

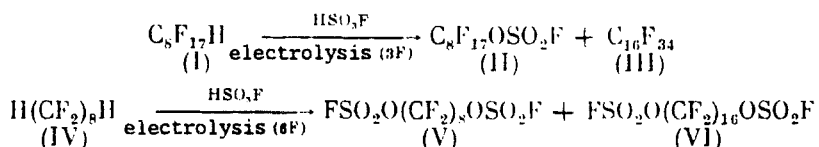
OXIDATIVE CONDENSATION OF MONO- AND DIHYDROPERFLUOROALKANES

V. M. Rogovik, V. F. Cherstkov,
N. I. Delyagina, S. R. Sterlin,
and L. S. German

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According to Germain et al. [1], the oxidative fluorosulfatization of 1-hydroperfluoroalkanes upon electrolysis in FSO_2OH , which proceeds through a free radical mechanism, leads to the formation of perfluoroalkyl fluorosulfates as the only reaction products.

We have established that the fluorosulfatization of hydroperfluoroalkanes upon their electrolysis in FSO_2OH under conditions when their concentration exceeds the current concentration of peroxydisulfuryl difluoride is accompanied by oxidative dehydrodimerization. Thus, perfluorohexadecane (III) is formed in the electrolysis of $\text{C}_8\text{F}_{17}\text{H}$ (I) in FSO_2OH , while α,ω -bis(fluorosulfato)perfluorohexadecane (VI) is formed in the electrolysis of $\text{H}(\text{CF}_2)_8\text{H}$ (IV).



This reaction is the first example of the oxidative dehydrodimerization of hydroperfluoroalkanes. A mixture of 21 g (50 mmoles) (I) and 40 ml HSO_3F , containing 3 g NaSO_3F , was subjected to electrolysis in a diaphragmless cell with a vitreous carbon anode and titanium cathode for 20 h at 0.2 A. Treatment of the reaction mixture gave 18.4 g (71%) (II), bp 156-157°C and 2.8 g (14%) (III), mp 124-125°C (125-126°C [2]). Found: C, 18.50; H, 66.02%. Calculated for $\text{C}_8\text{F}_{18}\text{SO}_3$: C, 18.53; F, 66.02%. Under analogous conditions, 20 g (50 mmoles) (IV) upon electrolysis at 0.2 A over 40 h gave 17.5 g (58%) (V), bp 89-92°C (11 mm) (90-93°C (10 mm [3])) and 6.1 g (24%) (VI), bp 134-137°C (3 mm). Found: C, 19.08; S, 6.52%. Calculated for $\text{C}_{18}\text{F}_{34}\text{O}_6\text{S}$: C, 19.20; S, 6.40%.

LITERATURE CITED

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3. German Federal Republic Patent No. DE 3,128,113 A1 (1983).

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