

Received: May, 2011

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

N.A.Mayorova <sup>a</sup>, N.D.Kagramanov <sup>b</sup>, V.A.Grinberg <sup>a</sup>, S.R.Sterlin <sup>b</sup>

<sup>a</sup>The establishment of Russian Academy of Sciences A.N.Frumkin Institute of Physical Chemistry and Electrochemistry RAS Russian Federation, 119991 Moscow, Leninskii pr. 31, Fax: (495) 9520846, E-mail: [vgrinberg@phyche.ac.ru](mailto:vgrinberg@phyche.ac.ru)

<sup>b</sup>The establishment of Russian Academy of Sciences A.N.Nesmeyanov Institute of Organoelement Compounds RAS, Russian Federation, 119991 Moscow, Vavilova st. 28, Fax: (499) 135 6549, E-mail: [lsg@ineos.ac.ru](mailto:lsg@ineos.ac.ru)

**Abstract:** The electrochemical cross-dimerization of perfluorovaleric and perfluoro-2-propoxypropionic acids conducted in the presence of butadiene afforded a mixture of cross- and homodimers characterized by abnormally high percentage of the compounds containing perfluoro-2-propoxyethyl 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 electro-synthesis; 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:H<sub>2</sub>O = 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 electro-synthesis obtained from acid II and butadiene were described in [3]).



over  $\text{MgSO}_4$  to 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  $\text{C}_8\text{F}_{18}$  (**III**) (m/z, reference): 362  $[\text{C}_8\text{F}_{14}]^+$ ; 331  $[\text{C}_7\text{F}_{13}]^+$ ; 319  $[\text{C}_6\text{F}_{13}]^+$ ; 281  $[\text{C}_6\text{F}_{11}]^+$ ; 243  $[\text{C}_6\text{F}_9]^+$ ; 231  $[\text{C}_5\text{F}_9]^+$ ; 219  $[\text{C}_4\text{F}_9]^+$ ; 181  $[\text{C}_4\text{F}_7]^+$ ; 169  $[\text{C}_3\text{F}_7]^+$ ; 131  $[\text{C}_3\text{F}_5]^+$ ; 119  $[\text{C}_2\text{F}_5]^+$ ; 112  $[\text{C}_3\text{F}_4]^+$ ; 100  $[\text{C}_2\text{F}_4]^+$ ; 81  $[\text{C}_2\text{F}_3]^+$ ; 69  $[\text{CF}_3]^+$  (100%); 62  $[\text{C}_2\text{F}_2]^+$ ; 50  $[\text{CF}_2]^+$ .

Mass-spectrum for  $\text{C}_4\text{F}_9\text{-CF}(\text{CF}_3)\text{OC}_3\text{F}_7$  (**IV**) (m/z, reference): 504  $[\text{M-F}]^+$ ; 319  $[\text{C}_6\text{F}_{13}]^+$ ; 297  $[\text{C}_6\text{F}_{11}\text{O}]^+$ ; 231  $[\text{C}_5\text{F}_9]^+$ ; 181  $[\text{C}_4\text{F}_7]^+$ ; 169  $[\text{C}_3\text{F}_7]^+$ ; 147  $[\text{C}_3\text{F}_5\text{O}]^+$ ; 131  $[\text{C}_3\text{F}_5]^+$ ; 119  $[\text{C}_2\text{F}_5]^+$ ; 100  $[\text{C}_2\text{F}_4]^+$ ; 69  $[\text{CF}_3]^+$  (100%); 59  $[\text{C}_2\text{FO}]^+$ .

Mass-spectrum for  $[\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)]_2$  (**V**) (m/z, reference): 385  $[\text{C}_7\text{F}_{15}\text{O}]^+$ ; 363  $[\text{C}_7\text{F}_{13}\text{O}_2]^+$ ; 285  $[\text{C}_5\text{F}_{11}\text{O}]^+$ ; 263  $[\text{C}_5\text{F}_9\text{O}_2]^+$ ; 219  $[\text{C}_4\text{F}_9]^+$ ; 197  $[\text{C}_4\text{F}_7\text{O}]^+$ ; 169  $[\text{C}_3\text{F}_7]^+$ ; 147  $[\text{C}_3\text{F}_5\text{O}]^+$ ; 131  $[\text{C}_3\text{F}_5]^+$ ; 119  $[\text{C}_2\text{F}_5]^+$ ; 100  $[\text{C}_2\text{F}_4]^+$ ; 69  $[\text{CF}_3]^+$  (100%); 62  $[\text{C}_2\text{F}_2]^+$ ; 50  $[\text{CF}]^+$ .

## References

1. H.J.Schafer "Recent Contributions of Kolbe Electrolysis to Organic Synthesis" // Electrochemistry IV, Akademie-Verlag, Berlin, Topics Current Chemistry vol.152. p.105 (1990)
2. V.F.Cherstkov, V.A.Grinberg, S.R.Sterlin, Yu.B.Vasil'ev, L.S.German, E.I.Mysov, Izv. Akad. Nauk SSSR, Ser. Khim., 1991, 1141 (Russ.Transl.).
3. N.A. Mayorova, N.D.Kagramanov, V.A.Grinberg, S.R.Sterlin, Fluorine Notes N 4(65), 2009 July-August
4. N.A. Mayorova, N.D.Kagramanov, V.A.Grinberg, S.R.Sterlin, Russ.J.Electrochem., in press.
5. V.A.Grinberg, S.R.Sterlin, Russ.Chem.Bull., 2005, 54, N 8, 1942 (Engl. Transl.).
6. Nonhebel D.C., Walton J.C.Free-Radical Chemistry. University Press. Cambridge. 1974. P. 62