_3CO)_2O$, $(ClCF_2CO)_2O$, $(C_2F_5CO)_2O$, and $(C_3F_7CO)_2O$. For



the reaction was much slower, requiring several days. When the same amounts of $(CF_3CO)_2O$ and $S_2O_6F_2$ were condensed into a 500-ml. Pyrex glass bulb and allowed to react at 100°, the time required for complete reaction was at least three times longer than for a 100-ml. bulb. Liquid and gaseous phases were present in both the 100-ml. and 500-ml. reaction vessels, but much less liquid was present when the larger bulb was used.

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