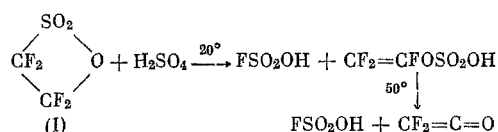


FLUORINE-CONTAINING β -SULTONES
 COMMUNICATION 42. NEW METHOD FOR PREPARATION OF
 FLUOROSULFONIC ACID

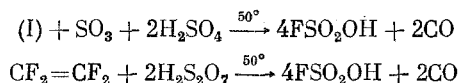
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It is known that the reaction of tetrafluoroethane- β -sultone (I) with H_2SO_4 gives FSO_3H and the labile trifluorovinylsulfuric acid, which decomposes at $50^\circ C$ into FSO_3H and the difluoro ketone [1], which in turn decomposes rapidly to give CO and tetrafluoroethylene [1, 2]



The latter when reacted with SO_3 is easily converted to (I) [3, 4]. In view of what has been said it is logical to assume that the following processes can be realized:

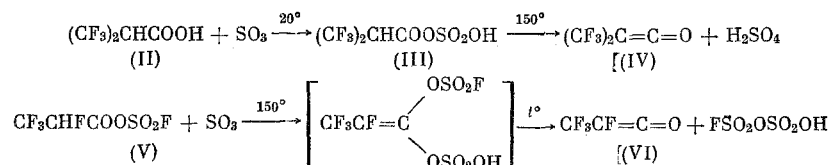


A description of such reactions is the subject of the present communication.

It proved that CO is evolved when a solution of (I) in 30% oleum is heated above 20° , the amount of which reaches the theoretical amount when a mixture with the composition (I) : SO_3 : H_2SO_4 = 1 : 1 : 2 is heated up to 50° . FSO_3H was isolated in over 90% yield when the residue was fractionally distilled.

The second process, based on the use of tetrafluoroethylene, arouses much more interest. The passage of this compound through pyrosulfuric acid (50% oleum), heated up to 50° , results in the quantitative evolution of CO and the formation of analytically pure FSO_3H , which makes it possible to regard this reaction as a method for the preparation of FSO_3H .

Previously it was shown that the reaction of α -hydrohexafluoroisobutyric acid (II) with SO_3 gives the stable α -hydrohexafluoroisobutyrylsulfuric acid (III), the hydrolysis of which leads to the stable hexafluoro-dimethylketene (IV) [5]. In like manner, the reaction of α -hydrotetrafluoropropionyl fluorosulfate (V) with SO_3 gives the labile trifluoromethylfluoro ketone (VI), which was isolated as the isomeric trifluoroacryloyl fluoride [6]



The formation of these fluorine-containing ketones from the derivatives of α -hydropolyfluorocarboxylic acids is undoubtedly associated with the relative lability of the α -C-H bond. It is possible to

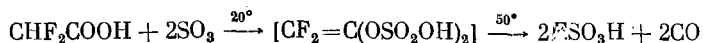
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assume that the simplest homolog of these acids, namely difluoroacetic acid, is capable of reacting in a similar manner to give the unstable difluoroketene, which on decomposition gives CO and tetrafluoroethylene (or tetrafluoroethane- β -sultone or FSO₃H).

Actually, an exothermic reaction is observed when difluoroacetic acid is mixed with SO₃ in a 1:2 ratio, which is accompanied by the evolution of CO and tetrafluoroethylene (GLC), and the formation of FSO₃H (nitron test).

A similar result is also achieved by running the process in an autoclave. It is clear that this process is multistep, and that one of the intermediate products is difluoroketene, which is probably formed by the decomposition of the unstable difluoroethylidene-bis-sulfuric acid (cf. above).



As a result, the end product of the reaction of difluoroacetic acid, difluoroketene, tetrafluoroethylene, and tetrafluoroethane- β -sultone (under the appropriate conditions) with SO₃ is FSO₃H, the yield of which is limited mainly by the amount of difluoromethylene groups in the starting compound. It is possible to assume that this process is also typical for other compounds, in which the difluoromethylene group is connected by either a single or a double bond to a monatomic carbon grouping.

EXPERIMENTAL METHOD

Reaction of Tetrafluoroethane- β -sultone with Oleum. To a stirred solution of 4.0 g of SO₃ in 9.8 g of 100% H₂SO₄ at ~20° was slowly added 9.0 g of tetrafluoroethane- β -sultone in drops; here slight heat evolution was observed and the formation of a homogeneous viscous mass. Subsequent slow heating from 20 to 50° in an hour resulted in the evolution of 2.0 liters (89%) of CO (GLC and test with PdCl₂). The residue was fractionally distilled to give 18.2 g (91%) of FSO₃H.

Reaction of Tetrafluoroethylene with Pyrosulfuric Acid. In a Teflon reactor, equipped with a dropping funnel, a gas-inlet tube and a reflux condenser, was placed 96.0 g of 100% H₂SO₄. With cooling in an ice-salt mixture, 80.0 g of freshly-distilled SO₃ was slowly added in drops. Then 12 liters of dry tetrafluoroethylene was passed in at 50° at such a rate as to assure its complete solution (10-20 ml/min). Here 22.5 liters of CO was evolved. The residue represented 200 g (100%) of colorless analytically pure FSO₃H.

Reaction of Difluoroacetic Acid with SO₃. To 9.6 g of difluoroacetic acid at 40-50° was slowly added (in 2-2.5 h) 16.0 g of SO₃ in drops. Here 18 liters of CO was evolved. Fractional distillation of the residue gave 14.8 g (74%) of FSO₃H.

A mixture of the same reactants was heated in a steel autoclave at 40-50° for 2 h. Here we collected 21 liters of CO and obtained 16.2 g (81%) of FSO₃H.

CONCLUSIONS

1. The reaction of tetrafluoroethylene with pyrosulfuric acid leads to the quantitative formation of analytically-pure fluorosulfonic acid.
2. The reaction of difluoroacetic acid with sulfur trioxide leads to the formation of carbon monoxide and fluorosulfonic acid.

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