KINETICS OF ANODIC AND CHEMICAL REACTIONS
IN KOLBE'S ELECTROSYNTHESIS

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Kolbe's electrosynthesis takes place at the anode during the electrolysis of salts of carboxylic acids and can be generally represented by the following equation

\[ 2\text{RCOO}^- + 2e^- \rightarrow R - R + 2\text{CO}_2 \] (1)

Until now a large number of studies devoted mainly to the effect of the electrolysis conditions on the yield of dimerc product R-R have been carried out, and a great many mechanisms have been proposed for reaction 1 [1-3]. The kinetics of anodic reactions in Kolbe's electrosynthesis have scarcely been investigated. The present study is an attempt at filling to a certain extent the existing gaps in the investigations of Kolbe's electrosynthesis.

EXPERIMENTAL

Polarization curves and i-t curves were taken on vibrating and rotating platinum disc electrodes, the curves were recorded by means of PE-312 and PO-5122 polarographs [4]. The design of the cells and the rotating electrode did not differ substantially from that described in the literature [5]. We also took polarization curves on a stationary macroelectrode and analyzed the electrolysis products collected at various controlled values of the anode potential.

The equipment consisted of a potentiostatic system with manual adjustment. The pH and the electrolyte concentration were kept constant. Before the gas samples were taken, the electrolyte was saturated with gas of the same composition from an auxiliary cell. Before each experiment, the electrode was polarized anodically with a current of 0.02 A/cm² for 30 min in a 1 M NaOOCCl₄ solution. The preliminary polarization produced an anode surface in such a state that the current at constant potential hardly changed over a period of several hours. The gases were analyzed in a VTI-2 gas analyzer. The methanol content in the electrolyte was determined by means of the procedure described in the literature [6]. Reproducible polarization curves were obtained by applying the method of alternating cathodic-anodic activation of the platinum anode. The neat reproducibility of the results was due not only to the use of this method, but also to the high purity of the original solutions.

The polarization curve taken on a platinum disc electrode in a solution of sodium acetate rises through the potential range between 1.8 and 2.1 V (with reference to a normal hydrogen electrode), after which, having passed through a maximum, it drops at potentials above 2.2 V, and finally rises much more steeply (Fig. 1). The polarization curve taken on the stationary platinum macroelectrode by applying the compensation method does not show a maximum. As demonstrated in Fig. 2, the first weakly inclined part of the polarization curve obtained in this case is superseded by the second characteristic platform. An examination of the way in which the position of the maximum depends on the number of revolutions of the disc electrode shows that over a broad range of acetate concentrations the intensity of mixing has no effect whatever on the rate of the process. This suggests that the maximum of the current in the first part of the polarization curve taken in the acetate solution is of kinetic origin.

Analysis of the gases liberated at the anode during electrolysis of an acetate solution reveals that at potentials corresponding to the first part of the polarization curve only oxygen is liberated at the anode. At potentials corresponding to the second part of the curve, CO₂, C₂H₆, and CH₃OH (besides oxygen) are formed at the anode; this points to discharging of acetate anions.

Plotted in semilogarithmic coordinates, the first part of the curve, which corresponds to liberation of oxygen, is a straight line. The coefficient b of Tafel's equation varies between 0.120 and 0.6, and depends markedly on the
Fig. 1. Polarization curve in 0.1 N NaOOCCH$_3$ on a rotating electrode and i-t curves at $\varphi = \text{const.}$, in various regions of the polarization curve.

Fig. 2. Polarization curve taken in 1 N NaOOCCH$_3$ + CH$_3$COOH on a Pt macroelectrode up to pH = 6. Yield of anodic products at current densities corresponding to the various points indicated on the curve: 1, 2, 3, 4, 5) 100% O$_2$; 3', 4', 5') traces of CO$_2$ and C$_2$H$_6$; 6) 0% C$_2$H$_6$, 68.5% O$_2$, 8.25% CO$_2$, 12.7% CH$_3$OH; 7) 0% C$_2$H$_6$, 30.7% O$_2$; 8) 1.97% C$_2$H$_6$, 11.6% O$_2$; 9) 37.3% C$_2$H$_6$, 6.679% O$_2$, 10) 60.8% C$_2$H$_6$, 6.08% O$_2$, 11.8% CH$_3$OH, 11) 81.3% C$_2$H$_6$, 4.29% O$_2$. 12) 89.1% C$_2$H$_6$, 0.24% O$_2$, 5.5% CH$_3$OH.

Composition of the solution and on the rate at which the polarization curve is taken. This indicates that at the potentials corresponding to the first part of the polarization curve not only water molecules are discharged but the state of the electrode surface is also changed owing to adsorption of carboxylic anions as noted by Antropov [7], or to formation of oxidic anion compounds on the surface. The surface state of the electrode changes slowly with time. As can be seen in Fig. 1, the rate of the anodic reaction is found to decrease with time, and tends to a limiting value, if the potential relieved before the taking of the i-t curve corresponds to the first part of the polarization curve. The change in current density with time at constant potential satisfies the exponential law $i_t = i_0 + Ce^{-kt}$. The rise in potential with time at constant current density can be represented as $\varphi = \text{const} + bt$, an expression similar to that reported by Bockris and Solc [8] for the changes in current density and potential with time during liberation of oxygen from sulfuric acid solutions. The position of the first part of the polarization curve hardly depends on the acetate concentration in the solution. In concentrated solutions the overvoltage of oxygen liberation even rises slightly, probably owing to a lowering of the activity of water. With increasing acetate concentration the coefficient b increases slightly; this is analogous to the effect observed by Efimov and Izgaryshov [9] during liberation of oxygen from sulfuric acid solutions. Up to a pH of 11.5, variation of the pH of the solution has no effect at all on the position and the shape of the polarization curve. When the pH exceeds the above value, the overvoltage of oxygen liberation diminishes. This phenomenon is probably due to the fact that in acid, neutral, and weakly alkaline solutions of sodium acetate at potentials corresponding to the first part of the polarization curve, oxygen is liberated by the discharging of water molecules according to the following scheme:

$$H_2O \rightarrow e^- + OH^- + H^+$$
$$4OH^- \rightarrow O_2 + 2H_2O$$

Hence, the position of this part does not depend on the pH. At pH > 11.5, oxygen is already liberated by the discharge of OH$^-$ ions.

$$OH^- \rightarrow e^- + OH^-$$
$$4OH^- \rightarrow O_2 + 2H_2O$$

Consequently, in sodium acetate solutions the transition from oxygen liberation by discharging of water molecules to oxygen liberation by discharging of OH$^-$ ions takes place only at a pH > 11.5.

If the discharging of water molecules were not retarded by a change in the state of the electrode surface, then at nearly all current densities liberation of oxygen would be observed and reactions requiring higher anodic potentials would be impossible in aqueous solutions. However, liberation of oxygen is retarded by a change in the state of the electrode surface caused by adsorption of carboxylic anions, or by formation of oxidic anion compounds on the