FLUOROSULFONYL-CONTAINING HETEROCYCLIC COMPOUNDS

V.* PYROLYTIC TRANSFORMATIONS OF HEXAFLUOROISOBUTENYLIDENE SULFATE

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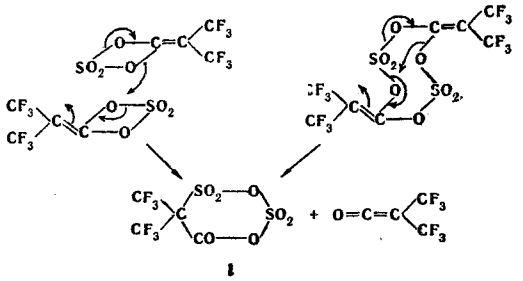
When hexafluoroisobutenylidene sulfate is heated above 80°C, hexafluorodimethylketene is liberated and the inner anhydride of hexafluoro-α-pyrosulfoisobutyric acid (I) is formed. On storage, anhydride I is spontaneously isomerized to hexafluoroisobutenylidene pyrosulfate, which is converted to the mixed anhydride of pentafluoromethacrylic and fluoropyrosulfonic acids on heating above 130° for many hours. On heating above 160°, I is decarboxylated to give hexafluoropropane-2,2-disulfonic acid anhydride, which is inclined to isomerize to pentafluoropropene-2-pyrosulfonyl fluoride.

It has been shown [2] that the sulfotrioxidation of hexafluorodimethylketene gives hexafluoroisobutenylidene sulfate, which exists in the liquid state as an equilibrium mixture of the monomer and dimer.

When the preparation is diluted with inert solvents or when the liquid preparation is heated to the boiling point (+49°), the equilibrium is shifted to favor the monomer. It seemed of interest to study the behavior of hexafluoroisobutenylidene sulfate under conditions in which the temperature exceeds the boiling point; this problem is also discussed in the present communication.

It was found that at 70-80° (in a sealed ampul) hexafluoroisobutenylidene sulfate undergoes a number of transformations: the F^{19} NMR spectra contains, in addition to two previous signals of the monomer and dimer, other singlets in the regions of trifluoromethyl and sulfonyl fluoride groups and a number of multiplets. Moreover, the degree of conversion of hexafluoroisobutenylidene sulfate increases as the heating time increases; a similar pattern is also observed under more severe temperature conditions. As a consequence, it was found that pyrolysis of hexafluoroisobutenylidene sulfate is accompanied by a number of secondary processes, as a result of which compounds of various structural types are formed.

The products of primary pyrolytic conversion of hexafluoroisobutenylidene sulfate – hexafluorodimethylketene and the inner anhydride of hexafluoro-α-pyrosulfoisobutyric acid (I) – could be isolated after brief heating of the preparation above 120° in a sealed glass ampul. The formation of these compounds is the result of "autosulfonation" of hexafluoroisobutenylidene sulfate; the process can be represented as intermolecular in monomer or as intramolecular in dimer.



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*See [1] for communication IV.

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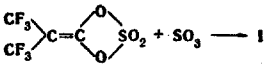
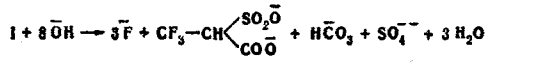
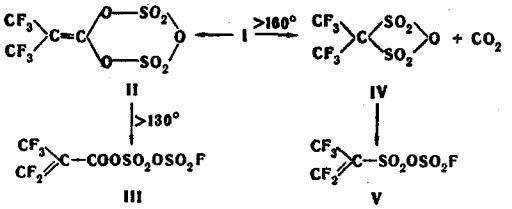
The correctness of these schemes is apparent from the following facts. It is known that hexafluoroisobutenylidene sulfate is characterized by the ability to sulfotrioxidize metal halides, ethers, amines [3], and even olefins [1]; in all cases, hexafluorodimethylketene is liberated. On the other hand, hexafluoroisobutenylidene sulfate can be sulfonated; this is confirmed by reaction with free sulfur trioxide, during which anhydride I is also formed.



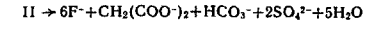
The structure of this compound was proved by F^{19} NMR spectroscopy and the results of alkaline hydrolysis.



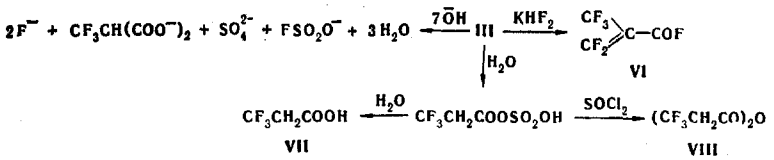
On prolonged storage, anhydride I is isomerized to hexafluoroisobutenylidene pyrosulfate (II).



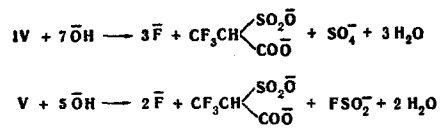
The structure of this compound is also confirmed by F^{19} NMR spectroscopy and the results of alkaline hydrolysis.



Six-membered cyclic ketenal pyrosulfate II is considerably more stable than four-membered hexafluoroisobutenylidene sulfate I. It does not form a dimer, and its pyrolytic lability is manifested only on heating for many hours above 130°; in this case, there is a new isomerization to give the mixed anhydride (III) of pentafluoromethacrylic and fluoropyrosulfonic acids. Various chemical transformations – reaction with potassium bifluoride and controllable alkaline and neutral hydrolysis – were used to prove the structure of this compound. The isolated pentafluoromethacrylyl fluoride, β,β,β-trifluoropropionic acid, and its anhydride (VI, VII, and VIII) were identified by gas–liquid chromatography and F^{19} NMR spectroscopy.



If the primary product of pyrolysis of hexafluoroisobutenylidene sulfate – anhydride I – is heated at 160-180°, it undergoes further decomposition: carbon dioxide is liberated. Moreover, the compound initially formed is the unstable hexafluoropropane-2,2-disulfonic acid anhydride (IV), which spontaneously isomerizes to pentafluoropropene-2-pyrosulfonyl fluoride (V) – relatively slowly at room temperature and rapidly at 160°. For proof of the structure of these two isomeric compounds, their alkaline hydrolysis was analyzed.

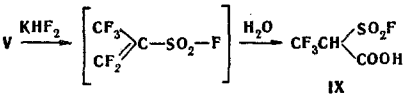


In addition, the structure of the latter isomer (the stable one) is confirmed by the F^{19} NMR spectrum and conversion of it to β,β,β-trifluoro-α-fluorosulfonylpropionic acid.

TABLE 1. Characteristics of the Isolated Compounds

Comp.	mp, °C	bp, °C	d_4^{20}	n_D^{20}	Found, equiv. OH⁻ with respect to phenolphthalein	Found, equiv. OH⁻ with respect to Methyl Orange	Found, equiv. F⁻	F^{19} NMR spectrum δ*, ppm	F^{19} NMR spectrum J, Hz
II	—	121	1,8200	1,3602	12,98	12,05	5,90	−15,2 s	
I	—	109	1,8402	1,3540	7,95	6,94	2,89	−14,8 s	
IV	—	142	1,8520	1,3622	7,03	6,98	3,03	−13,8 s	
VI	—	51	—	—	4,93	4,83	2,80	m	
III	43	105	—	—	7,21	7,12	2,14	m	
V	—	133	1,8260	1,3360	5,18	5,10	2,09	−144,0 s	
								−23,4 m	11,3
								−3,7 m	22,6
VII	0	153	—	—	1,10	0,95	0,0	−15,0 t	11,0
VIII	—	137	—	—	2,15	1,92	0,0	−12,2 t	8,0
IX	55	—	—	—	3,09	2,98	0,95	−138,0 s	
								−9,2 d	7,5

*Symbols: s, singlet; d, doublet; t, triplet; m, multiplet.



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Thus a chain of pyrolytic transformations that leads to a complex mixture of thermolysis products is realized when hexafluoroisobutenylidene sulfate is heated.

The physical properties of the isolated products are presented in Table 1.

EXPERIMENTAL

The F^{19} NMR spectra were recorded with a model R-20 Hitachi-Perkin-Elmer spectrometer with a field intensity of 14,092 Gauss and an operating frequency of 56.456 MHz; 20% solutions of the preparations in carbon tetrachloride (I, II, IV, and VI), in acetonitrile (III, V, VIII, and IX), or in water (VII) were used. The chemical shifts (δ, external standard) presented in Table 1 were measured relative to trifluoroacetic acid.

Inner Anhydride of Hexafluoro-α-pyrosulfoisobutyric Acid (I). A. A 25.6 g (0.1 mole) sample of hexafluoroisobutenylidene sulfate was heated in a sealed glass ampul at 120 ± 5° for 1 h. The contents were then fractionated to give 6.5 g (73%) of hexafluorodimethylketene and 13.0 g (77%) of I as a colorless fuming liquid. Found,%: C 14.2; F 34.0; S 18.4. $C_4F_6O_7S_2$. Calculated,%: C 14.2; F 33.7; S 18.8.

B. A mixture of 8.0 g (0.1 mole) of freshly distilled sulfur trioxide and 17.8 g (0.1 mole) of hexafluoroisobutenylidene sulfate was heated in a steel autoclave to 150 ± 5°. It was then cooled rapidly and distilled to give 30.4 g (90%) of I.

Hexafluoroisobutenylidene Pyrosulfate (II). Anhydride I was stored in a glass vessel at room temperature for 4-5 days. Fractionation gave II (87%) as a colorless fuming liquid. Found,%: C 14.1; F 33.9, S 18.6. $C_4F_6O_7S_2$. Calculated,%: C 14.2; F 33.7; S 18.8.

Mixed Anhydride (III) of Pentafluoromethacrylic and Fluoropyrosulfonic Acids. Pyrosulfate II was heated in a sealed glass ampul at 130-140° for 10-12 h. Subsequent fractionation gave III (62%) as white low-melting crystals. Found,%: C 14.5; F 34.0; S 18.4. $C_4F_6O_7S_2$. Calculated,%: C 14.2; F 33.7; S 18.8.

A solution of 16.9 g (0.05 mole) of anhydride III in 30 ml of dry chlorobenzene was added slowly dropwise to 7.8 g (0.1 mole) of potassium bifluoride. Distillation of the mixture yielded 11.7 g (76%) of pentafluoromethacrylyl fluoride, which was identified from its physical properties [4], by GLC, from its IR spectrum ($\nu_{C=C}$ 1700 cm^{-1}, $\nu_{C=O}$ 1835 cm^{-1}), and from the results of alkaline hydrolysis.

Hydrochloric acid (sp. gr. 1.19) was added slowly dropwise to 33.8 g (0.1 mole) of anhydride III, during which the formation of a crystalline substance was observed; the reaction was stopped when the crystals began to dissolve. Filtration on a glass filter yielded 11.0 g (53%) of crystalline β,β,β-trifluoropropionylsulfuric acid (alkali equivalents found 3.03). The product was distilled, and the fraction with bp 60-80° (50 mm) was selected; refractionation yielded 4.1 g (32%) of β,β,β-trifluoropropionic acid. Found,%: C 27.7; H 2.9; F 43.8. $C_3H_3F_3O_2$. Calculated,%: C 28.2; H 2.4; F 44.5.

An 11.9 g (0.1 mole) sample of thionyl chloride was added slowly dropwise to a mixture of 10.5 g (0.05 mole) of β,β,β-trifluoropropionylsulfuric acid and 3.7 g (0.05 mole) of potassium chloride. Fractionation of the mixture yielded 4.0 g (67%) of β,β,β-trifluoropropionic anhydride, which was identified by GLC, F^{19} NMR, and alkalimetry.

Hexafluoropropane-2,2'-disulfonic Acid Anhydride (IV). A 33.8 g sample of I was heated to 180° in a steel autoclave, after which the contents were rapidly cooled to room temperature and distilled to give 26.1 g (89%) of IV as a fuming liquid with light-green opalescence. Found,%: C 12.5; F 38.2; S 21.3. $C_3F_6O_5S_2$. Calculated,%: C 12.1; F 38.8; S 21.8.

Pentafluoropropene-2-pyrosulfonyl Fluoride (V). Anhydride IV was heated at 160° for 10 h. Fractionation yielded V (84%) as a light-green liquid. Found,%: C 12.4; F 38.5; S 21.9. $C_3F_6O_5S_2$. Calculated,%: C 12.2; F 38.8; S 21.8.

A 14.5 g sample of V, cooled to 0°, was added with shaking to 3.5 g of potassium bifluoride. Subsequent distillation yielded a fraction passing over at 50-75° (7.0 g). This fraction was dissolved in 10 ml of chloroform, and 1 ml of water was added to the solution at 60°. Cooling of the solution to 0° gave a precipitate which, on workup, gave 5.9 g (69%) of β,β,β-trifluoro-α-fluorosulfonylpropionic acid as white prism-shaped crystals with mp 55°. Found,%: C 17.4; H 1.2; F 36.6; S 15.0. $C_3H_2F_4O_4S$. Calculated,%: C 17.4; H 1.0; F 36.3; S 15.2.

Alkalimetry. A weighed sample (0.03-0.06 g) of the preparation was dissolved in 10-20 ml of 0.1 N potassium hydroxide, and the solution was then allowed to stand 10-15 min. The excess alkali was then titrated with 0.1 N hydrochloric acid, initially with respect to phenolphthalein and then, with alkali, with respect to Methyl Orange. The fluoride ion content in the alkaline hydrolyzate was determined by a thoriometric method. The analytical results are presented in Table 1.

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