FLUOROSULFONYL-CONTAINING HETEROCYCLIC COMPOUNDS

II.* PROPERTIES OF HEXAFLUOROISOBUTENYLIDENE SULFATE

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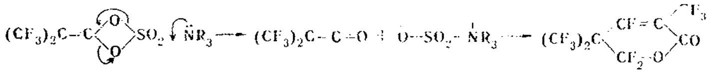
The reactions of hexafluoroisobutenylidene sulfate with tertiary amines, ethers, sulfolane, and alkali metal halides were studied. Hexafluorodimethylketene is liberated, and the reagent is sulfotrioxidized during the reaction of hexafluoroisobutenylidene sulfate with these nucleophilic compounds. Hexafluoroisobutenylidene sulfate is an electrophilic compound of the quasicomplex type, which contains a labile sulfotrioxide grouping.

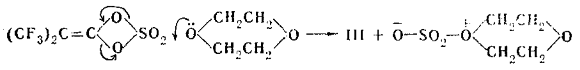
It has been demonstrated that hexafluoroisobutenylidene sulfate (I) [1] is formed in quantitative yield in the reaction of hexafluorodimethylketene with sulfur trioxide. Compound I is extremely reactive and reacts vigorously with various nucleophilic compounds – water, alcohols, ethers, esters, alkyl halides, aldehydes, ketones, amines, olefins, etc. Some of these reactions are examined in the present communication.

Hexafluoroisobutenylidene sulfate decomposes exothermically at 0°C under the influence of tertiary amines. When excess amine was used in an inert solvent, the dimeric (to hexafluorodimethylketene) unsaturated δ-lactone (II) and the aminosulfotrioxide were obtained. The generation of hexafluorodimethylketene (III), which is inclined to dimerize in the presence of tertiary amines [2], undoubtedly precedes the formation of the δ-lactone.

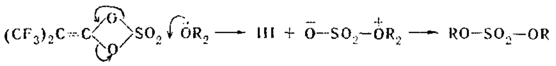


I III II

Ketene III and dioxane sulfotrioxide are similarly formed in the reaction of hexafluoroisobutenylidene sulfate with dioxane.



If a noncyclic ether is used as the nucleophilic reagent, the sulfotrioxide complex isomerizes to the sulfate compound. Thus the ketene and diethyl sulfate were isolated from the reaction of hexafluoroisobutenylidene sulfate with diethyl ether.



An exothermic reaction, accompanied by the quantitative liberation of ketene and the formation of a crystalline precipitate, occurs when hexafluoroisobutenylidene sulfate is dissolved in anhydrous sulfolane. A similar precipitate is also formed in the reaction of free sulfur trioxide with sulfolane; it has been assumed [3] that this crystalline substance is a 1:1 adduct. In our experiments, on the basis of alkalimetry, it was

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*See [1] for communication I.

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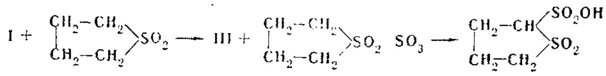
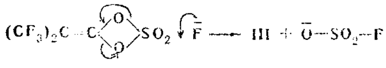
demonstrated that this quasicomplex compound is unstable and isomerizes on heating; the final reaction product is apparently α-sulfolanesulfonic acid.



Ketene is generated and potassium fluorosulfate forms when hexafluoroisobutenylidene sulfate or its solutions in inert solvents are shaken with potassium fluoride.



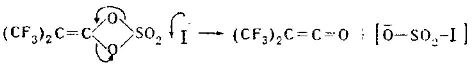
It is interesting that hexafluoroisobutenylidene sulfate is absolutely inert to dry potassium chloride and can even be distilled over this salt. This phenomenon becomes understandable if one considers that alkali metal chlorosulfates are unstable and dissociate to metal chlorides and sulfur trioxide [4]. The latter is capable of sulfonating ketene if it is generated in the first step of the reaction, and hexafluoroisobutyenylidene sulfate would be again formed. On the whole, the starting system is regenerated; the observed effect is the absence of a reaction.

$$\mathrm{I + KCl \longrightarrow III + [KO{-}SO_2{-}Cl] \qquad [KO{-}SO_2{-}Cl] \longrightarrow [SO_3] + KCl}$$

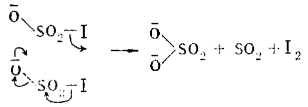
$$\mathrm{III + [SO_3] \longrightarrow I}$$

When a solution of hexafluoroisobutenylidene sulfate in an inert solvent is shaken with potassium bromide or iodide, an intense coloration of the mixtures is observed, and gaseous reaction products are evolved. In analytical experiments with potassium iodide it was demonstrated by the hyposulfite method that one mole of hexafluoroisobutenylidene sulfate causes the liberation of one equivalent of iodine. If the reaction mixture is treated rapidly with aqueous acetic acid, the color disappears. Hexafluorodimethylketone and sulfur trioxide were isolated in preparative experiments.

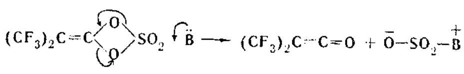
It can be assumed that, as in the previous cases, ketene is liberated and the reagents undergo sulfooxidation in the first stage of the process, for example,



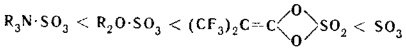
The iodosulfate and bromosulfate formed are unstable and rapidly decompose. It is possible that their destruction is realized in the crystal via a push–pull mechanism.



Thus, in the reactions under consideration, hexafluoroisobutenylidene sulfate acts as an effective electron-acceptor compound that contains an extremely labile sulfotrioxide grouping. Sulfotrioxidation of the reagent used occurs in all of the investigated cases.



The sulfotrioxidizing capacity of hexafluoroisobutenylidene sulfate considerably exceeds that of such substances as pyridine sulfotrioxide and dioxane sulfotrioxide and is inferior only to free sulfur trioxide.



$$\mathrm{R_3N{\cdot}SO_3 < R_2O{\cdot}SO_3 < (CF_3)_2C{=}C\langle{}^{O}_{O}\rangle SO_2 < SO_3}$$

Owing to this, hexafluoroisobutenylidene sulfate can be used for the sulfonylation of various halgen-, oxygen-, and nitrogen-containing compounds. It was subsequently found that it is a convenient reagent also for C-sulfonation; reactions of this type will be examined in a separate communication.

EXPERIMENTAL

Reaction with Triethylamine. A 25.8-g (0.1 mole) sample of hexafluoroisobutenylidene sulfate was added slowly dropwise with stirring at 0°C to a solution of 10.1 g (0.1 mole) of triethylamine in 20 ml of anhydrous methylene chloride. The reaction was exothermic and gave a crystalline precipitate. The precipitate was removed by filtration and recrystallized twice from water to give 17.4 g (96%) of triethylamine sulfotrioxide with mp 92° C. This product did not depress the melting point of an authentic sample. The mother liquor was fractionated to give 16.7 g (94%) of δ-lactone II, which was identified from its physical properties [2] and by F^{19} NMR spectroscopy.

Reaction with Dioxane. A 25.8-g sample of hexafluoroisobutenylidene sulfate was added slowly dropwise with stirring at 0° C to 10 ml of anhydrous dioxane. The reaction was exothermic and gave a crystalline precipitate. The reaction mixture was heated to 20° C, and dry nitrogen was bubbled through it for 1 h. The gaseous products that evolved during the reaction were condensed in a trap cooled with acetone–dry ice. The condensate was fractionated to give 12.8 g (72%) of hexafluorodimethylketene, which was identified by NMR spectroscopy. The crystalline precipitate was isolated from the reaction mixture by filtration under nitrogen and was washed repeatedly with anhydrous methylene chloride to give 10.7 g (64%) of dioxane sulfotrioxide, which was identified by alkalimetry. Found: equivalent weight (E) 82.3. Calculated: E 84.0.

Reaction with Diethyl Ether. A 25.8-g sample of hexafluoroisobutenylidene sulfate was added slowly dropwise with stirring at 0° C to 10 ml of anhydrous ether. The reaction was exothermic, and the mixture became colored. Fractionation of the mixture gave 12.1 (68%) of hexafluorodimethylketene and 9.4 g (61%) of diethyl sulfate, which was identified from its physical properties and molecular weight and by gas-liquid chromatography (GLC). Found: mol. wt. 151. Calculated: mol. wt. 154.

Reaction with Sulfolane. A 25.8-g sample of hexafluoroisobutenylidene sulfate was added slowly dropwise under dry nitrogen to 20 ml of anhydrous sulfolane at 18-20° C. The reaction was exothermic and produced a white crystalline precipitate and gases, which were condensed in a trap cooled with acetone–dry ice. Fractionation of the condensate gave 15.0 g (85%) of hexafluorodimethylketene. The crystalline precipitate was separated from the reaction mixture by filtration under nitrogen and was washed repeatedly with anhydrous methylene chloride to give 15.2 g (76%) of sulfolane sulfotrioxide. Found: S 31.8%; E (alkalimetry) 104. $C_4H_8O_5S_2$. Calculated: S 32.0%; E 100. The product partially liquified even during brief storage at room temperature. On heating above 40-50° C for 1 h, the precipitate was completely converted to a yellow viscous liquid, which was found to be α-sulfolanesulfonic acid. Found: S 31.8%; E (alkalimetry) 192. $C_4H_8O_5S_2$. Calculated: S 32.0%; E 200.

Reaction with Potassium Fluoride. A 25.8-g (0.1 mole) sample of hexafluoroisobutenylidene sulfate was added dropwise with stirring at 0° C to a suspension of 5.8 g (0.1 mole) of potassium fluoride in 10 ml of of methylene chloride (chloroform, carbon tetrachloride, or dichloroethane). Dry nitrogen was then bubbled through the mixture for 1 h. The liberated hexafluorodimethylketene [16.4 g (92%)] was collected in a trap. The precipitate was separated by filtration and recrystallized from 50% alcohol to give 13.2 g (96%) of potassium fluorosulfate. Found: F 14.0; S 23.0%. KFO_3S. Calculated: F 13.8; S 23.2%. A qualitative nitrone test was positive.

Reaction with Potassium Bromide and Iodide. A) A solution of hexafluoroisobutenylidene sulfate (0.1-0.2 g) in 10 ml of anhydrous dichloroethane was shaken vigorously for 5 min with 1 g of potassium iodide, during which the mixture became lilac-violet. After 1 h, 1 ml of acetic acid and 10 ml of water were added to the mixture. After 15 min, the mixture was titrated with 0.1 N sodium hyposulfite with starch as the indicator. Found: I 0.96 g-eq.

B) Similarly, 0.85 g-eq of Br was found in the reaction with potassium bromide.

C) A 25.8-g (0.1 mole) sample of hexafluoroisobutenylidene sulfate was added dropwise with stirring to a mixture of 32.2 g (0.2 mole) of potassium iodide and 20 ml of anhydrous dichloroethane (carbon tetrachloride, chloroform or methylene chloride). The gaseous products were condensed in a trap cooled with acetone–dry ice. Fractionation of the condensate gave 2.4 g of sulfur dioxide (75%), which was identified from its molecular weight and by GLC, and 15.0 g (84%) of hexafluorodimethylketene, which was identified by GLC and F^{19} NMR spectroscopy.

D) Similarly, sulfur dioxide (70%) and hexafluorodimethylketene (91%) were isolated from the reaction with potassium bromide.

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