7. H. Pines and J. Manassen, in: A. A. Balandin and A. M. Rubinshtein (editors), Catalysis. Stereochemistry and Mechanism of Organic Reactions [Russian translation], Mir (1968), p. 56.
8. A. I. Maksimov, I. I. Levitskii, and Kh. M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 1033.
9. K. Tanabe, Solid Acids and Bases: Their Catalytic Properties, Academic Press, New York (1970).
10. V. I. Yakerson, L. I. Lafer, and A. M. Rubinshtein, in: Problems in Kinetics and Catalysis [in Russian], Vol. 16, Nauka (1975), p. 49.
11. M. Kraus and K. Kochloefl, Collect. Czech. Chem. Commun., 32, No. 6, 2320 (1967).
12. R. Hoffmann, J. Chem. Phys., 39, 1397 (1963).
13. P. R. Andrews, Theor. Chim. Acta, 14, 261 (1969).

ELECTROSYNTHESIS OF DIESTERS OF SATURATED
DICARBOXYLIC ACIDS FROM OXALIC ACID AND ETHYLENE

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The electrolysis of oxalic acid in a methanol solution on a Pt anode in the presence of 1,3-butadiene is known to result in the formation of unsaturated dicarboxylic acids and their diesters [1]. The intermediate participation of $\dot{C}OOH$ radicals in this reaction has been postulated [2].

We have found that the analogous electrolysis with the use of ethylene (ET) as a radical acceptor makes it possible to obtain a mixture of the diesters of saturated dicarboxylic acids $CH_3OCO(CH_2)_nCOOCH_3$ (Ia-Ie), where n = 0 (a), 2 (b), 4 (c), 6 (d), and 8 (e), with a preparative yield.
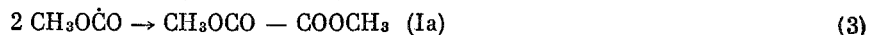
Addition to ethylene does not occur in a DMFA medium. This suggests that the preliminary step in a methanol medium is the formation of the monoester of oxalic acid (II):
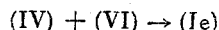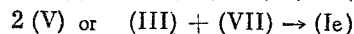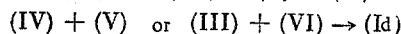
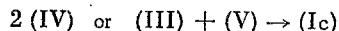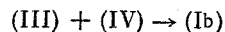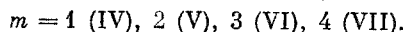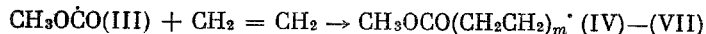$$HOOC - COOH + CH_3OH \rightleftarrows CH_3OCO - COOH(II) + H_2O \tag{1}$$

The anodic oxidation of the anion of monoester II results in the generation of methoxycarbonyl radicals (III):

$$CH_3OCO - COO^- \xrightarrow{e} CH_3O\dot{C}O(III) + CO_2 \tag{2}$$
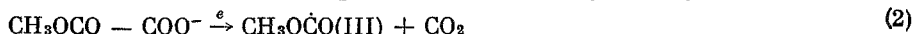
These radicals are added to ethylene in analogy to the other electrochemically generated radicals we previously studied [3-6] and recombine to form the diester of oxalic acid (Ia):

$$2 CH_3O\dot{C}O \rightarrow CH_3OCO - COOCH_3 \quad (Ia) \tag{3}$$

$$CH_3OCO - COOCH_3 + HOOC - COOH \rightleftarrows 2 CH_3OCO - COOH \quad (II) \tag{4}$$

The possible reversible equilibrium (4) together with reaction (3) probably lowers the current efficiency for higher diesters, but does not alter the yield. The key step in the formation of the latter is clearly the addition of radical III to ethylene. It is followed by the ordinary acts of chain propagation and termination:

$$CH_3O\dot{C}O(III) + CH_2 = CH_2 \rightarrow CH_3OCO(CH_2CH_2)_m^{\cdot} \quad (IV)-(VII)$$
$$m = 1 \ (IV), \ 2 \ (V), \ 3 \ (VI), \ 4 \ (VII).$$
$$(III) + (IV) \rightarrow (Ib)$$
$$2 \ (IV) \ \text{or} \ (III) + (V) \rightarrow (Ic)$$
$$(IV) + (V) \ \text{or} \ (III) + (VI) \rightarrow (Id)$$
$$2 \ (V) \ \text{or} \ (III) + (VII) \rightarrow (Ie)$$
$$(IV) + (VI) \rightarrow (Ie)$$

Diesters Ib-Ie were isolated from the electrolyte and identified (Table 1). The total yield of diesters significantly exceeds their yield in the case of the addition of radicals generated as a result of the electrooxidation of the monoesters of glutaric acid or adipic acid to ethylene [6]. One of the reasons for this is apparently the electrophilic nature of radical III, whose properties are reminiscent of the properties of the CF_3 radical and

TABLE 1. Composition of the Mixture of Electrolysis Products as a Function of the Current Density

Current density, A/dm^2	Concentration of $CH_3OOC(CH_2)_nCOOCH_3$ in electrolysis product, %				
	$n=0$	$n=2$	$n=4$	$n=6$	$n=8$
0.5 *	29,0	25,0	31,3	12,0	2,7
10,0†	46,2	21,3	26,4	5,8	1,3

*With consideration of the return of the dimethyl oxalate to the cycle, the total yield is 94%.
†The total yield is 70%.

which forms an addition product with ethylene with a high yield [5]. Another reason is associated with the adsorbability of monoester II on the anode, which is poor in comparison to the monoesters of higher acids containing a comparatively long hydrocarbon chain. As a result, the adsorption of ethylene is hampered to a lesser extent.

The fact that there is competitive adsorption of ethylene and the substrate being oxidized on the surface of the anode was confirmed by us by studying the kinetics of the electrooxidation of oxalic acid in MeOH.

As the ethylene pressure is increased, the oxidation currents decrease with maintenance of the shape of the curve over the entire range of potentials, including the second ascending branch of the curve, which corresponds to the evolution of oxygen. When the ethylene pressure is 60 atm, the rate of oxidation at φ_{max} decreases by a factor of 1.6 (Fig. 1). In control experiments with an argon pressure of 60 atm and a partial pressure of ethylene equal to 1 atm, no decrease in the oxidation rate occurs.

Increasing the ethylene pressure slightly displaces the maximum of the curve toward more positive potentials. This displacement reaches its largest magnitude $\Delta\varphi = 100$ mV when the ethylene pressure is 60 atm. The initial portion of the $\varphi - \log i$ curve recorded in a solution of oxalic acid remains linear when ethylene is introduced (Fig. 2a), its slope remaining unchanged. However, the presence of ethylene probably causes an increase in the overvoltage of the anodic processes in the first and second segments of the polarization curve as a result of its adsorption on the electrode [7]. At the same time, the rate of the electrode processes at $\varphi = $const drops with increasing ethylene pressure ($p_{C_2H_4}$) raised to a fractional power, i.e., $i = Bp_{C_2H_4}^{-\alpha}$ where α varies as the potential is increased from 0.7 to 0.

This type of influence of ethylene is typical of particles adsorbed on a dimensionally heterogeneous surface which do not participate in the electrode process [7-11]. The slight displacement of the potential of the maximum as the ethylene pressure is increased (see Fig. 1) may apparently be attributed to the mutual competition between the oxalate anions, ethylene, and the chemisorbed oxygen. A similar effect was previously observed in [10].
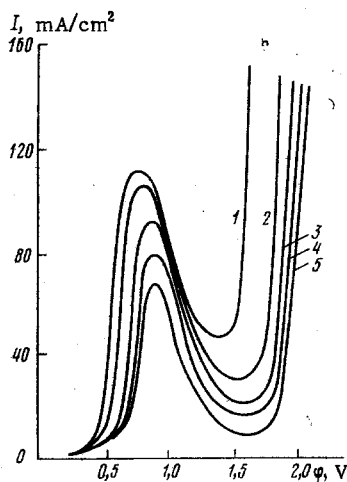

Fig. 1. Anodic polarization curves on a Pt electrode in an aqueous 0.5 M $H_2C_2O_4$ + 0.5 M H_2SO_4 solution with an ethylene pressure, atm: 1) 0; 2) 3; 3) 15; 4) 30; 5) 60.
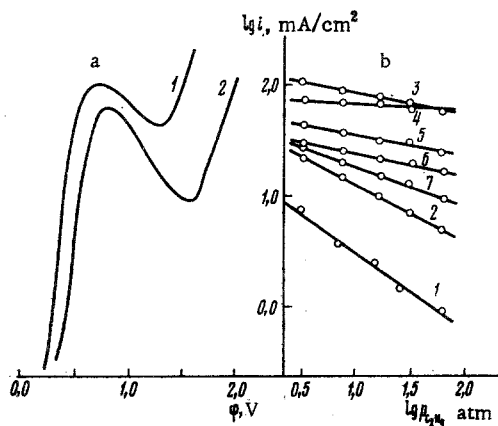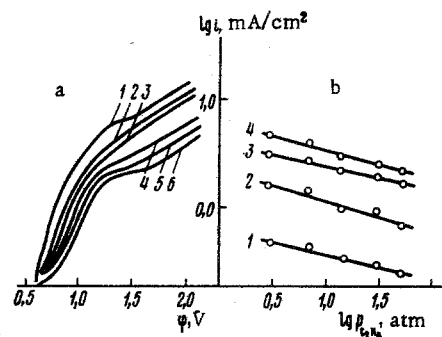
Fig. 2

Fig. 3

Fig. 2. Anodic polarization curves on a Pt electrode in an aqueous 0.5 M $H_2C_2O_4 + 0.5$ M H_2SO_4 solution (a) in the absence of ethylene (1) and when its pressure is equal to 60 atm (2); dependence of the rate of anodic processes in the same solution on the ethylene pressure (b) at the potentials, V: 1) 0.5; 2) 0.6; 3) 0.8; 4) 1.0; 5) 1.2; 6) 1.4; 7) 1.6.

Fig. 3. Anodic polarization curves on a Pt electrode in a methanolic 0.05 M $H_2C_2O_4$ solution (a) at various ethylene pressures and dependence of the rate of anodic processes on the ethylene pressure in a system at various potentials (b). a. Ethylene pressure, atm: 1) 0; 2) 3; 3) 7; 4) 15; 5) 30; 6) 60. b. Potentials, V: 1) 0.8; 2) 1.0; 3) 1.2; 4) 1.4.

The rate of the electrooxidation of oxalic acid in methanolic solutions has been observed [8] to be lower than that in aqueous solutions. The inhibition of the oxidation in water—methanol solutions with high concentrations of the alcohol is due to a decrease in the first dissociation constant of oxalic acid, as well as, possibly reaction (1). The nature of the influence of the ethylene pressure on the polarization curve in MeOH (Fig. 3) is similar to that considered above for aqueous solutions. It should be noted that the oxidation currents of MeOH amount to only an insignificant fraction of the total anodic current.

Thus, ethylene, like 1,3-butadiene [9], does not take direct part in the electrode process. Competing for the surface of the electrode with the solvent and the substrate undergoing oxidation upon adsorption, it only lowers their oxidation rates. However, as was previously shown, the electrochemically generated radicals react with the sorbed ethylene. Therefore, as its adsorption is increased, the yield of the addition products increases in analogy to the previously studied cases [3-6]. An increase in the current density lowers their yield (see Table 1).

EXPERIMENTAL

The PMR spectra were obtained on a Perkin—Elmer R-12 instrument, and the external reference was TMS. The GLC analysis was carried out on an LKhM-8M chromatograph, and the stationary phase was 20% QF-1 on Shimalite. The preparative recovery of the products obtained was carried out on a Carlo Erba instrument, the stationary phase being QF-1 on Chromosorb W.

The boiling points were determined according to Sivolobov's method.

Electrosynthesis of Diesters I. A 50 ml portion of a 10% solution of $(COOH)_2$ in MeOH was poured into a 100 ml Teflon cell placed in a stainless-steel autoclave. The autoclave was hermetically sealed, and ethylene was admitted to a pressure of 65 atm. From 0.08 to 0.1 F of electricity was passed through the electrolyte, which was stirred by a magnetic stirrer, with maintenance of a current density (in different experiments) of 0.2 to 10 A/dm². At the conclusion of the electrolysis the excess gas was blown out, the autoclave was opened, and the electrolyte was evaporated in a vacuum at ~20°C. The residue was diluted with ether, washed three times with water, and dried over $MgSO_4$. After the evaporation of the ether, the mixture was analyzed and separated by GLC. The analysis was carried out (see Table 1) at 192°C, and the separation was carried out under the conditions of a programmed temperature from 160 to 220°C with a heating rate of 5 deg/min. Dimethyl succinate (Ib), bp 194-197°C, compare [12]. PMR spectrum (δ, ppm): 3.25 (s, 4 H, CH_2) and 3.40 (s, 6 H, CH_3). Dimethyl adipate (Ic), bp 229-231°. A known specimen boils in the same range. PMR spectrum (δ, ppm): 1.49 (s, 4 H, CH_2CH_2COO), 2.14 (bs, 4 H, CH_2COO), 3.37 (s, 6 H, CH_3).

Dimethyl suberate (Id), bp 263-264°C, compare [12]. PMR spectrum (δ, ppm): broadened singlets at 1.22 (4 H, γ-CH$_2$), 1.45 (4 H, β-CH$_2$), 2.09 (4 H, α-CH$_2$), 3.37 (s, 6 H, CH$_3$). Dimethyl sebacate (Ie), bp 291-292°C, compare [12].

Kinetics of the Electrooxidation of Oxalic Acid. A special three-electrode cell placed in an autoclave was used. The possibility of introducing a bridge from the reference electrode directly into the inner space of the autoclave was provided for in its design. A saturated calomel reference electrode was used in the measurements in methanol solutions, and a mercurous sulfate electrode was used in the measurements in a 1 N H$_2$SO$_4$ electrolyte background. All the reagents used were subjected to additional purification, i.e., by recrystallization or fractional distillation.

Before the recording of a polarization curve the electrode was subjected to a single cycle of cathodic-anodic polarization for 3 min at $\varphi_c = -0.8$ and $\varphi_a = +0.1$ V (in the measurements in 1 N H$_2$SO$_4$) or $\varphi_c = -0.3$ and $\varphi_a = +0.5$ V (in the measurements in MeOH). Such treatment guaranteed the reproducibility of the results. The discrepanices in the values of the current at $\varphi = $ const did not exceed 2% for 6-10 consecutively recorded potentiodynamic polarization curves. The curves were recorded with linear variation of the potential at a rate of 3 mV/sec. When the polarization curves were recorded in the presence of ethylene under pressure, the solution was preliminarily saturated with ethylene for 1 h.

CONCLUSIONS

1. The electrolysis of the methanolic solutions of oxalic acid on a Pt anode in the presence of ethylene under pressure produces a mixture of diesters of succinic acid, adipic acid, suberic acid, and sebacic acid with a preparative yield (70-95%).

2. According to the data from the investigation of the kinetics of the electrooxidation of oxalic acid in the presence of ethylene, the latter does not take part in the electrochemical stage of the process. Being adsorbed on the surface of the electrode, ethylene participates in secondary reactions with electrochemically generated radicals.

LITERATURE CITED

1. M. Ya. Fioshin, L. A. Mirkind, L. A. Salmin', and A. G. Kornienko, Zh. Vses. Khim. O-va., 10, 238 (1965).
2. A. G. Kornienko, L. A. Mirkind, and M. Ya. Fioshin, Elektrokhimiya, 3, 1370 (1967).
3. K. G. Karapetyan, L. S. Kanevskii, A. M. Skundin, Yu. B. Vasil'ev, E. P. Kovsman, and G. N. Friedlin, Elektrokhimiya, 12, 1622 (1976).
4. K. G. Karapetyan, I. V. Proskurovskaya, A. A. Bezzubov, L. S. Kanevskii, A. M. Skundun, and Yu. B. Vasil'ev, Elektrokhimiya, 13, 544 (1977).
5. V. A. Grinberg, V. R. Polishchuk, E. I. Mysov, L. S. German, L. S. Kanevskii, V. V. Tsodikov, and Yu. B. Vasil'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 1977, 2825.
6. Yu. B. Vasil'ev, L. S. Kanevskii, K. G. Karapetyan, E. P. Kovsman, A. M. Skundin, G. A. Tarkhanov, and G. N. Freidlin, Elektrokhimiya, 14, 770 (1978).
7. K. G. Karapetyan, S. I. Andruseva, E. P. Kovsman, O. A. Khazova, L. S. Kanevskii, and Yu. B. Vasil'ev, Elektrokhimiya, 15, 487 (1979).
8. A. G. Kornienko, L. A. Mirkind, and M. Ya. Fioshin, Elektrokhimiya, 6, 1592 (1970).
9. A. G. Kornienko, L. A. Mirkind, and M. Ya. Fioshin, Elektrokhimiya, 4, 69 (1968).
10. L. A. Mirkind, M. Ya. Fioshin, and V. I. Romanov, Zh. Fiz. Khim., 38, 2223 (1964).
11. L. A. Mirkind, M. Ya. Fioshin, and D. Constantinescu, Elektrokhimiya, 2, 193 (1966).
12. Dictionary of Organic Compounds [Russian translation], IL (1949).