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Cross-dimerization of Perfluorovaleric and Perfluoro-2-propoxypropionic acids in the Presence of Butadiene

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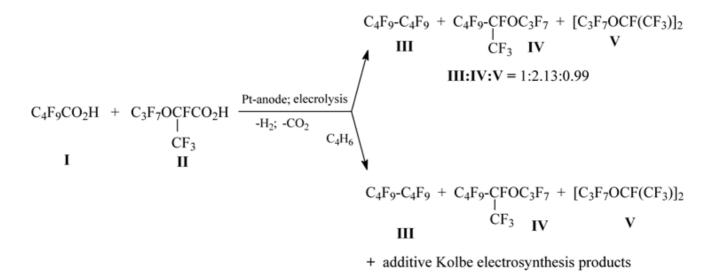
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Abstract:The electrochemical cross-dimerization of perfluorovaleric and perfluoro-2propoxypropionic acids conducted in the presence of butadiene afforded a mixture of cross- and homodimers characterized by abnormally high percentage of the compounds containing perfluoro-2propoxyethyl group. Presumably the result obtained reflects the competitive adsorption of electrolytes' components on the anode surface in the course of which butadiene preferably displaces perfluorovalerate-anion from anode.

Keywords:perfluorovaleric acid; perfluoro-2-propoxypropionic acid; Kolbe elrctrosynthesis; butadiene.

The electrochemical oxidation of two carboxylic acids that possess close physico-chemical characteristics – first of all the pK_a values – leads to the formation of homo- and cross Kolbe dimers in a ratio determined only by the concentrations of starting acids RCOOH and R'COOH and obeys the rule R-R:R-R':R'-R' = [RCOOH]²:2[RCOOH].[R'COOH]:[R'COOH]² [1]. Thus the anodic oxidation of equimolar mixture of perfluorovaleric (I) and perfluoro-2-propoxypropionic acid (II) resulted in the preparation of homo- and cross-dimers mixture in the ratio III:IV:V= 1:2,13:0,99 that is close to the theoretical ratio of these products [2].

Now we have established that this reaction [Pt-10%Ir anode; MeCN:H₂O = 9:1] conducted in the presence of butadiene after passing of 0.5 F electricity per 1 mole of acid afforded a mixture of compounds III-V in the ratio III:IV:V= 1:3,3:2,2 (The products of additive Kolbe electrosynthesis obtained from acid II and butadiene were described in [3]).



III:IV:V = 1:3.3:2.2

The electrolysis conducted at the incomplete conversion of the starting acids allows to estimate the current rates of perfluorovalerate-anion (**Ia**) and perfluoro-2-propoxypropionate-anion (**IIa**) electro-oxidation under given conditions by the ratio of products obtained by recombination of fluoroalkyl radicals generated in the course of oxidation.

The sharp decrease of compounds' IIIshare in a mixture of III-Vevidently indicates that in the presence of butadiene anion **Ia** oxidizes considerably slower than anion **Ia**.

Most probably the result obtained reflects the competitive adsorption of electrolytes' components on the anode surface in the course of which butadiene preferably displaces perfluorovalerate-anion from anode; the concentration of anion **IIa** hereat doesn't change virtually. Two-fold decrease of the current yield of additive Kolbe electrosynthesis products obtained from acid **I** and butadiene also witnesses the diminution in concentration of anion **Ia** the anode in the presence of butadiene [4].

The nature of different adsorption energy of anions **Ia-IIa** is not entirely clear. It can be assumed that the enhanced adsorption energy of anion **IIa** is rather connected with the presence of oxygen atom in the main chain of the molecule that performs a role of an additional nucleophilic centre in spite of the electron withdrawing influence of fluoroalkyl substituents. To a certain extend such assumption ties up with our observations of the enhanced persistence and hence reduced reactivity of perfluorinated α -alkoxyalkyl radicals (**VI**) in comparison with their perfluoroalkyl analogues [5]. It was postulated that this phenomenon could be explained within the frame of the scheme reported in [6] according to which an oxygen atom at a-position towards paramagnetic centre reveals sufficiently high electron donating ability to form mesomeric structure (**VII**):

$$R_{f} \stackrel{\bullet}{\text{O-CFR}}_{f} \Longrightarrow R_{f} \stackrel{+\bullet}{\text{O-CFR}}_{f}$$

The study of the competitive adsorption of fluoroalkyl and oxafluoroalkyl carboxylic acids will be continued.

Experimental

The mass spectra were recorded on VG ANALYTICAL 70-70E (70 eV) and Finnigan Polaris/GCQ Plus (70 eV) spectrometers.

The electrolysis of acids I and II in the presence of buradiene

A mixture of 4.76 g (18 mmol) of acid I, 6.0 g (18 mmol) of acid II, 30 ml of aq. MeCN (MeCN:H₂O = 9:1) and 0,48 g (7.2 mmol) 85% KOH was loaded into a glass undivided electrochemical cell equipped with a water-cooled jacket, reflux condenser, inlet tube and magnetic stirrer. Anode – Pt-10%Ir (15.5 cm²); the anode current density 64.5 mA/cm²; cathode – stainless steel. The butadiene was bubbled through electrolyte at a rate 30 ml/min. After passing 0.48 A-h of electricity (0.5 F/mole of acid) at 20°C the lower layer of electrolyte was separated, washed with aq. NaHCO₃ solution, 10% aq. HCl, dried

over MgSO₄to give 1.5 g of a mixture that contained 80% compounds III-V(III:IV:V= 1:3.3:2.2) (according to GLC and CMS data).

Mass-spectrum for C_8F_{18} (III) (m/z, reference): 362 $[C_8F_{14}]^+$; 331 $[C_7F_{13}]^+$; 319 $[C_6F_{13}]^+$; 281 $[C_6F_{11}]^+$; 243 $[C_6F_9]^+$; 231 $[C_5F_9]^+$; 219 $[C_4F_9]^+$; 181 $[C_4F_7]^+$; 169 $[C_3F_7]^+$; 131 $[C_3F_5]^+$; 119 $[C2F_5]^+$; 112 $[C_3F_4]^+$; 100 $[C_2F_4]^+$; 81 $[C_2F_3]^+$; 69 $[CF_3]^+$ (100%); 62 $[C_2F_2]^+$; 50 $[CF_2]^+$.

Mass-spectrum for C_4F_9 -CF(CF₃)OC₃F₇ (**IV**) (m/z, reference): 504 [M-F]⁺; 319 [C₆F₁₃]⁺; 297 [C₆F₁₁O]⁺; 231 [C₅F₉]⁺; 181 [C₄F₇]⁺; 169 [C₃F₇]⁺; 147 [C₃F₅O]⁺; 131 [C₃F₅]⁺; 119 [C₂F₅]⁺; 100 [C₂F₄]⁺; 69 [CF₃]⁺ (100%); 59 [C₂FO]⁺.

Mass-spectrum for $[C_3F_7OCF(CF_3)]_2$ (V) (m/z, reference): 385 $[C_7F_{15}O]^+$; 363 $[C_7F_{13}O_2]^+$; 285 $[C_5F_{11}O]^+$; 263 $[C_5F_9O_2]^+$; 219 $[C_4F_9]^+$; 197 $[C_4F_7O]^+$; 169 $[C_3F_7]^+$; 147 $[C_3F_5O]^+$; 131 $[C_3F_5]^+$; 119 $[C_2F_5]^+$; 100 $[C_2F_4]^+$; 69 $[CF_3]^+$ (100%); 62 $[C_2F_2]^+$; 50 $[CF]^+$.

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