# Reports of the Academy of Sciences of the USSR

M. Ya. Fioshin, Yu. B. Vasil'ev, and E. T. Gaginkina

1960

SovietRxiv

## Abstract

## Full Text

Reports of the Academy of Sciences of the USSR
1960. Volume 135, No. 4

### PHYSICAL CHEMISTRY

**M. Ya. Fioshin, Yu. B. Vasil' ev, and E. T. Gaginkina**

# ON THE INFLUENCE OF THE NATURE OF THE CATION ON THE KOLBE ELECTROSYNTHESIS

*(Presented by Academician A. N. Frumkin on 26 VI 1960)*

It has already been noted in the literature that the cation of the salt of a carboxylic acid has a considerable influence on the yield of products formed at the anode in the Kolbe electrosynthesis ([1–3]). The influence of the nature of cations on the anodic process has also been observed in a number of other anodic reactions proceeding at high potentials. Izgaryshev and co-workers noted the influence of the nature of cations on the yield of persulfuric acid during anodic oxidation of sulfuric acid and related this influence to a change in the degree of hydration of hydrosulfate ions ([4,5]). Erdey-Gruz and Shafarik believe that cations added to sulfuric acid in the form of sulfates alter the overvoltage of oxygen at the anode, owing to their influence on the water molecules adsorbed in the double layer ([6,7]).

Kolbe electrosynthesis proceeds at high anodic potentials and, as in the case of the electrosynthesis of persulfuric acid, is associated with the dimerization reaction of free radicals formed as a result of the discharge of anions ([8]). However, although in the electrosynthesis of persulfuric acid a number of regularities have been found in the changes in anodic polarization and product yields as functions of the nature of the cation, and attempts have been made to explain the observed phenomena, this cannot be said of the Kolbe electrosynthesis. Although the dependence of the yield of hydrocarbons on the nature of the cation of the carboxylic-acid salt has been noted, no regularities have been found, and there is no satisfactory explanation in the literature for the existence of this dependence. It was therefore of interest to study the influence of cations on the anodic process in the Kolbe electrosynthesis. Using the method described earlier ([8]), we studied the behavior, on a rotating platinum anode, of acetates of the following cations: $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $Rb^+$, $Cs^+$, $(CH_3)_4N^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Tl^+$, $Tl^{3+}$, $Co^{2+}$, $Mn^{2+}$, $Pb^{2+}$. At the same time, on a stationary smooth platinum electrode, using an apparatus that made it possible to analyze the gas at individual points of the polarization curve, we studied the influence

Figure 1

Figure 1: Figure 1

of the nature of the cations on the yield of the main products of the Kolbe electrosynthesis—carbon dioxide and ethane.

As we established earlier ([8]), the Kolbe electrosynthesis proceeds at potentials more positive than the potentials corresponding to oxygen evolution. On the polarization curve, the onset of discharge at the anode of the carboxylic-acid anions is preceded by an oxygen-evolution wave and a maximum, the appearance of which is connected with inhibition of the oxygen-evolution process as a result of adsorption of anions. As the polarization curves showed, the nature of the cation strongly affects the first section, corresponding to the process of oxygen evolution as a result of discharge of water molecules, which leads to a sharp change in the maximum current (Fig. 1). Its influence on the second section of the curve, corresponding to discharge of acetate ions, is very insignificant.

Figures 2 and 3 show the dependence of the logarithm of the maximum current on the logarithm of the acetate concentration. In concentrated solutions the nature of the cation has little effect on the maximum current. However, the more dilute the solution, the more significant this effect becomes, which is difficult to explain by the dehydrating action of the cation on the anion.

Fig. 1. Polarization curves $\varphi$—lg $I$ for 0.1 $N$ acetates of alkali metals.
$I$—$KOOCCH_3$, $II$—$NaOOCCH_3$, $III$—$LiOOCCH_3$

Proceeding from these considerations, we selected 0.2 $N$ acetate solutions for carrying out electrolyses with the aim of collecting and analyzing the gases.

When considering the dependence of the maximum current on the nature of the cation, the connection of this phenomenon with the radius of the cation is striking. The larger the radius of the cation, the lower the maximum current, i.e., the earlier inhibition of the oxygen-evolution process occurs and discharge of acetate ions begins. Thus, one should expect that, in the electrolysis of an acetic-acid salt whose cation has the maximum radius, the maximum yield of the principal products of the Kolbe electrosynthesis will be obtained. The nature of the cation affects not only the maximum current, but also its dependence on concentration, expressed by the relation

$$I_{\max} = \frac{A}{C^n} \tag{8}$$

i.e., on the magnitudes $A$ and $n$. The larger the radius of the cation, the lower the maximum current and the smaller its dependence on concentration. Table 1 well illustrates the influence of the nature of the cation on the anodic process in Kolbe synthesis as a function of the magnitude of the cation radius.

Figure 2

Figure 2: Figure 2

Fig. 2. Dependence of the logarithm of the maximum current on the logarithm of the acetate concentration

It follows from Table 1 that, in the electrolysis of acetates whose cations have the largest radius, the maximum yield of Kolbe electrosynthesis products is observed. Attainment of the maximum yield corresponds to the greatest decrease in the maximum current, i.e., to the strongest suppression of the oxygen-evolution process.

The influence of the nature of the cations on the anodic process is probably connected with adsorption of cations in the electric double layer. To clarify this question we measured the shift of the electrode potential from the initial value in the potential range from 0.5 to 2.0 V relative to the normal hydrogen electrode upon addition of cations to solutions of acetates of other cations. In studies of additions of the cations $K^+$, $Rb^+$, $Cs^+$, and $(CH_3)_4N^+$ to a $0.1\,N$ lithium acetate solution and to a $1\,N$ sodium acetate solution, a linear dependence of the adsorption-

**Table 1**

Dependence of the yield of carbon dioxide and ethane on the nature of the cation. Anodic current density 10 A/dm$^2$, acetate concentration 0.2 N

| Cation | $I_{max}$ at $C = 0.1\,N$, $\mu$A | $n$ | Current yield of the dimerization product $C_2H_6$, % | Cation radius $r$, Å | Cation | $I_{max}$ at $C = 0.1\,N$, $\mu$A | $n$ | Current yield of the dimerization product $C_2H_6$, % | Cation radius $r$, Å |
|---|---|---|---|---|---|---|---|---|---|
| $Li^+$ | 46,8 | 0,63 | 64,0 | 0,60 | $(CH_3)_4N^+$ | 11,2 | 0,205 | 76,2 | – |
| $Na^+$ | 38,9 | 0,63 | 66,2 | 0,95 | $Mg^{2+}$ | 61,5 | 0,54 | – | 0,65 |
| $K^+$ | 22,4 | 0,49 | 68,2 | 1,33 | $Ca^{2+}$ | 51,1 | 0,56 | 61,1 | 0,99 |
| $NH_4^+$ | 17,35 | 0,42 | 68,7 | 1,43 | $Sr^{2+}$ | 38,9 | 0,515 | 61,7 | 1,13 |
| $Rb^+$ | 15,85 | 0,380 | (66,4) | 1,48 | $Ba^{2+}$ | 30,9 | 0,46 | 68,3 | 1,35 |
| $Cs^+$ | 13,5 | 0,280 | – | 1,99 | | | | | |

···shift $\Delta\varphi$ from the logarithm of the concentration of the added cation, i.e., $\Delta\varphi = b \lg C$. A similar dependence was found by Erdley-Grúz and Shafarik [7].

Fig. 3. Dependence of the logarithm of the maximum current on the logarithm of the concentration for acetates of divalent metals

Figure 3: Fig. 3. Dependence of the logarithm of the maximum current on the logarithm of the concentration for acetates of divalent metals

This dependence was observed only at very low additive concentrations (from $10^{-6}$ to $10^{-2}\,N$). When the additive concentration exceeds a certain value, a further increase in concentration no longer causes a shift of the potential.

The greater the difference in the radii of the background cation and the introduced acetate, the stronger the potential shift, caused by adsorption, in the positive direction. The larger the radius of the cation, the lower the concentration at which no further shift of the potential is observed.

Analogously, the maximum current corresponding to inhibition of the oxygen-evolution process also changes. In this case it is observed that the introduced acetate lowers the maximum current only when the radius of its cation is greater than the radius of the cation of the acetate serving as the background. For example, if tetramethylammonium or cesium acetates are added to a sodium acetate solution, a sharp decrease in the maximum current is observed. If, however, acetates whose cations have a smaller radius than the background cations are introduced, this produces no effect, i.e., no change in the maximum current or shift of the potential is observed.

**Fig. 3.** Dependence of the logarithm of the maximum current on the logarithm of the concentration for acetates of divalent metals

The observed phenomenon can probably be explained only by assuming that the cations participate in the construction of the electrical double layer at the anode. The introduction into solution of the acetate of a cation having a larger radius and, consequently, a greater adsorption capacity on the given electrode apparently leads to its preferential adsorption on the electrode. Additions of a cation having a lower adsorption capacity than the background cation do not lead to a change in the structure of the double layer or to a shift of the potential. Consequently, according to the adsorption activity of cations on smooth platinum, they may be arranged in the following series:

$$(CH_3)_4N^+ > Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > Li^+.$$

In Obrucheva' s work ([9]) the conclusion is drawn that cations whose electron shell does not have a noble-gas configuration can exhibit strongly pronounced specific adsorption. Specific adsorbability of $Cs^+$ on the surface of Hg, on which $F^-$ ions are adsorbed, was found in the work of Damaskin, Nikolaeva-Fedorovich, and Frumkin ([10]).

We also studied the specific action of cations of variable valence, $Tl^+$, $Co^{2+}$,

$Mn^{2+}$, $Pb^{++}$, and showed that the action of these cations is connected not with their activity as "catalysts for the decomposition of hydrogen peroxide," as Glasstone and Hickling ([1]) supposed, but with a change in the state of the electrode surface in the presence of these cations. The surface changes as a result of the formation on the electrode of a deposit of the oxides of these metals ($MnO_2$ and $PbO_2$). The occurrence of a new electrode process at the electrode is also possible ($Co^{2+} - e \to Co^{3+}$, $Tl^{+} - 2e \to Tl^{3+}$).

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
6 VII 1960

## REFERENCES

[1] S. Glasstone, A. Hickling, *Electrolytic Oxidation and Reduction*, London, 1935, p. 279.
[2] O. Walker, J. Weiss, Trans. Farad. Soc., **31**, 1011 (1935).
[3] F. Fichter, R. Zumbrunn, Helv. chim. Acta, **10**, 878 (1927).
[4] N. Isgarischew, S. Berkmann, Zs. Elektrochem., **28**, 40 (1922).
[5] N. A. Izgaryshev, A. A. Petrova, ZhFKh, **24**, 881 (1950).
[6] T. Erdey-Gruz, I. Shafarik, Transactions of the 4th Conference on Electrochemistry, Moscow, 1959, p. 263.
[7] T. Erdey-Gruz, J. Safarik, Acta chem. Acad. sci. Hung., **13**, 159 (1957).
[8] M. Ya. Fioshin, Yu. B. Vasiliev, DAN, **134**, No. 4 (1960).
[9] A. D. Obrucheva, DAN, **120**, 1072 (1958).
[10] B. B. Damaskin, N. V. Nikolaeva-Fedorovich, A. N. Frumkin, DAN, **121**, 129 (1958).

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