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As is known, the Brown—Walker reaction, consisting in anodic condensation occurring during the electrolysis of aqueous or alcoholic solutions of salts of monoesters of dicarboxylic acids:

$$2\mathrm{ROOC(CH_2)_nCOO^-} \xrightarrow{-2e} \mathrm{ROOC(CH_2)_{2n}COOR} + 2\mathrm{CO_2} \qquad (1)$$

is a convenient method for the synthesis of diesters of carboxylic acids, and, in particular, of the dimethyl ester of sebacic acid ($R = \mathrm{CH_3},\ n = 4$) ([1,2]).

When carrying out the anodic condensation of monoesters of adipic acid, as was established earlier ([3–5]), along with the main product—the diester of sebacic acid—a number of by-products are present in the solution (esters of allylacetic, valeric, and oxyvalerianic acids, dimethyl adipate, and small amounts of the ester of tricarballylic acid). Although the principal regularities of the formation of diesters of sebacic acid in both aqueous and alcoholic solutions have been studied in considerable detail ([1,4]), the literature contains no systematized information on the dependence of the nature and yields of the by-products on the electrolysis conditions. The absence of such information hinders the compilation of a general scheme of the electrochemical and chemical reactions leading to the formation of the main and by-products of the Brown—Walker electrosynthesis.

As the object of investigation we chose the monomethyl ester of adipic acid, the sodium salt of which was subjected to electrolysis in aqueous or alcoholic solutions having compositions corresponding, as did the electrolysis regimes, to the conditions optimal for the formation of dimethyl sebacate ([7–9]). The electrolysis was carried out in a cylindrical glass vessel using concentrically arranged platinum meshes as electrodes.

Isolation of sebacic acid, the content of which was then recalculated as dimethyl sebacate, was carried out by the method described earlier ([6]). The methyl ester of allylacetic acid was determined by the bromine number ([10]). The methyl ester of valeric acid and dimethyl adipate were determined from the difference between the amount of neutral product in each experiment and the sum of the esters of allylacetic acid and dimethyl sebacate in the same experiment. The separate contents of the methyl ester of valeric acid and dimethyl adipate were

Fig. 1

Figure 1: Fig. 1

determined by a calculation method, based on comparison of the ester numbers of the electrolysis products. The amount of the ester of oxyvalerianic acid was calculated from the difference between the weights of the reacted monomethyl adipate and that monomethyl adipate which went into the formation of dimethyl sebacate and the above-listed by-products. The possibility of formation of the ester of tricarballylic acid was not taken into account in the calculation because of the small amounts of this product. The contents of oxygen and CO_2 in the gases were determined by an absorption method. Hydrogen was determined by combustion. The material balance was compared with the balance of the amount of electricity expended on the formation of the main and by-products of electrolysis.

The main results of the investigations are presented in Figs. 1—3. From consideration of these figures, the following conclusions can be drawn. Stabilization of the substance and current yields of dimethyl sebacate is achieved in the anodic condensation of monomethyl adipate in an aqueous solution of its salt.

(Fig. 1a, curves 1, 2) owing to stabilization of the total current yield of by-products (Fig. 1a, curve 3) at a definite current density. This fact is undoubtedly a reflection of a change in the ratio between the rates of two electrochemical reactions occurring at the anode during electrolysis: the main reaction, oxidation of the anion,

$$\mathrm{CH_3OOC(CH_2)_4COO^-} - \mathrm{e} \rightarrow \mathrm{CH_3OOC(CH_2)_4COO^{\cdot}} \tag{2}$$

and the side reaction of water oxidation

$$\mathrm{H_2O} - \mathrm{e} \rightarrow \mathrm{OH^{\cdot}} + \mathrm{H^+}. \tag{3}$$

Using the example of the anodic condensation of monomethyl malonate in an aqueous medium, it was shown that, upon reaching a certain value of the current density, the rate of reaction 2 ceases to change (11). This point corresponds to a transition into a region in which the yield of the dimeric product does not depend on the anodic current density. Although the total amount of electricity consumed in the formation of all by-products becomes constant (curve 3, Fig. 1a), the ratio between them changes quite substantially with a further increase in the anodic current density (Fig. 1b, curves 1-4).

Fig. 1. a—dependence of the substance yield (1), current yield (2) of dimethyl sebacate, and total current yield of by-products (3) on the anodic current density; b—dependence of the current yields of the methyl esters of allylacetic (1),

Fig. 2

Figure 2: Fig. 2

valeric (2), oxovaleric (3), and dimethyl adipate (4) acids on the anodic current density in aqueous medium.

Among the gaseous products of electrolysis of aqueous solutions of sodium monomethyl adipate, only very small amounts of oxygen were found (about 2%), which by no means correspond to the low current yields of dimethyl sebacate.

This may indicate a low rate of recombination of hydroxyl radicals with formation of oxygen and makes it possible to suppose that side chemical reactions involving the $OH\cdot$ radicals and the oxidation products of the monomethyl adipate anion proceed on the anode surface. As is seen from equations (4) and (5), these reactions can lead to the formation of at least two by-products—the methyl esters of allylacetic and oxovaleric acids:

Fig. 2. a—dependence of the substance yield (1), current yield (2) of dimethyl sebacate, and total current yield of by-products (3) on the concentration of methanol; b—dependence of the current yields of the methyl esters of allylacetic (1), valeric (2), oxovaleric (3), and dimethyl adipate (4) acids on the concentration of methanol.

$$CH_3OOC(CH_2)_2CH_2C\dot{H}_2 + OH^{\cdot} \rightarrow CH_3OOC(CH_2)_2CH = CH_2 + H_2O, \quad (4)$$

$$CH_3OOC(CH_2)_4^{\cdot} + OH^{\cdot} \rightarrow CH_3OOC(CH_2)_4OH. \quad (5)$$

It is characteristic here that, with increasing anodic current density, the current yield of the methyl esters of allylacetic and oxovaleric acids becomes—

···are stabilized at the same current densities as is the yield of dimethyl sebacate. Stabilization of the current yields of the indicated by-products corresponds to the current density at which the rate of formation of $OH\cdot$ radicals on the anode surface becomes constant. It is possible that some amount of allylacetic acid ester may be formed as a result of a disproportionation reaction:

$$2CH_3OOC(CH_2)_4^{\cdot} \rightarrow CH_3OOC(CH_2)_2CH{=}CH_2 + CH_3OOC(CH_2)_3CH_3. \quad (6)$$

Reaction (6), however, cannot explain the presence in the solution of appreciable amounts of valeric acid ester, which, especially at low current densities, clearly exceed the amounts equivalent, according to reaction (6), to the ester of allylacetic acid. Probably the formation of valeric acid ester is not, to any noticeable extent, connected with reaction (6), but proceeds by abstraction of hydrogen from water molecules:

$$CH_3OOC(CH_2)_3CH_2^{\cdot} + H_2O \rightarrow CH_3OOC(CH_2)_3CH_3 + OH^{\cdot} \qquad (7)$$

Fig. 3. a—dependence of the substance yield (1), current yield (2) of dimethyl sebacate, and total current yield of by-products (3) on the anodic current density in an alcoholic solution; **b**—dependence of the current yields of the esters of allylacetic acid (1), valeric acid (2), oxivaleric acid (3), and dimethyl adipinate (4) on the anodic current density in an alcoholic solution

As the anodic current density is increased and water molecules are displaced from the anode surface (^{12}), accompanied by an increase in the concentration of $CH_3OOC(CH_2)_4^{\cdot}$ radicals, the rate of reaction (7) decreases, while the rate of the dimerization reaction leading to the formation of dimethyl sebacate increases, as is seen from Fig. 1. The greatest uncertainty arises in explaining the mechanism of formation of dimethyl adipinate. Probably, in an aqueous medium a transesterification reaction occurs:

$$2CH_3OOC(CH_2)_4COOH \rightarrow CH_3OOC(CH_2)_4COOCH_3 + HOOC(CH_2)_4COOH, \qquad (8)$$

as a result of which, along with dimethyl adipinate, adipic acid actually found in the analysis is formed in the solution. If all the dimethyl adipinate arose by reaction (8), one could expect its yield to decrease with increasing current density, i.e., with shortening of the electrolysis time. However, as follows from Fig. 1b, the opposite picture is observed.

When methanol is added to the solution, a fairly sharp increase occurs in the yields of dimethyl sebacate both by current and by substance (Fig. 2a), which is associated with suppression of reaction (3) (^{13}). Noteworthy is the fact that, with increasing methanol concentration in the solution, the current yields of those by-products of electrolysis decrease in whose formation, according to the assumptions made above, $OH\cdot$ radicals participate. This is connected with a decrease in the rate of reaction (3), accompanied by a fall in the concentration of $OH\cdot$ radicals on the anode surface and, consequently, also with a decrease in the rates of reactions (4) and (5).

Owing to the displacement of water molecules from the anode surface, which occurs as a result of methanol adsorption, the yield of valeric acid ester formed by reaction (7) decreases, as is seen from curve 2 in Fig. 2b. The total current yield of by-products, as follows from curve 3 in Fig. 2a, decreases with increasing methanol concentration, which corresponds to the fact of increa-

decrease in the yield of dimethyl sebacate in alcoholic solutions as compared with aqueous ones $^{(13)}$. Figure 3 presents the dependence of the yields of the products of anodic condensation of monomethyl adipate on the current density in alcoholic solutions containing about 0.15% water. Owing to the absence, in alcoholic solutions at the anode surface, of appreciable concentrations of $OH^{\cdot}$ radicals, other pathways must probably be proposed for the formation of the side products of electrolysis which, in aqueous solutions, could be formed by reactions involving hydroxyl radicals. The possibility cannot be excluded that, as in aqueous solution, the disproportionation reaction (6) occurs, explaining the appearance in solution of equivalent amounts of the esters of allylacetic and valerianic acids. However, to explain the observed deviation from the equivalent ratio of the latter, it is necessary to consider other pathways for the formation of these products as well. Direct oxidation of the radical $CH_3OOC(CH_2)^{\cdot}_4$ at the anode is possible, leading to the formation of the ester of allylacetic acid:

$$CH_3OOC(CH_2)_2CH_2CH_2^{\cdot} - e \rightarrow CH_3OOC(CH_2)_2CH = CH_2 + H^+. \quad (9)$$

The material balance, as well as the balance of the amount of electricity, show that dimethyl adipate in alcoholic solutions must be formed as a result of a reaction proceeding with participation of the radical $CH_3OOC(CH_2)_4COO^{\cdot}$. It is stated in the literature that carboxylate and, in particular, acetate free radicals cannot exist in solution for any appreciable length of time, decomposing at rates close to the rates of their formation and with considerable thermal effects (14). However, there are indications of the possibility of stabilizing free radicals as a result of their adsorption on solid surfaces, without a noticeable decrease in chemical activity or in the activation energy of subsequent reactions of some radicals (15). Stabilization of the radical $CH_3COO^{\cdot}$ on the surface of a platinum anode is assumed by some authors who have studied Kolbe electrosynthesis (16). From what has been said, it follows that the possibility is not excluded that the radical $CH_3OOC(CH_2)_4COO^{\cdot}$, stabilized on the anode surface as a result of adsorption, participates in the formation of dimethyl adipate, for example by reaction with methanol:

$$CH_3OOC(CH_2)_4COO^{\cdot} + CH_3OH \rightarrow CH_3OOC(CH_2)_4COOCH_3 + OH^{\cdot}. \quad (10)$$

The $OH^{\cdot}$ radicals formed in this process may participate in the formation of the ester of oxyvalerianic acid (reaction (5)). It is interesting to note that the minimum on the curve for the dependence of the total yield of side products (curve 3, Fig. 3a) corresponds to the optimum material yields of dimethyl sebacate at an anodic current density of 5–7 A/dm^2 in alcoholic solution.

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