HEXAFLUOROISOBUTENYLIDENE SULFATE

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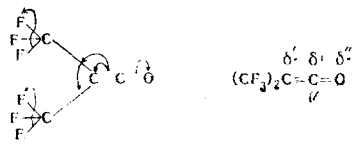
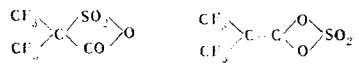
Hexafluoroisobutenylidene sulfate was obtained by treatment of hexafluorodimethylketene with sulfur trioxide. In the condensed phase, the product is a monomer–dimer equilibrium system. The heat and constant of equilibrium dimerization of hexafluoroisobutenylidene sulfate were estimated.

It is known that fluorine-containing β-sultones and β-pyrosultones are formed in the reaction of polyfluoroolefins with sulfur trioxide (see [1-3], for example). The corresponding β-alkoxy-containing compounds were similarly obtained when alkyl polyfluoroalkenyl ethers were treated with sulfur trioxide [4]. In all cases, the addition of sulfur trioxide to a multiple bond is realized in accordance with the polarity of the reacting substances. Both polyfluoroolefins and alkyl polyfluoroalkenyl ethers apparently act as electron-donor reagents with respect to sulfur trioxide, and the electron-donor character of the multiple bond in the ethers prevails over the electron-donor character of the ether oxygen. However, this position is not so indisputable in the case of hexafluorodimethylketene, the electron density distribution in which can be represented by the scheme



Owing to this sort of polarization, the addition of various addends to hexafluorodimethylketene is conceivable at both the carbon–carbon bond and at the carbonyl group. A study of the addition of sulfur trioxide to hexafluorodimethylketene therefore seemed of definite theoretical interest; the results of this investigation are examined in the present communication.

The reaction of hexafluorodimethylketene with sulfur trioxide occurs at even 0°C. Under these conditions, only one reaction product, which, according to analytical data, is a 1 : 1 adduct, was isolated. The structure of the adduct can apparently be described either by anhydride (I) or sulfate (II) structures.



I II

α-Hydrohexafluoroisobutyric and sulfuric acids are formed in the neutral hydrolysis of the adduct. This result forces us to reject the mixed anhydride structure I and can be explained only by the fact that the adduct is hexafluoroisobutenylidene sulfate (II).

$$\text{II} + 2\,H_2O \longrightarrow (CF_3)_2CHCOOH + H_2SO_4$$

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TABLE 1. Dependence of the Position of the Monomer–Dimer Equilibrium on Temperature

Equilibrium parameters		Temp., °C		
		34,5	50	70
Concn., %	Monomer	51,6	56,4	63,1
	Dimer	48,4	43,6	36,9
Concn., M	Monomer	3,58	3,92	4,38
	Dimer	1,68	1,52	1,28
K, liter/mole		0,132	0,0983	0,0667
$2+\lg K$		1,12	0,993	0,824

TABLE 2. Dependence of the Position of the Monomer–Dimer Equilibrium on the Adduct Concentration in CCl_4

Adduct concn., %	Concn., M		K, liter/mole
	monomer	dimer	
100	3,58	1,68	0.131
53	2,13	0,668	0,147
27,2	1,21	0,265	0,181
13,8	0,639	0,113	0,276
6,96	0,342	0,0461	0,394
3,5	0,182	0,0174	0,530

This conclusion is also in complete agreement with the results of the alkaline hydrolysis of the adduct, in which 11 equivalents of alkali are consumed, and six equivalents of fluoride ion and sulfate ion are detected in the hydrolyzate.*

$$\text{II} + 11\,^{-}OH \longrightarrow 6\,F^{-} + [HC(COO^{-})_3] + SO_4^{2-} + 5\,H_2O$$

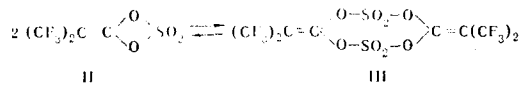
Such profound destruction of the adduct required an estimate of the stability of the starting hexafluorodimethylketene and α-hydrohexafluoroisobutyric acid and its anhydride under the conditions of alkaline hydrolysis. The results are in complete agreement.

$$(CF_3)_2C{=}C{=}O + 9\,^{-}OH \longrightarrow 6\,F^{-} + [HC(COO^{-})_3] + 4\,H_2O$$

$$(CF_3)_2CHCOOH + 9\,^{-}OH \longrightarrow 6\,F^{-} + [HC(COO^{-})_3] + 5\,H_2O$$

Thus there is no doubt that the adduct has the ketenal sulfate structure. At the same time, two singlet signals, which correspond to two nonequivalent trifluoromethyl groups, were unexpectedly detected in its F^{19} NMR spectrum. Moreover, it was found that the relative intensities of the signals of the chemical shift depend inversely on the temperature condition. When the temperature is raised, the integral intensity of one signal ($\delta_A = -12.7$ ppm relative to trifluoroacetic acid) increases, while the other ($\delta_B = -15.5$ ppm) decreases; just the opposite of this is observed when the temperature is lowered. These facts indicate that the adduct in the liquid state is an equilibrium mixture of two substances.

The quantitative characteristics of this equilibrium as a function of temperature (Table 1) and of the adduct concentration in various solvents (Tables 2 and 3) were obtained by NMR spectroscopy. We found that the chemical shifts remained constant as the adduct concentration changed, while the change in the integral intensity of the δ_A signal relative to the δ_B signal can be expressed by a quadratic function. This observation made it possible to assume that monomer (II) and dimer (III) forms of the adduct participate in the equilibrium.



Using the dependence of the position of the equilibrium on the temperature (Table 1), we estimated the thermal effect of the equilibrium reaction on the basis of the van't Hoff equation by a graphical method to give $\Delta H = -4$ kcal/mole. The relatively low thermal effect is explained by the fact that chemical bonds of close or even identical polarity are broken and formed during the dimerization; this satisfactorily confirms the participation of monomer II and dimer III in the equilibrium. The δ_A signal of -12.7 ppm is characteristic for the monomer, while the δ_B signal of -15.5 ppm is characteristic for the dimer. An additional confirmation of this conclusion was afforded by the results of a measurement of the relative intensities of the signals of solutions of the adduct. Both the solvents and the adduct concentrations were varied in the experiments (Tables 2 and 3); the temperature of the solutions was held constant at +34.5°. In all

*The percentage of methanetricarboxylic acid anion in the hydrolyzate, which is probably unstable and decomposes to give equivalent amounts of bicarbonate and malonate ions, was not determined.

$$[HC(COO^{-})_3] + H_2O \longrightarrow HCO_3^{-} + H_2C(COO^{-})_2$$

The bicarbonate ion is monobasic with respect to phenolphthalein, while the malonate ion is dibasic.

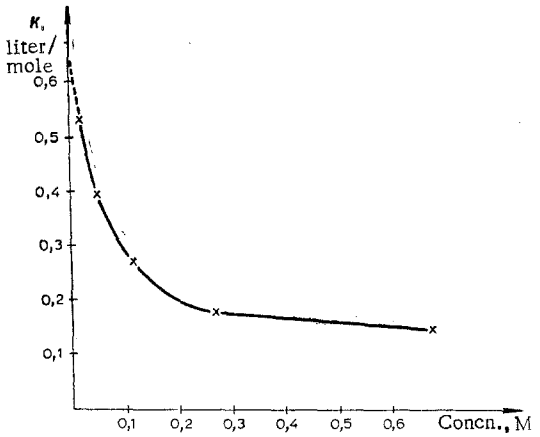


Fig. 1. Dependence of the monomer–dimer equilibrium constant on the adduct concentration in CCl_4.

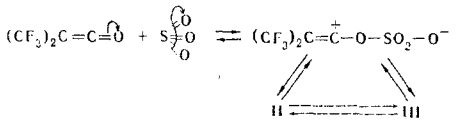
TABLE 3. Dependence of the Position of the Monomer–Dimer Equilibrium on the Adduct Concentration in Polar Solvents

Solvent	Adduct concn., %	Concn., M	
		monomer	dimer
—	100	3,58	1,68
$CHCl_3$	54,6	2,60	0,428
	28,6	1,43	0,148
	13,9	0,706	0,0570
	7,45	0,403	0,00163
	3,72	0,213	0,00014
$(CH_3)_2SO_4$	21,3	0,804	0,180
	10,9	0,508	0,0344
	5,6	0,285	0,0026

cases, the relative intensity of the monomer signal increases as the adduct concentration decreases, while the signal of the dimer decreases; this is in complete agreement with the probability of their formation in the equilibrium system.

Of course, the capacity of the monomer–dimer system for shifting the equilibrium to the left on dilution depends on the nature of the solvent. Thus comparable effects of shifts in the equilibrium are achieved in nonpolar carbon tetrachloride (Table 2) for considerably higher dilutions than in the polar solvents chloroform or dimethyl sulfate (Table 3). The observed effect of the solvents is associated with their different solvating capacities, which, in this system, are highest for polar solvents and lowest for nonpolar solvents. In all cases, this solvent effect does not make it possible to rigorously estimate the equilibrium constant. Thus, even in carbon tetrachloride, this constant changes by more than a factor of four as the adduct concentration changes from 100 to 3.5%. This value can be roughly estimated only by extrapolation to infinite dilution. This approximate evaluation was accomplished by a graphical method (see Fig. 1) on the basis of the data obtained in carbon tetrachloride; the equilibrium constant was found to be 0.6–0.65 liter/mole.

The results of physicochemical investigation and the known general concepts regarding the mechanism of sulfur trioxide addition to unsaturated compounds [5, 6] make it possible to propose the following scheme for the reaction of hexafluorodimethylketene with sulfur trioxide:



In the first step of the reaction, a dipolar ion is formed and can be stabilized by cyclization via two routes: intramolecularly to form a four-membered "monomer" and intermolecularly to form an eight-membered "dimer"; the formation of "trimers" and other higher associates is unlikely. It is interesting to note that a similar phenomenon was observed in the addition of sulfur trioxide to tetrafluoroethylene, in which a four-membered β-sultone and an eight-membered β-sultide formed simultaneously [2]. It can be assumed that the equilibrium association of the monomer and the dissociation of the dimer are realized through a dipolar ion, although the direct interconversion of these ketenal sulfates cannot be rejected. Moreover, the eight-membered compound proves to be thermodynamically more favorable, which is in agreement with the stereochemical concepts. Heating shifts the equilibrium to favor the monomer, which, being more volatile, can be isolated by distillation of the adduct.

The formation of hexafluoroisobutenylidene sulfate during the addition of sulfur trioxide to the ketene is in agreement with the known transformations of the latter. Thus hexafluorodimethylketene reacts with

TABLE 4. Results of the Alkaline Hydrolysis of Some Fluorine-Containing Compounds

Compound	No. of equivalents	
	OH^-	F^-
Hexafluoroisobutenylidene sulfate	11,15	6,06
Hexafluorodimethylketone	9,10	5,95
α-Hydrohexafluoroisobutyric acid	9,00	6,02
α-Hydrohexafluoroisobutyric anhydride	17,80	12,23

vinyl ethers [7], butadiene [8], silanes [9], and geminal diamines [10] by addition at the carbonyl group to form adducts of the ketenal type. The initial act in the extensively investigated reactions of hexafluorodimethylketene with nucleophilic reagents containing a labile hydrogen atom [11-14] is apparently addition at the carbonyl group; the adduct (anion or molecule) then rearranges to give the corresponding α-hydrohexafluoroisobutyric acid derivative. The isolation of α-hydrohexafluoroisobutyric acid derivatives in the latter reactions is associated with the lability of the enol compound of the ketenal type. It is natural that hexafluoroisobutenylidene sulfate, which is a ketenal, is extremely labile. This is manifested in its capacity for dimerization and hydrolysis and also for reaction with very many reagents. The various transformations of hexafluoroisobutenylidene sulfate will be examined in subsequent communications.

EXPERIMENTAL

Hexafluoroisobutenylidene Sulfate. A total of 23.7 g (0.297 mole) of freshly distilled sulfur trioxide was added in the course of an hour with shaking and ice cooling to 54.0 g (0.303 mole) of hexafluorodimethylketene in a flask equipped with a dry ice-cooled reflux condenser. The reaction was extremely exothermic. Subsequent fractionation isolated 75.0 g (97%) of hexafluoroisobutenylidene sulfate as a colorless, fuming (in air) liquid with bp 49°, d_4^{20} 1.7910, and n_D^{20} 1.3382. Colorless needle-shaped crystals formed when the liquid was cooled below −60°. Found: C 18.4; F 44.3; S 12.5%; MR_D 31.13. $C_4F_6O_4S$. Calculated: C 18.6; F 44.3; S 12.4%; MR_D 31.08.

Hydrolysis. Water [1.8 g (0.1 mole)] was added to 12.9 g (0.05 mole) of ice-cooled hexafluoroisobutenylidene sulfate. The reaction was exothermic. The liquid phase (sulfuric acid) was decanted. The residue (9.5 g, quantitative yield) was α-hydrohexafluoroisobutyric acid with mp 55°.

Alkalimetry. A weighed sample of the preparation (0.01-0.3 g) was dissolved in 20-30 ml of 0.1 N potassium hydroxide, and the excess alkali was back-titrated with 0.1 N hydrochloric acid (with respect to phenolphthalein). The percentage of fluoride ions (thoriometry) and sulfate ions (by a volumetric method) was determined in the hydrolyzate (see Table 4).

NMR Spectrometry. The F^{19} NMR spectra were recorded with an Hitachi-Perkin-Elmer spectrometer with a field strength of 14,092 Gauss at 56.456 MHz with a resolution of $3 \cdot 10^{-8}$. The chemical shifts (δ) were measured in parts per million relative to trifluoroacetic acid (external standard): 22.0 ppm for hexafluorodimethylketene, δ_A −12.7 ppm for hexafluoroisobutenylidene sulfate, and δ_B −15.5 ppm for its dimer. The position of the equilibrium was estimated on the basis of the relative integral intensities (Tables 1-3).

Dimerization Parameters. The quantitative characteristics of the equilibrium in liquid hexafluoroisobutenylidene sulfate were obtained by NMR spectroscopy at various temperatures (Table 1). The equilibrium constants were calculated assuming the presence of a monomer−dimer system:

$$K = \frac{[\text{dimer}]}{[\text{monomer}]^2}, \text{ [liter/mole]}.$$

The heat effect of the equilibrium dimerization (ΔH = −3970 cal/mole) was calculated on the basis of the log K = f(1/T) graph and the van't Hoff equation.

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