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POLYFLUOROALKYL SULFITES: PREPARATION AND PROPERTIES

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SUMMARY

The first polyfluoroalkyl sulfite esters have been prepared and characterized. These materials show considerably greater resistance to thermal decomposition, hydrolysis, and oxidation than non-fluorinated alkyl sulfites.

INTRODUCTION

Alkyl sulfite esters have been known for some time[1], although as a class of compounds they have been much less studied than the higher oxidation state sulfates, and no fluoroalkyl derivatives have been reported. These circumstances, coupled with recent interest in fluorinated >S=O derivatives[2-6] and the present availability of polyfluorinated alkanols, prompted us to synthesize the first polyfluoroalkyl sulfites and to compare their properties with those of the previously reported hydrocarbon analogs.

Although the polyfluoroalkanols alone (i.e., in the absence of a base) were surprisingly unreactive toward thionyl chloride, reaction of polyfluoroalkanol-amine adducts with thionyl chloride provided a facile route to the fluorinated sulfite esters:

$$R_fOH{\cdot}NEt_3 + SOCl_2 \rightarrow [R_fO]_2SO + Et_3N{\cdot}HCl, \quad \text{where}$$
$$R_f = CF_3CH_2,\ HC(CF_3)_2,\ CH_3C(CF_3)_2,\ C(CF_3)_3.$$

The fluoroalkyl sulfites were found to be significantly more stable than their non-fluorinated analogs.

RESULTS AND DISCUSSION

The direct, high-yield synthesis of polyfluoroalkyl sulfites via the reaction of $SOCl_2$ with polyfluoroalcanol-amine adducts in the absence of solvents was found to be a convenient method of of preparation. Although the intermediate 1:1 alcohol-amine adducts employed for this purpose were not studied in detail, they can probably best be described as covalent in each case[7]. Attempts to utilize ether as a solvent for these reactions, or to use other bases such as alkali metal fluorides, invariably led to lower yields of the sulfites and required much longer reaction times. Yields were also markedly affected by the order of addition when employing the amine adducts; reactions in which the amine was added to the thionyl chloride or in which the alcohol and amine were not premixed afforded much lower yields. This result was found to arise from a side reaction involving the $SOCl_2$ and free amine, although the nature of this reaction was not investigated. Other side reactions, such as the formation of the polyfluoroalkyl chlorides from the intermediate mono-substituted derivatives, were not found to be significant.

The polyfluoroalkyl sulfites are colorless liquids which freeze below room temperature to form white solids; boiling points, vapor pressures, and analytical data for these compounds are found in Table I. The higher Trouton constants and boiling points for the partially fluorinated derivatives, compared to the perfluoro-t-butyl case, may suggest some association involving hydrogen bonding. All of the fluoroalkyl sulfites were substantially more stable thermally than their unfluorinated analogs. For example, each of the fluorinated esters was recovered unchanged after heating for 22 hrs. at 200°C in Pyrex, whereas ordinary sulfites decompose readily under much less drastic conditions. In order to obtain a more quantitative comparison, a sample of the non-fluorinated isopropyl sulfite, $[HC(CH_3)_2]S{=}O$, prepared by the alcohol-amine-$SOCl_2$ method, was examined and found to begin to decompose within 2 hr. at 180°; after 15 hrs., ~80% of the material had decomposed to $HC(CH_3)_2OH$, $H_2C{=}C(H)CH_3$, and SO_2. In contrast, the fluorinated isopropyl sulfite $[HC(CF_3)_2O]_2S{=}O$ was heated at 180° for 100 hrs. and recovered without a trace of decomposition.

TABLE I. ANALYTICAL DATA

	$[CH_3CH_2O]_2SO$	$[HC(CF_3)_2O]_2SO$	$[CH_3C(CF_3)_2O]_2SO$	$[C(CF_3)_3O]_2SO$
Elemental Analysis[a]				
Carbon	19.41 (19.52)	18.41 (18.86)	23.04 (23.43)	18.38 (18.55)
Hydrogen	1.86 (1.64)	0.45 (0.53)	1.48 (1.47)	-
Sulfur	13.06 (13.03)	8.50 (8.39)	7.54 (7.82)	5.73 (6.19)
Fluorine	47.62 (46.31)	59.97 (59.66)	54.90 (55.58)	67.30 (66.00)
Vapor Pressure Data (Log P=A-b/T)				
a	8.44	8.36	8.43	7.75
b	2321	2216	2448	2018
ΔH_{vap} (kcal/mol)	10.68	10.14	11.2	9.24
ΔS_{vap} (eu)	25.6	25.1	25.0	22.3
B.p. (°C)	144.3	131.3	174.8	141.4
Yields (%)	74.0	81.2	65.4	68.7
G. C. Conditions				
Injector (°C)	160	125	155	130
Column (°C)	115	80	115	90
Flow (cc/min)	50	50	60	50

[a] Theoretical values in parentheses.

Table II. SPECTRAL DATA[a] (cm^{-1})

Infrared Spectra

$[CF_3CH_2O]_2SO$ 2980(w), 1453(w), 1410(m), 1293(ms), 1258(m), 1230(ms), 1183(vs), 1057(ms), 1024(vs), 969(ms), 852(mw), 790(brd,m), 725(brd,m), 649(w), 579(vw), 532(w)

$[HC(CF_3)_2O]_2SO$ 2991(w), 2975(w), 1368(s), 1303(s), 1287(sh, ms), 1265(sh,ms), 1242(vs), 1215(sh,s), 1180(w), 1119(s), 1081(m), 1045(s), 905(m), 879(m), 809(m), 761(s), 715(m), 692(ms), 590(w), 555(w), 530(w)

$[CH_3C(CF_3)_2O]_2SO$ 1467(w), 1400(w), 1385(w), 1311(s), 1272(sh,mw) 1259(sh,m), 1243(sh,s), 1232(vs), 1170(w), 1131(s), 1096(s), 929(ms), 801(w), 773(mw), 722(mw), 715(mw), 664(vw), 635(vw), 531(vw), 485(vw), 462(w)

$[C(CF_3)_3O]_2SO$ 1307(vs), 1288(vs), 1267(vs), 1231(sh,vw), 1192(vw), 1126(sh,w), 1090(w), 998(s), 984(s), 812(vw), 794(vw), 777(w), 759(vw), 732(m), 578(vw), 554(w), 538(vw)

Raman Spectra

$[CF_3CH_2O]_2SO$ 2990(24.0), 2947(82.1), 2843(7.9), 2770(7.0), 1454(18.8), 1414(3.1), 1295(12.7), 1285(13.1), 1232(33.6), 1172(13.1), 1039(11.8), 1012(10.5), 965(15.7), 847(100), 778(21.0), 702(6.1), 663(17.0), 645(20.5), 589(14.4), 550(19.7), 535(24.5), 473(3.9), 430(3.5), 380 (9.6), 364(10.5), 240(23.6), 224(18.8), 215(14.4), 150(6.1)

$[HC(CF_3)_2O]_2SO$ 2967(18.1), 1383(9.3), 1368(13.1), 1301(11.0), 1245(19.0), 1207(8.0), 1116(5.5), 1078(4.6), 1040(5.1), 908(5.9), 889(96.2), 806(2.5), 760(3.8), 734(100), 717(31.2), 691(7.2), 658(22.4), 569(20.3), 558(20.3), 551(8.9), 517(5.1), 474(6.3), 461(5.1), 413(9.3), 369(8.0), 331(54.0), 300(18.1), 260(11.0), 253(8.9), 229(24.1), 195(11.4), 144(9.7), 115(27.0)

$[CH_3C(CF_3)_2SO$	3020(16.4), 2960(86.5), 2897(12.2), 2765(3.2), 1467(13.2), 1395(7.1), 1315(9.8), 1363(10.3), 1257(25.4), 1220(7.0), 1126(3.2), 996(3.7), 920(5.3), 877(4.2), 795(3.4), 748(100), 718(10.8), 700(7.7), 655(8.2), 626(18.5), 602(11.6), 565(9.0), 534(8.5), 495(6.1), 462(2.6), 338(25.1), 314(18.3), 295(9.8), 244(5.3), 216(9.6), 192(7.7), 150(5.3)
$[C(CF_3)_3O]_2SO$	1298(30.3), 1268(9.3), 1227(3.1), 1191(0.9), 1150(0.9), 1119(0.9), 995(2.2), 785(7.7), 730(15.2), 717(9.9), 658(18.3), 581(5.6), 554(9.3), 535(13.9), 332(8.4), 316(39.0), 246(13.3), 224(9.6), 194(2.2), 167(5.6),

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[a] Relative intensity in parentheses.

The polyfluoroalkyl sulfites were also substantially more resistant to hydrolysis than the unfluorinated sulfites. A sample of $[HC(CH_3)_2O]_3S{=}O$ was found to be ~80% hydrolyzed to $HC(CH_3)_2OH$ and SO_2 after 16 hr. at 100° with an equimolar amount of water, whereas the completely fluorinated $[C(CF_3)_3O]_2S{=}O$ showed no hydrolysis after 16 hr. at 100°, and the partially fluorinated $[HC(CF_3)_2O]_2S{=}O$ and $[CF_3CH_3O]_2S{=}O$ were completely recovered after exposure to water for 16 hr. at 125°. In a longer term reaction, $[CF_3CH_2O]_2S{=}O$ was found to be only ~13.5% hydrolyzed after 92 hr. at 125°. The miscibility of the esters with water during the hydrolysis was also differed significantly in that the fluorinated samples were miscible at the onset of the study at room temperature, but the unfluorinated $[HC(CH_3)_2O]_2S{=}O$ was not completely miscible even after an hour at 100°C.

Infrared and Raman spectral data for the fluoroalkyl sulfites are tabulated in Table II. The C-H stretching vibrations are expectedly weak in the gas phase infrared spectra but reasonably strong in the Raman spectra. The assignment of the S=O stretching frequency is rather difficult owing to the overlap of the C-F stretching region. An attempt to estimate the probable stretching region was made by utilizing the Kagarise[8] empirical carbonyl stretching frequency relationship to estimate the effective electronegativities of the fluorinated alkoxy groups from the C=O frequencies of the corresponding fluoroalkyl chloroformates[9]. When the calculated effective electronegativity of each group was superimposed on the Szmant and Emerson[10] curve, the S=O stretching frequency was estimated to be between 1215 and 1240 cm^{-1}. This estimated range appears reasonable in comparison to the unfluorinated analogs which have strong S=O stretches[11] at approximately 1200 cm^{-1}. Assignments of other frequencies with any degree of certainty were not possible owing to overlap of bending and skeletal modes and the C-F stretches and deformations.

The mass spectra of the polyfluoroalkyl sulfites primarily reflect fragmentation of the alkyl and alkoxy groups. The appearance of a parent ion was noted only in the bis(trifluoroethyl) sulfite derivative, and this amounted to less than 1% of the trifluoroethyl base peak. Although the m/e 69 peak (CF_3^+) is usually very intense for derivatives containing CF_3^- groups, it was <20% for $[CF_3CH_2O]_2SO$. With the other derivatives, the CF_3^+ peak is the second most intense, except for the case of $[C(CF_3)_3O]_2SO$, where it is the base peak. Other major identifying peaks which are characteristic of these derivatives are m/e's corresponding to $R_fOS(O)^+$ or $R_fOSO_2^+$ in addition to SO_2^+ and SO^+.

The nmr spectra of the fluoroalkyl sulfite esters, summarized in Table III, show typical second-order effects arising from the nonequivalence of groups attached to the α-alkoxy carbon. These effects have been observed with the other >S=O derivatives[6,12-15] and are attributed to the existence of an asymmetric center at the sulfur atom. In the $[CF_3CH_2O]_2SO$ case, for example, the CF_3- group appears as a simple triplet but the CH_2- group appears as an ABX_3 spectrum. With the $HC(CF_3)_2O$- and $CH_3C(CF_3)_2O$-esters, the protons appear as simple heptets, but the CF_3- groups, when proton-decoupled, are A_3B_3 spectra, each consisting of two AB patterns. Because of these complexities, the data of Table III only represent the "evident" chemical shifts and coupling constants; a more detailed analysis of the spectra is in progress and will be given at a later date.

Unsuccessful attempts were made to oxidize the bis(perfluoro-t-butyl) sulfite ester to the bis(perfluoro-t-butyl) sulfur oxy-

TABLE III. NMR SPECTRAL DATA

	Chemical Shift[a] and		Coupling Constants (Hz)
$[CF_3CH_2O]_2SO$	CF_3 74.7 (t)	H 4.2	$J_{CF_3-H} \sim J_{CF_3-H'} = 8.0$
		H′4.4	$J_{H-H'} = 12.4$
$[HC(CF_3)_2O]SO$	CF_3 73.3	H 5.1 (hept)	$J_{CF_3-CF_3'} = 9.5$
	CF_3' 74.1		$J_{CF_3-H} \simeq J_{CF_3'-H} = 5.6$
$[CH_3C(CF_3)_2O]SO$	CF_3 74.8	CH_3 1.97 (hept)	$J_{CF_3-CF_3'} = 9.5$
	CF_3' 77.9		$J_{CF_3-H} \simeq J_{CF_3'-H} = 1.1$
$[C(CF_3)_2O]_2SO$	CF_3 70.5(S)		

[a] ^{19}F chemical shifts in ppm relative to $CFCl_3$; H chemical shifts in ppm downfield from TMS.

difluoride, $(R_fO)_2S(O)F_2$, <u>via</u> the Sauer-Shreeve ClF fluorination-oxidation reaction[6] and by direct fluorination. (The perfluoro-t-butyl derivatives was chosen with the expectation that it would be the least prone to side chain reactions and cleavage.) In both the ClF and the F_2 reactions, the products isolated in addition to unreacted sulfite were a result of cleavage either from direct reaction of the ClF and F_2 with the alkyl chain or from decomposition of a possible "hypohalite" intermediate produced by S-O bond cleavage:

$$[C(CF_3)_3O]_2SO \xrightarrow{XF} SOF_2 + [C(CF_3)_3OX] \rightarrow CF_3X + (CF_3)_2CO$$

where X = Cl or F.

The decomposition of R_fOX derivatives to give these products has been cited previously[17, 18]. These results are somewhat surprising in view of the ease with which perfluoroalkyl sulfoxides are oxidized to $(R_f)_2S(O)F_2$ by ClF and in view of the expected shielding of the S-O bond by the perfluoro-t-butyl group.

EXPERIMENTAL SECTION

Starting Materials: Thionyl chloride (Fisher Scientific Co.) was pumped in vacuo while held at -78° to eliminate SO_2; triethylamine (Eastman Organic Chemicals) was dried with CaO. The polyfluorinated alcohols CF_3CH_2OH, $HC(CF_3)_2OH$, $CH_3C(CF_3)_2OH$, and $C(CF_3)_3OH$ were obtained from PCR, Inc., and used as received. The ClF (Ozark-Mahoning) and F_2 (Matheson Gas Products) were also used as received. Elemental analyses were performed by PCR, Inc.

Apparatus: Gases and volatile liquids were handled in conventional Pyrex glass or stainless steel vacuum apparatus, and quantities were determined by PVT measurements. Infrared spectra were taken with a Perkin-Elmer Model 457 Spectrophotometer using an 8.5 cm Pyrex cell with KBr optics; Raman spectra were recorded from samples in sealed Pyrex capillaries with a Jarrell-Ash Model 500 Laser-Raman Spectrometer (4880 Å exciting line). Mass spectra were obtained on a Hewlett-Packard Model 5930A Spectrometer operating at 70 eV. The ^{19}F nmr spectra were recorded on a JEOL Model MH-100 instrument using $CFCl_3$ as an internal standard, and the ^{1}H nmr spectra were recorded on both the MH-100 and a Varian Model HA100 nmr spectrometer using TMS as a standard. Reaction products were initially separated crudely via fractional condensation using -23, -45 and -196° traps and then were purified by glc using a GOW-MAC Model 69-550 gas chromatograph fitted with an 8 ft x 0.25 in o.d. stainless steel column packed with 15% DCQF-1 on Chromosorb P.

General Preparation of Bis(polyfluoroalkyl) Sulfites: Each of the sulfites was made in essentially the same manner. The alcohol and amine in 1:1 ratio[7] were mixed in a 20 ml Pyrex reactor equipped with a Teflon stopcock and left at room temperature for 10-15 minutes with occasional agitation. In each case except

$C(CF_3)_3OH$, the mixture remained liquid. The alcohol-amine mixture was then cooled to -196°, the $SOCl_2$ (0.5 parts) was condensed in vacuo into the reactor, and the latter was then slowly warmed to room temperature in a -196° cooled dewar and kept at 25° for ~14 hr. with periodic shaking. The volatile contents were removed on a vacuum line and separated by fractional condensation. Final purification was effected by gas chromatography; the conditions used for each ester are found in Table I with the corresponding yields. The reactions were run using between 4 and 20 mmole of alcohol, with little change in the yields.

Reactions of Bis(polyfluoroalkyl) Sulfites:

1. Hydrolysis: Approximately 0.5 mmole of ester was condensed into a 20 ml Pyrex reactor fitted with a glass-Teflon valve, then accurately weighed. The vessel was then charged with 1 atm. of helium and an equivalent amount of distilled water was injected from a microliter syringe. The ester-water mixture was frozen to -196°, the helium was removed by pumping, and the vessel was heated in an oil bath to the desired temperature. Reaction progress was monitored by the appearance of SO_2 and alcohol infrared bands, followed by fractionation. The hydrolysis data are given in the Results and Discussion section.

2. Reaction with ClF: A 30 ml Hoke cylinder was charged with 1.0 mmole of $[C(CF_3)_3O]_2SO$ and 2.4 mmole ClF, then slowly warmed to room temperature in an empty -196° dewar. After 14 hr. at 25°, the reaction mixture was examined, but only unreacted starting material was found. The reaction was then heated at ~65° for 4 hr. (which produced only traces of unidentifiable material) and finally held for an additional 10 hr. at 65°; subsequent fractionation resulted in the identification of CF_3Cl, $(CF_3)_2CO$, SOF_2, and ~30% of the unreacted starting material.

3. Reaction with F_2: Approximately 0.75 mmole $[C(CF_3)_3O]_2SO$ and 1.0 mmole F_2 were added to a 30 ml Hoke cylinder. After a slow warm-up to room temperature in a dewar cooled to -196°, the vessel was left ~6 hr., then refrozen to -196°. An infrared spectrum of the non-condensable gases indicated CF_4 was present. After removal of the non-condensable gases, the reaction mixture was fractionated and CF_4, $(CF_3)_2CO$, SOF_2, and ~65% unreacted sulfite ester were identified as the only products.

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