# INVESTIGATION OF THE MECHANISM OF SOME ANODIC PROCESSES BY A COMBINATION OF ELECTROCHEMICAL AND LABELLED ATOM METHODS

M. A. Gerovich* and R. I. Kaganovich

The M. V. Lomonosov Moscow State University, Chemical Faculty

A series of recent papers [1] shows that there is a promising future for a simultaneous combination of the method of labelled atoms with electrochemical methods, for investigating the structure of the electrical double layer and the mechanism of electrochemical reactions. Use of the heavy oxygen isotope has proved extremely valuable for investigating the mechanism of anodic processes. Interesting results were obtained in this field by V. I. Veselovskii and K. I. Rozental', who used the heavy oxygen isotope ($O^{18}$) to determine the degree of participation of surface oxides in the process of evolution of oxygen, with polarizations up to 1.5 v.

In this paper we used the oxygen isotope $O^{18}$ to study the mechanism of anodic oxidation of the sulfate ion to persulfate, and also of the anodic evolution of oxygen at a platinum electrode from concentrated solutions of $H_2SO_4$ and $HClO_4$.

## I. REACTION OF ANODIC FORMATION OF PERSULFATE

In investigating this process [2], our object was to make use of the heavy oxygen isotope to decide between the two main different mechanisms of anodic persulfate formation discussed in the literature – by means of electrons according to the scheme

$$HSO_4^- - e \rightarrow H^+ + SO_4^-$$

or

$$SO_4^{2-} - e \rightarrow SO_4^- \qquad (1)$$

$$2SO_4^- \rightarrow S_2O_8^{2-}$$

or by means of atoms, where the $SO_4^{2-}$ ion is oxidized by platinum oxide, the hydroxyl radical or hydrogen peroxide, formed by the primary electrochemical process, according to the scheme

$$\left.\begin{aligned} nH_2O + Pt - 2ne &\rightarrow PtO_n + 2n\,H^+;\\ PtO_n + HSO_4^- &\rightarrow HSO_5^- + PtO_{n-1};\\ HSO_5^- + HSO_4^- &\rightarrow S_2O_8^{2-} + H_2O; \end{aligned}\right\} \qquad (2)$$

$$\left.\begin{aligned} 2H_2O - 2e &\rightarrow 2OH + 2H^+;\\ HSO_4^- + 2OH\ (\text{or}\ H_2O_2) &\rightarrow HSO_5^-. \end{aligned}\right\} \qquad (3)$$

With this object, we electrolyzed a solution of $K_2SO_4$ in water, containing heavy oxygen. The potassium persulfate, formed at the anode, was decomposed thermally, and the oxygen evolved was analyzed by mass spectrometry.

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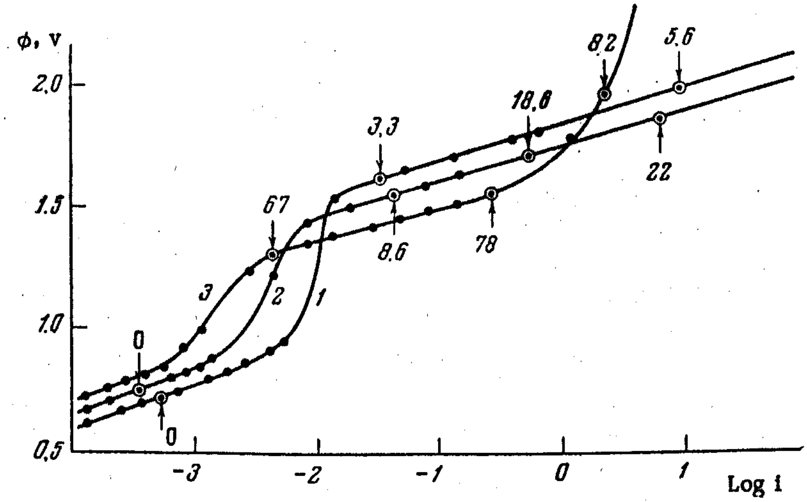
* Deceased.

Results of Isotopic Analysis of the Original Water and $K_2S_2O_8$ Obtained by Electrolysis

| Anolyte composition | $O^{18}$ in water, mole % | Decomposition of $K_2S_2O_8$, % | $O^{18}$, in $O_2$ mole % |
|---|---|---|---|
| 5% solution of $K_2SO_4$ in 0.1 N KOH | 0.200 | 90.9 | 0.200 |
| 5% solution of $K_2SO_4$ in 0.1 N KOH | 0.613 | 86.2 | 0.200 |
| 5% solution of $K_2SO_4$ in 0.15 N $H_2SO_4$ | 0.613 | 91.0 | 0.200 |
| 5% solution of $K_2SO_4$ in 0.1 N KOH | 1.23 | 78.4 | 0.198 |



Anodic polarization curves of a platinum electrode in perchloric acid. 1) 5.8 N $HClO_4$; 2) 7.6 N $HClO_4$; 3) 10 N $HClO_4$. The numbers show the share of the acid anion in the evolution of oxygen (as percentages). The current density, i, is expressed in amp/$cm^2$.

The results, given in the table, show that in none of the samples investigated was there any enrichment of the oxygen in the $O^{18}$ isotope, which indicated that the oxygen of the water was not taking part in the anodic oxidation of the sulfate ion.

Analysis of the oxygen from persulfate, obtained by electrolysis of labelled sulfate in ordinary water, showed its enrichment with $O^{18}$. We could deduce from these results that the electron mechanism for the formation of persulfate was more probable. It should be noted, however, that, to obtain a final confirmation of this view, it is necessary to exclude another, although less probable, mechanism which is also consistent with the results obtained – the transfer of a hydrogen atom from the $HSO_4$ – ion to the anode surface and subsequent combination of the atom with adsorbed oxygen. This possibility is now being investigated.

## II. REACTION OF ANODIC EVOLUTION OF OXYGEN

Polarization curves [3], recorded by us with a platinum anode in concentrated solutions of $HClO_4$ and $H_2SO_4$, over the current density range $0.7 \times 10^{-5}$ to 0.7 amp/$cm^2$, showed three well defined parts, characterized by different angles of slope to X axis*. Analysis of these curves, for example, those of $HClO_4$, showed that, over the region 0.3 to 0.9 v, the overvoltage was directly proportional to the logarithm of the current density, with a coefficient b = 0.16 v. Further increase in current, corresponded to an abrupt increase in overvoltage, amounting to 0.8 v for a small change in current density, after which the curve became rectilinear again with a slope close to that of the first part of the curve. Let us consider the effect of acid concentration on the course of the electrochemical reaction. A comparison of curves 1-3 of Fig. 1, corresponding to 5.8, 7.6 and 10 N $HClO_4$, shows that

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*Similar curves for sulfuric acid were obtained in papers by N. A. Izgaryshev and E. A. Efimov [4] and by V. L. Kheifets and I. R. Rivlin [5].

the anodic overvoltage, in the region of current density corresponding to the lower part of the curve, increased with increasing acid concentration, but that the increase in overvoltage, corresponding to the transition from the lower to the upper part of the curve at the point noted, considerably decreased. Moreover, the point, at which the slope of the polarization curve altered, shifted in the direction of lower current density with increasing concentration of acid. The marked increase in overvoltage occurred at higher current densities in $H_2SO_4$ than in $HClO_4$. The above relation between overvoltage and concentration and composition of solution indicates that, in the region of current density corresponding to the lower part of the curve, the kinetics of the process of evolution of oxygen were determined, not only by the rate of decomposition of surface oxides, whose potential would completely determine the value of the overvoltage in the absence of influence by the composition of the solution, but also by the rate of discharge of water molecules, which is indeed one of the slow stages. The subsequent abrupt increase in overvoltage, in the next part of the curve, is probably associated with a change in the condition of the electrode surface.

It appeared to us, that, with a retarded electrochemical stage, an increase in the extent of coverage of the electrode surface with adsorbed reaction products must produce an increase in overvoltage to a value close to the equilibrium potential of the adsorbed layer, as was suggested by A. N. Frumkin and N. A. Aladzhalova [6] for the hydrogen overvoltage on palladium. Considering the above described relations between increase in overvoltage and anion concentration, we formed the hypothesis that acid was concerned in increase in oxidation of the surface. We used the method of labelled atoms to check this hypothesis, carrying out the electrolysis with $HClO_4$ labelled with $O^{18}$, and subsequently analyzing the oxygen liberated for its $O^{18}$ content by mass spectrometry. We reckoned that, if our hypothesis as to the participation of the acid anion in the evolution of oxygen was correct, then the oxygen collected at overvoltages corresponding to the upper part of the polarization curve should be enriched in $O^{18}$, while oxygen collected at overvoltages corresponding to the lower part of the curve should be of normal composition. The isotopic analysis results for oxygen liberated in the electrolysis of $HClO_4$ solutions of three concentrations (5.8, 7.6 and 10 N), at different polarizations, showed that oxygen collected at overvoltages of 0.65-0.8 v (lower part of the curve) did not contain more than the normal amount of $O^{18}$. This showed that the $ClO_4^-$ ion did not take part in the anodic formation of oxygen.

However, when a change was made to higher overvoltages of 1.4-2.0 v (upper part of curve), there was a rise in the $O^{18}$ content, which was greater the higher the anion concentration and the higher the overvoltage. If the participation of acid in the process of oxygen evolution was expressed by the ratio of excess $O^{18}$ in the oxygen sample to the $O^{18}$ in the original acid, then, for the lower part of the curve, this was equal to nil, and, for the upper part of the curve at similar overvoltage values (1.55-1.6 v), was 3.6, 18.7 and 78 %,respectively, for 5.8, 7.6 and 10 N $HClO_4$. This is shown graphically in Fig. 1, where the percentage participation of the anion in the process of evolution of oxygen is given, together with the overvoltage at which electrolysis was carried out. The results obtained confirmed the above hypothesis that a change to high overvoltage is accompanied by a change in mechanism of the process of evolution of oxygen, associated with participation of the acid anion.

Let us consider the nature of this participation. The yellowing of the anolyte, observed in the electrolysis of 10 N $HClO_4$ at overvoltages exceeding 1.7 v, was evidently due to the formation of $ClO_2$, which could be explained by supposing that liberation of oxygen was due to decomposition of the $ClO_4$ radical, formed by discharge of the $ClO_4^-$ ion. However, analysis of the anolyte, after electrolysis at an overvoltage of 1.4 v (upper part of curve), when the participation of the anion amounted to about 70%, showed the absence of either $ClO_2$, thus, excluding the decomposition of the $ClO_4$ radical as a mechanism of the process, or the $ClO_3^-$ ion, thus, excluding another conceivable mechanism of interaction of the $ClO_4$ radical with water in the bulk of the solution and formation of the ion $ClO_3^-$ and oxygen, according to the scheme:

$$ClO_4^- \rightarrow ClO_4 + e;$$

$$4ClO_4 + 2H_2O \rightarrow 4\,ClO_3^- + 4H^+ + 3O_2.$$

Considering all these results, we arrived at the following hypothesis as to the nature of the participation of the acid anion in the process of evolution of oxygen. The abrupt increase in overvoltage, associated, as stated above, with adsorption of the anion, must evidently lead to powerful deformation of the latter. Because of this, conditions are established in which the acid anion takes part in a reaction of isotopic exchange with the platinum surface oxides, and thus, participates in the process oxygen evolution.

It should also be noted that the oxygen of the water, distilled off from the acid after electrolysis, had the normal isotopic composition, which showed the absence of any exchange between the electrolysis products and the water, and confirmed the irreversibility of the electrochemical stage of formation of oxides.

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*Original Russian pagination. See C. B. Translation.