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A Voltammetric Study of the Kolbe Synthesis with Perfluorinated Oxa Acids: Influence of the Structure of the Fluorocarbon Residue

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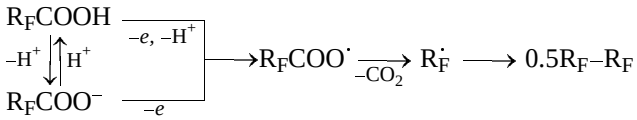
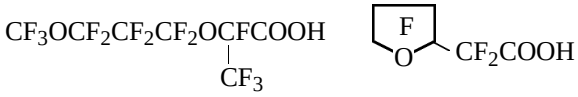
Abstract — The Kolbe synthesis with two perfluorinated oxa acids, perfluoro-3,7-dioxa-2-methyloctanoic and perfluorotetrahydro-α-furylacetic, was studied voltammetrically on platinum and glassy carbon anodes in water–acetonitrile and methanol–acetonitrile solutions. The influence exerted on the process by the acid concentration, degree of its neutralization, and solvent was studied. The solvent–anode system exerts a differentiating effect on the reactivity of perfluorinated acids under the conditions of the Kolbe synthesis.

The goal of this study was to elucidate the influence of structural elements of fluorocarboxylic acid molecules on their voltammetric characteristics under the conditions of the Kolbe synthesis. The primary step of this process is the discharge of acid molecules or anions [1].



Both acids studied, perfluoro-3,7-dioxa-2-methyloctanoic **I** and perfluorotetrahydro-α-furylacetic **II**, contain an oxa group relatively remote from the carboxy group.



I **II**

In **I**, however, the oxa group does not affect the flexibility of the acid residue and allows its deformation in an electric field of an electrical double layer, whereas the acid residue in **II** is rigid, and, furthermore, it contains no CF_3 groups favoring physical adsorption of fluorocarbon molecules on the electrode–electrolyte phase boundary. Despite significant differences, both acids under appropriate conditions form both homo- and cross Kolbe dimers (Table 1) [2–5].

The voltammetric measurements were performed as described in [6]. Platinum and glassy carbon were used as anode materials.

For acid **I**, we examined the solvent effect. As solvent we used MeCN–MeOH mixtures in 9 : 1 and 7 : 3 volume ratios and MeCN–H_2O mixtures (with methanol replaced by water). In the MeCN–MeOH 9 : 1 solvent, we also studied the dependence of the polarization on the concentration of acid **I** and on the degree α (%) of its neutralization by partial conversion to the sodium salt.

The polarization curves have the shape typical of the Kolbe synthesis. However, the current densities corresponding to the first Tafel portion and onset of the second Tafel portion noticeably depend on the electrolyte composition and anode material. First and foremost, the highest electrode potentials of the reactions are observed in water-containing solvents and on the glassy carbon anode (Fig. 1, curves *4*). In this respect, compound **I** is similar to other fluorocarboxylic acids, which are sorbed by electrodes from aqueous solutions more noticeably than from nonaqueous solutions but are displaced with water from the platinum anode to a greater extent.

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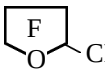
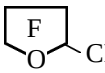
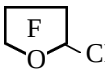
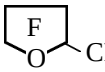
Table 1. Synthesis of Kolbe dimers R^1_F–R^2 from perfluorotetrahydro-α-furylacetic and 3,7-dioxa-2-methyloctanoic acids

R^1_F–COOH (**A**)	R^1_F–COOH (**B**)	Conditions: anode, total concentration of acids, α, additions, solvent, temperature, current density, **A** : **B** molar ratio	Yield based on **A**, %[a]	References
$F_3CO(CF_2)_3OCFCOOH$ (CF$_3$)	$F_3CO(CF_2)_3OCFCOOH$ (CF$_3$)	Glassy carbon; 1.2 M; α 6%; MeCN : H_2O = 7 : 3 (by volume); 20–22°C	85 (35)	[2]
$F_3CO(CF_2)_3OCFCOOH$ (CF$_3$)	CH_3COOH	Pt; 3.6 M; α 5%; MeCN : MeOH = 7 : 3 by volume); 20–22°C; 0.1 A cm^{-2}; 1 : 5	67 (87)	–
		Pt: (a) 2.5 M; MeCN : NeOH = 2 : 8; α 2%, 20°C; 0.32 A cm^{-2} (b) in MeCN : H_2O with glassy carbon; 1.5 M (c) α 5%; MeCN : MeOH = 7 : 3; 20°C, 0.15 A cm^{-2}	71 72 (88)	[3]
	$CF_3(CF_2)_2OCFCF_2OCFCOOH$ (CF$_3$ CF$_3$)	Glassy carbon; 1 M; MeCN : MeOH : Py[b] = 8 : 1 : 1; 20°C; 0.1 A cm^{-2}; **A** : **B** = 1 : 3 and 3 : 1	70[c]	[4]
	$CH_3OOC(CH_2)_4COOH$	Pt; 1 M, α 5%; MeOH : Py = 6.5 : 3.5; 20°C, 0.1 A cm^{-2}, **A** : **B** = 1 : 10	24	[5]

[a] The current efficiency (%) is given in parentheses. [b] Py is piridine. [c] Yield based on **B** 82%.

The influence of the acid concentration is very significant (Fig. 2). As already noted, the oxygen atom of the trifluoromethoxy group tends to specifically interact with the electrode (especially Pt) surface. Therefore, the first Tafel portion on Pt, especially in a concentrated solution of the acid in anhydrous solvent (1.8 M, Fig. 2a, curve *3*), is very strongly (by 0.5 V) shifted toward positive electrode potentials. There is virtually no transient region, and the slope is close to zero in the first portion and negative in the second portion. The polarization curves obtained on the platinum and glassy carbon anodes are in this case similar in shape. As the acid concentration is strongly decreased (to 0.6 M), the electrochemical behavior of the

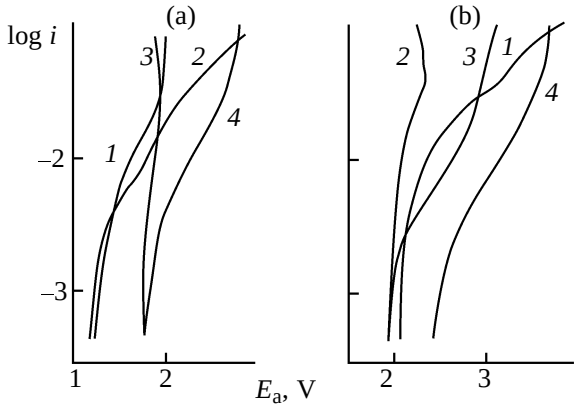


Fig. 1. Solvent effect on the voltammetric curves of acid **I** on (a) Pt and (b) glassy carbon electrodes. Acid concentration 1.2 M, degree of neutralization 6.0%. Solvent composition (molar ratio) MeCN : MeOH : H_2O: (*1*) 9 : 1 : 0, (*2*) 7 : 3 : 0, (*3*) 9 : 0 : 1, and (*4*) 7 : 0 : 3.

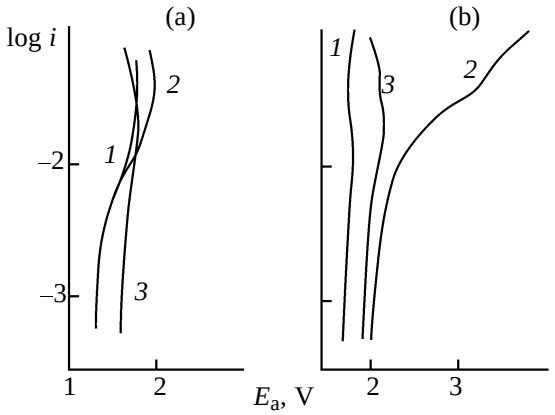


Fig. 2. Influence of the concentration of acid **I** on its voltammetric curves on the (a) Pt and (b) glassy carbon electrodes. Acid concentration, M: (*1*) 0.6, (*2*) 1.2, and (*3*) 1.8.

platinum and glassy carbon anodes becomes strongly different, wherteas the polarization of the platinum anode remains approximately the same. On the glassy carbon anode, the process is accompanied by a decreased overvoltage in both the second and the first portions (Fig. 2b, curve *1*), and the process rate is almost independent of the potential which is, apparently, determined by the physical adsorption only. Increased deceleration in the second portion with an increase in the acid concentration from 0.6 to 1.2 M (formation of specifically adsorbed layers) and the depolarization with a further increase in the acid concentration (probably due to micelle formation in solution) are typical of both anodes studied.

The influence of the degree of neutralization is shown in Fig. 3. Neutralization is accompanied by the breakdown of acid micelles; hence, the concentrations of both molecules and anions of the acid increase. These processes are differently manifested on the Pt and glassy carbon anodes. The Pt anode in the first Tafel portion at α 6% (Fig. 1a, curve *1*) shows a minimal overvoltage, because the concentration in the near-electrode space of, e.g., dimeric anions which are adsorbed and discharged on the active centers of the surface is in this case minimal. This can be accounted for by the fact that, in the course of neutralization, the concentration of acid molecules first decreases but then increases again because of the breakdown of the micelles. The glassy carbon anode has a weaker capability to chemisorb the solvent; in this case, with an increase in α, the polarization in the first Tafel portion smoothly grows in the entire range of acid concentrations, since the slow step of the process is the discharge of anions on the surface coated with a layer of adsorbed dimeric anions of the acid of the type $[(R_FCOO)_2H]^-$.

Variation of the concentration of nondissociated acid molecules depending on α affects the first Tafel portion of the Pt anode (see above), but on the glassy carbon anode is significantly manifested only in the second portion corresponding to the discharge of these species with the slow discharge step. At α 6% (Fig. 3b, curve *2*), the glassy carbon anode in the second portion exhibits superpolarization and appreciable (to 3 V) shift of the potential corresponding to the onset of the second portion toward positive values, because of the concentration hidrance of the discharge of the nondissociated molecules and their molecular dimers. At the same time, at the Pt anode exhibiting increased capability for destructive chemisorption, the concentration hindrance is not manifested, and the Kolbe product is formed by the Conway mechanism involving adsorbed radicals generated by the discharge of carboxylate ions; this significantly facilitates the process because of the gain in the adsorption energy. A gradual increase in the polarization of the Pt anode in the second portion with an increase in α from 2.4 to 6 and 8% (Fig. 3a, curves *1–3*) is due to the concentration hindrance to the discharge of the acid molecules and condensation of adsorbed radicals by the mechanism of electrochemical desorption (Table 2).

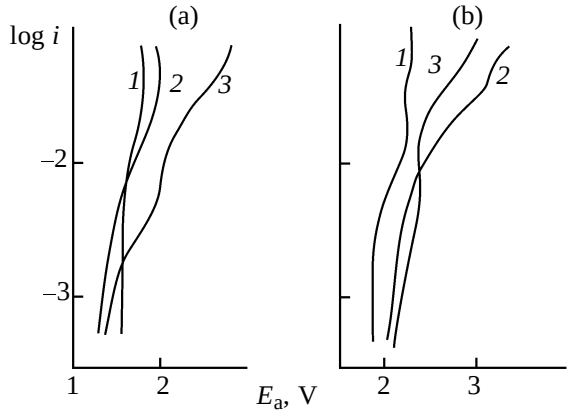


Fig. 3. Voltammetric curves of acid **I** on (a) Pt and (b) glassy carbon electrodes as influenced by the degree of its neutralization. Solvent MeCN–MeOH–H_2O, 9 : 1 : 0; concentration of **I** 1.2 M. Degree of neutralization, %: (*1*) 2.4, (*2*) 6.0, and (*3*) 8.0.

As in the case of **I**, the acid residue of **II** contains an oxa group that, in contrast to oxa groups in acids derived from hexafluoropropene oxide, has no adjacent carbon atom bearing the CF_3 substituent. In contrast to **I**, the oxa group in **II** is a part of a five-membered ring, and it does not impart flexibility to the carbon skeleton; when a carboxy group is present simultaneously in the molecule, the oxa group cannot interact with the anode surface. The interaction of the acid residue with the solvent molecules is preserved, though becomes weaker. All these features do not favor physical adsorption of the acid on the electrode. Taking into account weak chemisorption of the carboxylate group of fluoroacrboxylic acids, we can expect that the electrical double layer under the conditions of Kolbe electrosynthesis will be formed slowly and consider compound **II** as "anomalous."

In this case, the results of polarization measurements are difficult to interpret. However, consideration of the polarization curves is of certain interest.

The measurements on the Pt and glassy carbon anodes were performed in anhydrous (MeCN–MeOH) and water-containing (MeCN–H_2O) solvents. The results are shown in Fig. 4 (see also [7]).

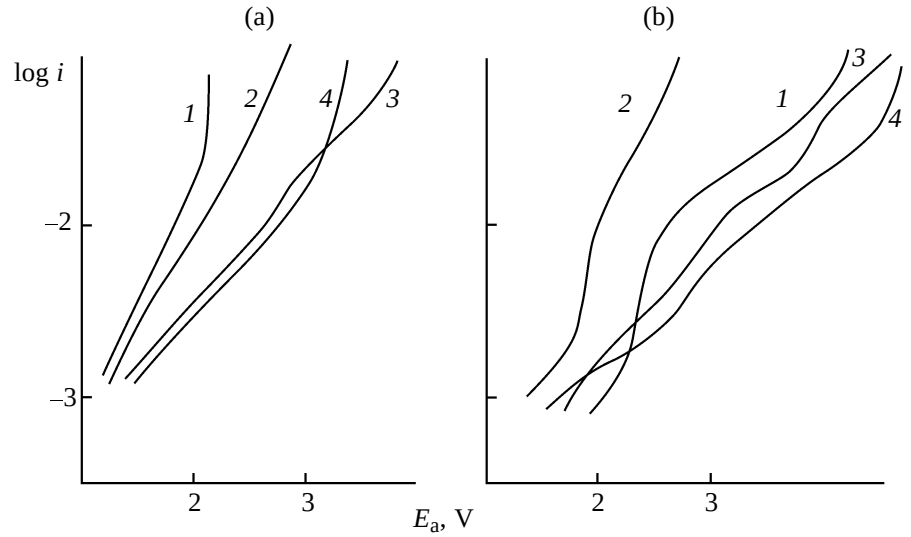


Fig. 4. Influence of the solution composition on the voltammetric curves of acid **II** on (a) Pt and (b) glassy carbon electrodes. Concentration of **II** 3 M, 20°C. Solvent MeCN–MeOH–H_2O; volume ratio: (*1*) 9 : 1 : 0, (*2*) 7 : 3 : 0, (*3*) 9 : 0 : 1, and (*4*) 7 : 0 : 3.

Figure 4 shows that, as with other fluorocarboxylic acids, the anode polarization in solutions of acid **II** in anhydrous (MeCN–MeOH) solvents is appreciably lower than in the solvents containing water. As the MeOH content is increased from 10 to 30%, the potential of the onset of the transient region on the glassy carbon anode shifts toward less positive values: from 2.72 to 2.27 V (vs. saturated calomel electrode; Fig. 4b, curves *1*, *2*). At the same time, replacement of 10% methanol by 10% water leads to a considerable increase in this potential (to 2.75 V, curves *1*–*3*), and with 30% water this potential becomes as high as 2.88 V (curves *2*–*4*). The slope of the second Tafel portion also changes: As the methanol content is increased from 10 to 30%, *b* decreases from 1.20 to 0.38 (Fig. 4b, curves *1*, *2*).

As for the Pt anode, its potentials in anhydrous solvents do not exceed 3 V (Fig. 4a, curves *1*, *2*), whereas in the presence of water they reach 3.4 V and more (Fig. 4a, curves *3*, *4*). Hence, in this case the molecules of **II**, in contrast to **I**, are not displaced by water from the near-anode space.

Comparison of the quantitative characteristics of the voltammograms recorded in different solvents, taking into account that oxidation of **II** in methanol is less hindered, suggests that methanol does not prevent interaction of the carboxy group of **II** with the anode surface, in contrast to water which binds the acid in solution into more stable hydrates.

Compound **II** differs from **I** in that with **II** the differentiating effect of the solvent–anode system is

Table 2. Steps of electrooxidation of 3,7-dioxa-2-methyloctanoic acid **I**

Solvent	Platinum anode	Glassy carbon anode
Anhydrous (MeCN–MeOH)	First Tafel portion	
	Strong chemisorption of acid. Slow discharge of acid anions	Slow discharge on the surface coated with $[(R_FCOO)_2H]^-$
	Second Tafel portion	
	Adsorption of various anions, slow electrochemical desorption	–
	Slow diffusion of discharging molecules and their dimers	–
Water-containing (MeCN–H_2O)	Lower polarization compared to glassy carbon	Higher polarization compared to Pt
	Stronger, compared to anhydrous solvents, physical adsorption and polarization	–

more pronounced. Indeed, here the general shape of the polarization curve is determined by the anode material, but the quantitative characteristics of the curve depend on the solvent. The polarization curve taken with the Pt anode differs from that taken with the glassy carbon anode in that it has no first Tafel portion; the polarization curve on Pt starts with the transient region. The second portion is seen in all the solvents. On the other hand, in the case of the glassy carbon anode, both the first and the second portions are well defined, since this anode only weakly chemisorbs oxygen-containing solvent molecules, whereas the physical adsorption of fluorinated radicals is preserved.

Along with the above-described quantitative features, in which acid **II** only slightly differs from the other fluorocarboxylic acids studied, we can note in this case specific distinctions between water-containing and anhydrous solvents, observed with the glassy carbon anode. In nonaqueous solvents (Fig. 4b, curves *1*, *2*), the first portion is very long (about unit of $\log i$), whereas in water-containing solvents it is very short (0.1–0.2 unit of $\log i$). This fact is indicative of the low activity of species discharged in the first portion in water-containing solvents.

The absence of the first Tafel portion on the Pt anode in solutions of **II** in both water-containing and nonaqueous solvents also indicates that the dimericion acid species is poorly competitive under the conditions of possible adsorption on Pt of the solvents and oxidation products (as far as specific interaction, i.e., chemisorption, is concerned). Also, presumably, in the course of the electrolysis the conditions for the Kolbe synthesis with acid **II** on the Pt anode in the second Tafel portion will become more favorable in nonaqueous media than in water because of the lower solvent basicity.

On the glassy carbon anode, because of the weak chemisorption of oxygen and oxygen-containing groups of the solvent, the discharge of **II** is principally possible in the entire range of potentials, including the potentials lower than the critical maximum for the Kolbe synthesis. However, a significant affinity of the acid residue containing no trifluoromethyl groups for the solvent, especially for the anhydrous solvent (MeCN–MeOH), makes the physical adsorption of the fluorocarbon molecules on the electrode–electrolyte boundary less efficient. The concentration hindrance may lead to predominant formation of by-products.

We studied how the concentration of **II** affects the polarization of the glassy carbon anode in MeCN–H_2O. With an increase in the acid concentration to 1 M, an adsorption layer of molecules and molecular dimers is formed; further increase in the acid concentration causes depolarization owing to micelle formation.

The dependence of the polarization on the degree of neutralization was described in one of the previous papers [7]; it was noted, in particular, that at α 5% the polarization is the highest throughout the polarization curve.

Thus, along with the regular trends common for all fluorocarboxylic acids, in the case of **II** we can note a differentiating effect exerted on the electrochemical behavior by the electrode–electrolyte system as a whole, rather than by the electrode material or solvent composition separately.

This study allows conclusions about effects exerted by structural elements of the acid residue of the examined fluorocarboxylic acids studied on the electrochemical properties of the acids under the conditions of the Kolbe synthesis: The oxa group in the linear part of the carbon chain favors chemisorption of the molecule (on Pt), and the trifluoromethyl group favors the physical adsorption on the metal–electrolyte boundary.

The Kolbe reaction with **I** can be performed on Pt and glassy carbon anodes in MeOH–MeCN and MeCN–H_2O (at α 5% and MeCN : H_2O = 9 : 1). However, in the case of **II**, interpretation of the polarization curves is difficult without knowing the results of preparative electrolysis.

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