# ANODIC PROCESSES DURING THE ELECTROLYSIS OF SALTS OF CARBOXYLIC ACIDS

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Figure 1

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## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# ANODIC PROCESSES DURING THE ELECTROLYSIS OF SALTS OF CARBOXYLIC ACIDS

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It has been noted repeatedly in the literature that the Kolbe reaction:

$$2\mathrm{CH_3COO^-} - 2e \rightarrow \mathrm{C_2H_6} + 2\mathrm{CO_2}$$

proceeds at the anode at potentials more positive than the oxygen-evolution potential ($^{1-9}$). In aqueous solutions such processes can occur only under conditions in which the oxygen-evolution process is inhibited.

A number of authors ($^{10-20}$), in studying the anodic process of oxygen evolution, observed at high potentials on a platinum electrode inhibition of this reaction and the appearance of a wave, the maximum current of which decreases with increasing solution concentration. In some works ($^{13}$) the inhibition is regarded as the result of a change in the state of the surface due to the formation of higher platinum oxides or compounds of platinum with the discharged ion (radical). Other authors believe that this phenomenon is connected with adsorption of the anion ($^{11,12,15}$).

We studied the anodic process during electrolysis of sodium acetate with a rotating platinum disk anode. The investigations were carried out both by recording polarization curves by the compensation method and by recording polarograms on PE-312 and Heyrovský polarographs. As a result of preliminary alternating cathodic-anodic polarization, the procedure for which is described in ($^{21}$), and of a high purity of the solutions, good reproducibility of the results was achieved—within 1% for currents and within 0.005 V for potentials.

**Fig. 1.** Polarograms of $\mathrm{NaOOCCH_3}$ on a Pt electrode.
*I*—background $0.575\,N$ $\mathrm{NaHCO_3}$;
*II*—background $+\,0.1\,N$ $\mathrm{NaOOCCH_3}$;
*III*—background $+\,0.2\,N$ $\mathrm{NaOOCCH_3}$;

Fig. 2. Polarization curves for solutions of sodium acetate of various concentration. I –0.1 N NaOOCCH3; II –0.2 N NaOOCCH3; III –0.6 N NaOOCCH3; IV –1 N NaOOCCH3; V –1.6 N NaOOCCH3; VI –3.0 N NaOOCCH3; VII –4.0 N NaOOCCH3. t = 25° C

Figure 2: Fig. 2. Polarization curves for solutions of sodium acetate of various concentration. I –0.1 N NaOOCCH3; II –0.2 N NaOOCCH3; III –0.6 N NaOOCCH3; IV –1 N NaOOCCH3; V –1.6 N NaOOCCH3; VI –3.0 N NaOOCCH3; VII –4.0 N NaOOCCH3. t = 25° C

$IV$–background $+\,0.3\,N$ $NaOOCCH_3$;
$V$–background $+\,1\,N$ $NaOOCCH_3$;
$t = 25°C$.

Figure 1 shows the anodic curves for sodium acetate in a background of $0.575\,N$ $NaHCO_3$. As is seen from Fig. 1, in the absence of added acetate the curve has a smooth rise, but if $NaOOCCH_3$ is added to the solution, a maximum appears on the polarogram. The first part of the curve in the presence of acetates always reproduces the background curve, while the second part lies beyond the background curve. The higher the acetate concentration, the lower the height of the maximum and the less positive the potentials at which the inhibition process is observed. All this indicates that the inhibition process is connected with the concentration of acetates in the solution and is not the result of formation of a higher oxygen oxide (absence of inhibition for the pure background). We investigated the influence of various

factors on the inhibition process. The independence of the maximum current from the rate of rotation of the electrode indicates the kinetic nature of this maximum.

Figure 2 presents the curves $\varphi$— $\lg I$ for pure solutions of $NaOOCCH_3$ of different concentrations. The curves have two linear sections. The first, from 1.8 to 2.1 V, with a slope coefficient of 0.220, corresponds, as analysis of the anode gases showed, to the process of oxygen evolution. The slight increase in overvoltage at high concentrations of sodium acetate for this section is probably connected with a decrease in the activity of water in concentrated solutions.

**Fig. 2.** Polarization curves for solutions of sodium acetate of various concentration.
$I$ –0.1 $N$ $NaOOCCH_3$; $II$ –0.2 $N$ $NaOOCCH_3$; $III$ –0.6 $N$ $NaOOCCH_3$; $IV$ –1 $N$ $NaOOCCH_3$; $V$ –1.6 $N$ $NaOOCCH_3$; $VI$ –3.0 $N$ $NaOOCCH_3$; $VII$ –4.0 $N$ $NaOOCCH_3$. $t = 25°C$

The anode gases on the second section of the curve contain $CO_2$, $C_2H_6$, and other products of Kolbe synthesis, which indicates the discharge of acetate anions. When the activity of acetate is changed tenfold, a parallel shift of the second section by 0.120 V toward less positive potentials is observed. The dependence of the current at constant potential on the activity of acetate for the second section of the polarization curve is a straight line passing through the origin, i.e., the process of discharge of acetate ions is a first-order reaction. The second section of the polarization curve, corresponding to discharge of the acetate ion, may be described by the following equation, obtained by us from experimental data:

$$\varphi' = 2.43 - 0.120 \lg a_{\mathrm{CH_3COO^-}} + 0.120 \lg I. \quad (1)$$

The transition to Kolbe electrosynthesis is possible only as a result of inhibition of the oxygen-evolution process, and the maximum on the curve at potentials 2.1-2.2 is a consequence of this phenomenon.

The magnitude of the current of this maximum falls with increasing acetate activity, and the dependence of $\lg I_{\max}$ on the logarithm of the activity is expressed by a straight line (Fig. 3), whence it follows that

$$I_{\max} = \frac{A}{a^n_{\mathrm{CH_3COO^-}}}, \quad (2)$$

where $A = \mathrm{const}$, and $n = 0.56$ for sodium acetate. With an increase in acetate activity by a factor of ten, the potential $\Phi$, at which inhibition occurs, is shifted by 120 mV toward lower potentials, i.e.,

$$\Phi = \Phi^0 - \frac{RT}{\alpha_2 F} \ln[\mathrm{CH_3COO^-}] = 2.134 - 0.120 \lg a_{\mathrm{CH_3COO^-}}. \quad (3)$$

The dependence of the potential at the onset of inhibition and of the maximum current on the activity of acetate indicates that inhibition is observed as a result of adsorption of acetate ions, which leads to a decrease in the surface concentration of water molecules (or $\mathrm{OH^-}$ ions) and, consequently, to a drop in current. This drop in current will continue until the potential of discharge of acetate ions is reached, after which a new rise in the polarization curve is observed, corresponding to Kolbe synthesis. On the reverse sweep, the maximum on the curve is not reproduced and hysteresis is observed—

lysis. Changing the rate of potential supply changes the magnitude of the maximum current and the depth of the drop.

Changing the pH of the solution up to pH 11.5 has absolutely no effect on the polarization curve or on the maximum current. At pH $> 11.5$, the first section of the polarization curve, corresponding to oxygen evolution, with an increase of pH by one unit shifts in parallel by 220 mV toward lower potentials. The position of the second section, corresponding to the discharge of acetate ions, does not change. This phenomenon is probably connected with the fact that in acidic, neutral, and weakly alkaline solutions of sodium acetate, oxygen is evolved in the first section as a result of the discharge of water molecules:

**Fig. 3.** Dependence of the logarithm of the maximum current on the logarithm of the activity of $NaOOCCH_3$; $t = 25°C$

**Fig. 4.** Effect of the pH of the solution on the maximum current:
*I*—in $0.6\,N$ $NaOOCCH_3$;
*II*—in $2.0\,N$ $NaOOCCH_3$; $t = 25°C$

$$H_2O - e \rightarrow OH + H^+$$

and therefore the position of this section does not depend on pH. At $pH > 11.5$, oxygen evolution already occurs as a result of the discharge of $OH^-$ ions:

$$OH^- - e \rightarrow OH.$$

Consequently, in sodium acetate solutions the transition from the process of oxygen evolution as a result of the discharge of water molecules to the process of discharge of $OH^-$ ions occurs only at pH 11.5.

From Fig. 4 it is clearly seen that the maximum current does not depend on pH up to pH 11.5, and with a further increase in pH the maximum current rises rapidly, i.e.,

$$\lg I_{\max} = \text{const} + \text{pH}. \tag{4}$$

The inhibiting potential $\Phi$ does not change at all over the entire range of pH values. It is known from the literature ([8,22]) that at $pH \geq 11$ the Kolbe reaction is suppressed, and oxygen becomes the main anodic product.

A change in temperature also strongly affects the composition of the products in Kolbe electrosynthesis. Our studies showed that with increasing temperature the height of the maximum current corresponding to the process of inhibition of oxygen evolution rises rapidly. The dependence of the logarithm of the maximum current on the reciprocal temperature is expressed by a straight line, i.e.,

$$\lg I_{\max} = A + \frac{B}{T}. \tag{5}$$

With increasing temperature, the inhibiting potential, according to expression (3), shifts slightly toward lower values.

Thus, we have established the regularities of the transition from the anodic process of oxygen evolution to Kolbe electrosynthesis as a result of inhibition of the first process due to adsorption of acetate anions. The influence of various conditions on the process of inhibition of oxygen evolution has been studied.

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*Note: Figure translations are in progress. See original paper for figures.*