## ELECTROCHEMICAL FLUOROSULFATION OF TETRAFLUOROETHYLENE

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Electrooxidation of certain fluoroolefins on platinum and glass-carbon in fluorosulfonic acid has been studied. The large difference in oxidation potentials of tetrafluoroethylene and the fluorosulfate anion makes it possible to carry out fluorosulfation via an ECEC mechanism. Potentiostatic preparative electrolysis at limiting-current potentials for oxidation of tetrafluoroethylene (E = 1.5 V) yields a mixture of  $\alpha, \omega$ -bis-fluorosulfates which is almost quantitative with respect to current, the main component being 1,2-bis(fluoro-sulfato)tetrafluoroethane.

Interaction of electrochemically generated peroxodisulfuryldifluoride (I) with fluoroolefins is a convenient preparative method for synthesis of various bisfluorosulfates which are formed both by addition of (I) to the double bond and as a result of fluorosulfate dimerization and oligomerization of fluoroolefins by the action of (I) [1, 2].

Traditionally the mechanism of electrochemical fluorosulfation is treated as anodic oxidation of the fluorosulfate anion with subsequent radical addition of the resulting (I) to the fluoroolefin [1]. In addition an alternative route is theoretically possible for formation of organic fluorosulfates in this process: preliminary anodic oxidation of the fluoroolefin and interaction of the resulting cation-radical with the  $FSO_3^-$  anion. A similar EC mechanism has been proposed for trifluoroacetoxylation or fluorosulfation of aromatic compounds [3, 4].

Obviously the path selected for fluorosulfation of fluoroolefins during electrolysis in fluorosulfonic acid will be determined by the difference in oxidation potentials of the  $FSO_3^-$  anion and the fluoroolefin.

The study of anodic oxidation of fluoroolefins (II) - (V) on glass-carbon and platinum electrodes showed that in fluorosulfonic acid the oxidation half-wave potential increases regularly on passing from tetrafluoroethylene to its mono- and disubstituted analogs (Table 1 and Fig. 1).

The increase in the difference in oxidation potentials of the fluorosulfate anion and olefins (II)-(IV) on replacing the glass-carbon anode by platinum is due both to a shift in the discharge potential of the fluorosulfate anion to the positive side resulting from formation of multilayer oxides on the platinum [5], and to a shift in the oxidation potential of the fluoroolefins to the negative side resulting from increase in their adsorbability on the platinum electrode. Oxidation of the fluoroolefins on glass-carbon and on platinum is characterized by an irreversible oxidation wave and has a predominantly diffusion character. At the same time the role of an adsorption stage is very clearly revealed during oxidation of tetrafluoroethylene on platinum in anhydrous trifluoroacetic acid. Here its oxidation potential is shifted by 1.0 V to the positive side compared with that in fluorosulfonic acid and oxidation of the olefin takes place simultaneously with discharge of the  $CF_3COO^-$  anion.

It is suggested that the potential shift to the anodic side is determined by stronger adsorption of  $CF_3COO^-$  compared with fluorosulfate, abruptly reducing the coverage of the

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Fig. 1. Anodic voltamperograms of a glass-carbon electrode in  $FSO_3H/0.25 \ M \ FSO_3K$  (1) and in the presence of fluoroolefins: (II) saturated solution at 1 atm (2); (III) saturated solution at 1 atm (3); (IV)  $1.3 \cdot 10^{-2} \ mole/liter$  (4); (V)  $2.5 \cdot 10^{-1} \ mole/liter$  (5). Rate of potential sweep 0.05 V/sec. Electrode surface  $3.1 \cdot 10^{-2} \ cm^2$ .

TABLE 1. Half-Wave Potentials for Oxidation of Certain Fluoroolefins and Potentials for Start of Discharge of the Fluorosulfate Anion in  $FSO_3H/0.25$  M  $FSO_3K$  on Smooth Platinum and Glass-Carbon

Compound	E <sub>1/2</sub> (GC)	E for start of FSO <sub>3</sub> dis- charge, V(GC)	E <sub>1/2</sub> (Pt)	E for start of FSO <sub>3</sub> dis- charge, V(Pt)
$CF_2=CF_2 (II)$ $CF_3CF=CF_2 (III)$ $CF_3CF_2CF_2CF=CF_2 (IV)$ $(CF_3)_2CFCF=CFCF_3 (V)$	$\begin{vmatrix} 1,3 \\ 1,9 \\ 1,9 \\ >2,0 \end{vmatrix}$	>1,95	1,2 1,8 1,8 >2,2	>2,2

surface by the olefin and increasing the oxidation potential of the double bond. Involvement of the electrode surface in this reaction is also corroborated by the fact that changing from glass-carbon to platinum appreciably lowers the rate of fluorosulfate oxidation (Fig. 2).

It is clear from the data shown in Table 1 and Fig. 2 that the greatest difference in oxidation potentials of the fluorosulfate anion and fluoroselfins is observed for tetra-fluoroethylene. On platinum this difference is 1.0 V. Thus, it is suggested that electrolysis in fluorosulfonic acid at an anodic potential no higher than the tetrafluoroethylene oxidation potential will not be accompanied by discharge of the FSO<sub>3</sub><sup>-</sup> anion and fluorosulfation of tetrafluoroethylene will proceed exclusively by an EC mechanism.\*

\*Electroactivity of perfluorooctene-1 during electrolysis in  $FSO_3H$  in a potentiostatic mode  $[E - 2.01 V (Cu/Cu^{2+})]$  was noted in [6]. It was found that the ratio of products formed in the course of the electrolysis, 1,2-bis(fluorosulfato)perfluorooctane and 7,8-bis(fluoro-sulfato)difluoromethylperfluorotetradecane, is the same as that from interaction of perfluorooctene-1 with (I). The reaction mechanism is not given, but identical composition of products from chemical and electrochemical reactions does not provide grounds for considering the given reaction as an example of fluorosulfation of fluoroolefins by an EC mechanism.



Fig. 2. Cyclic voltamperograms of a platinum electrode in  $FSO_3H/0.25$  M  $FSO_3K$  (1) and in the same solution saturated with (II) at 1 atm (2). Rate of potential sweep 0.05 V/sec. Electrode surface  $3.1 \cdot 10^{-2}$  cm<sup>2</sup>.

Preparative electrolysis at a controlled potential E = 1.5 V corresponding to the limiting current for tetrafluoroethylene oxidation confirmed this suggestion: with almost theoretical current efficiency a mixture was produced containing  $\alpha, \omega$ -bis-fluorosulfates (VIII)-(XI), the main component unexpectedly being 1,2-bis(fluorosulfato)tetrafluoroethane (VIII) (84%). The proportion of 1,4-bis(fluorosulfato)perfluorobutane (IX) was not more than 15%, although its formation in these conditions appeared the more probable. Formation of 1,6-bis(fluorosulfato)perfluorhexane (X) (0.5%) and bis( $\beta$ -fluorosulfatotetrafluoroethyl)sulfide (XI) (0.5%) was also observed.



The high yield of the bisfluorosulfate (VIII) indicates that fluorosulfation of tetrafluoroethylene during electrolysis in a potentiostatic mode, excluding formation of peroxide (I), proceeds mainly via an ECEC mechanism, according to which both the tetrafluoroethylene and radical (VII) formed as an intermediate undergo anodic oxidation and thus the oxidation wave observed (see Fig. 2) corresponds to a two-electron process. Oxidation of radical (VII) probably proceeds at a lower potential since only one oxidation wave is detected on the voltamperogram. Desorption of radical (VII) into solution and its subsequent recombination leads to formation of bis-fluorosulfate (IX), its interaction with tetrafluoroethylene yields the bis-sulfate (X), and with sulfur the sulfide (XI) results. Formation of elemental sulfur in the course of electrolysis of fluorosulfonic acid is mentioned in [2, 7].

There are examples in the literature of electrolysis of fluorosulfonic acid in the presence of fluoroolefins in a galvanostatic mode and at high anodic potentials [1, 2]. Here the determining factor for formation of bisfluorosulfates is undoubtedly anodic generation of (I). However, on the basis of the data obtained it may be stated that even in these conditions fluorosulfation of fluoroolefins, tetrafluoroethylene in the first instance, may proceed partially by an EC or an ECEC mechanism.

## EXPERIMENTAL

Mass spectra were recorded on a VGMS 70-70c spectrometer (70 eV). Compounds (VIII)-(X) were identified by GLC (FS-1265, 100°C) by comparison with known specimens obtained according to [1]. Polarization curves and cyclic voltamperograms were recorded using a PI-50 potentiostat with a PDA-1 two-coordinate recorder. The procedures used for the electrochemical measurements in fluorosulfonic acid have been described in [5]. Potentials were measured relative to a Pd/H<sub>2</sub> reference electrode in the same solution. The results of the electrochemical measurements are given in Table 1 and Figs. 1 and 2.

<u>Preparative Electrosynthesis of Fluorosulfates (VIII)-(XI)</u>. Potentiostatic electrolysis of a mixture of  $FSO_3H/0.25$  M  $FSO_3K$  in the presence of (II) was carried out at E = 1.5 V in a diaphragmless glass electrolyzer (platinum anode 20 cm<sup>2</sup>, nickel cathode 2 cm<sup>2</sup>, Pd/H<sub>2</sub> reference electrode) with mixing of the reaction mixture and constant bubbling of (II) at 22-25°C. The quantity of electricity was determined by integration of the *i* vs  $\tau$  curve recorded during electrolysis. After electrolysis the reaction mixture was poured over ice, the organic layer washed with water, dried over MgSO<sub>4</sub>, and distilled. In 6 h of electrolysis 0.6 A·h (0.022 F) electricity was passed. Vacuum distillation yielded 3.3 g of mixture containing (GLC) 84% (VIII), 14% (IX), 0.5% (X), and 0.5% (XI). The undistilled residue was 0.15 g. The overall yield with respect to current for (VIII)-(XI) was 94.2%.

Mass spectrum of (XI) (masses containing the main C and S isotopes), m/z ( $I_{rel}$ ,  $\mathfrak{F}$ ): 430 [M]<sup>+</sup> (10), 331 [M - FSO<sub>3</sub>]<sup>+</sup> (15), 281 [C<sub>3</sub>F<sub>7</sub>O<sub>3</sub>S<sub>2</sub>]<sup>+</sup> (28), 199 [C<sub>2</sub>F<sub>5</sub>O<sub>3</sub>S]<sup>+</sup> (51), 149 [CF<sub>3</sub>O<sub>3</sub>F]<sup>+</sup> (27), 132 [C<sub>2</sub>F<sub>4</sub>S]<sup>+</sup> (4), 119 [C<sub>2</sub>F<sub>5</sub>]<sup>+</sup> (100), 113 [C<sub>2</sub>F<sub>3</sub>S]<sup>+</sup> (50), 100 [C<sub>2</sub>F<sub>4</sub>]<sup>+</sup> (19), 83 [FSO<sub>2</sub>]<sup>+</sup> (73), 63 [CFS]<sup>+</sup> (18), 47 [CFO]<sup>+</sup> (22), 31 [CF]<sup>+</sup> (4).

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