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O_2 + H_2O = O_3 + 2H^+ + 2e.

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Abstract

Full Text

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ON THE NATURE OF SURFACE OXIDES OF PLATINUM FORMED DURING THE ANODIC DISCHARGE OF HYDROGEN PEROXIDE

Electrolysis of aqueous solutions containing hydrogen peroxide or peroxo acids is accompanied by the evolution of anodic O_2, which contains, as was found in earlier works (1–3), oxygen of the peroxide compound.* In this process, peroxide discharge is the dominant anodic reaction, and only after the peroxide concentration in the solution becomes sufficiently small (for example, a few g/liter H_2O_2 in 20% $KHSO_4$ (1)) does the discharge of water and HSO_4^- begin to predominate, with formation of O_2 from the oxygen of water (and of persulfate, retaining the oxygen of sulfate). In another work (2) it was shown that anodic ozone is formed from O_2 and the oxygen of water in exact accordance with the stoichiometric relation:

$$O_2 + H_2O = O_3 + 2H^+ + 2e. \tag{1}$$

These results are well explained by the ideas developed by V. M. Veselovskii (6) and A. N. Frumkin (7), according to which the primary stage of the anodic reaction is the formation of surface oxides of platinum, which, upon interaction with water, give anodic oxygen and ozone. However, our data (2, 3) lead to the conclusion that, in an electrolyte containing peroxide compounds, higher surface oxides of platinum are formed not only from water:

$$\mathrm{PtO} + 2H_2O = \mathrm{PtO}[OO] + 4H^+ + 4e, \tag{2}$$

but also from these peroxides:

$$\mathrm{PtO} + H_2O_2 = \mathrm{Pt}[OO] + 2H^+ + 2e, \tag{3}$$

$$\mathrm{PtO} + H_2O + HOOSO_3^- = \mathrm{PtO}[OO] + HSO_4^- + 2H^+ + 2e. \tag{4}$$

In studying the mechanism of the last reaction (4), cleavage of peroxomonosulfuric acid during its decomposition at the anode was established (3).

To study the behavior of the peroxide bond during the anodic decomposition of H_2O_2 and to elucidate the nature of the higher oxide of platinum formed in this process, we investigated the isotope-exchange reaction

$$O_2^{18} + O_2^{16} = 2O^{16}O^{18} \tag{5}$$

under the conditions of the anodic process. Its equilibrium constant

$$K = \frac{[O^{16}O^{18}]^2}{[O_2^{16}][O_2^{18}]}$$

corresponds practically exactly to the statistical distribution ($K = 4$), for which the ratio of isotopic molecules is:

$$\frac{[O_2^{18}]}{[O^{16}O^{18}]} = \frac{u^2}{2u(1-u)} \quad \text{and} \quad \frac{[O_2^{18}]}{[O_2^{16}]} = \frac{u^2}{(1-u)^2},$$

where

$$u = \frac{2[O_2^{18}] + [O^{16}O^{18}]}{2[O_2^{16} + O_2^{18} + O^{18}O^{16}]}$$

is the total atomic fraction of O^{18} in the oxygen. If mixtures of O_2 of different isotopic composition are taken, then the equilibrium of reaction (5) and the indicated ratio of isotopic varieties can be established only upon cleavage of the O—O bonds, without which no exchange of oxygen occurs between O_2 molecules of different isotopic composition.

The experiments were carried out in a U-shaped electrolyzer at a current density from 0.05 to 0.2 a/cm^2 on an anode made of platinum wire, at a potential difference of 12 V.

* Our data were confirmed in a later work by Devis et al. (4). In it, also, in agreement with the earlier published work (5), it was found that the hydrogen peroxide formed on a carbon cathode during electrolysis of alkaline solutions contains oxygen only from gaseous O_2 washing this electrode. In (4) it was also shown by the method described in the present article that, during the cathodic reduction of elemental oxygen to H_2O_2, no destruction of the O—O bond occurs.

The electrolyte used was a solution of $\mathrm{H_2O_2^{18}}$ in $2N$ $\mathrm{H_2SO_4^{16}}$, dissolved in water of natural isotopic composition. The isotopic analysis of the oxygen was carried out by V. G. Golovatyi on an MX-1302 instrument. Heavy hydrogen peroxide was prepared from $\mathrm{H_2O^{18}}$ in a glow discharge by the method developed by I. I. Vol' nov and co-workers (^{8}). The content of $\mathrm{O^{18}}$ in the peroxide was determined from the oxygen evolved from it under the action of $\mathrm{KMnO_4}$. In experiments 1-3

(Table 1) the H_2O_2 contained 11.1% O^{18}, and in experiments 4–5 it was diluted approximately in a 1 : 1 ratio with H_2O_2 of natural isotopic composition.

Table 1

Isotopic composition of anodic oxygen

No. of experiment	Electrolysis conditions	Source and amount of O_2, cm^3	Analysis of O_2 [36]/[34]	Analysis of O_2 [36]/[32]	u	Calculated equilibrium [36]/[34]	Calculated equilibrium [36]/[32]
1	5% $H_2O_2^{18}$ 20 min.	$H_2O_2^{18}$+ $KMnO_4$	0.0630	0.0159	0.111	0.0631	0.0159
1	5% $H_2O_2^{18}$ 20 min.	anod., 10	0.0635	0.0161	0.112	0.0634	0.0161
2	6% $H_2O_2^{18}$ 90 min.	anod.	0.0627	0.0144	0.104	0.0580	0.0135
3	1.6% $H_2O_2^{18}$ 30 min.	anod., 15	0.0625	0.0035	0.0668	0.0358	0.0051
4	–	$H_2O_2^{18}$+ $H_2O_2^{16}$+ $KMnO_4$	0.0612	0.0075	0.0610	0.0324	0.0042
4a	6% $H_2O_2^{18}$+ $H_2O_2^{16}$	anod., 15	0.0640	0.0073	0.0574	0.0304	0.0037
4b	0.7% H_2O^{18}+ $H_2O_2^{16}$	» 19	0.0615	0.0039	0.0334	0.0173	0.0012
4c	traces of $H_2O_2^{18}$+ $H_2O_2^{16}$	» 13	0.0258	0.0003	0.0060	0.0030	0.00004
5	–	$H_2O_2^{18}$+ $H_2O_2^{16}$+ $KMnO_4$	0.0627	0.0078	0.0618	0.0330	0.0044

No. of experiment	Electrolysis conditions	Source and amount of O_2, cm^3	Analysis of O_2 [36]/[34]	Analysis of O_2 [36]/[32]	u	Calculated equilibrium [36]/[34]	Calculated equilibrium [36]/[32]
5a	2.5% $H_2O_2^{18}$+ $H_2O_2^{16}$	anod., 13	0.0640	0.0068	0.0539	0.0285	0.0032
5b	0.5% $H_2O_2^{18}$+ $H_2O_2^{16}$	» 20	0.0515	0.0013	0.0134	0.0069	0.00019

Table 1 gives the mean values of u, found from the heights of the mass-spectrometric peaks [36], [34], and [32], as well as their ratios calculated for an equilibrium mixture.

In experiments 4–5, separate portions of O_2 were successively collected and analyzed at different time intervals from the beginning of electrolysis.

The data obtained confirm earlier observations (^{1,4}), according to which, at a considerable content of H_2O_2 in the electrolyte, the anodic oxygen has the isotopic composition of the oxygen in H_2O_2. As the concentration of H_2O_2 in the electrolyte decreases, increasing amounts of light oxygen from water are admixed with the anodic O_2. It is significant that the initial ratio $[O_2^{18}]/[O^{18}O^{16}]$ of the oxygen in $H_2O_2^{18}$ is retained in the anodic O_2 even upon addition of 50% light $H_2O_2^{16}$ and with a large decrease in the total O^{18} content in it. At the same time, as is seen from Table 1, this ratio differs sharply from the equilibrium one.

Thus, the data presented show that the anodic decomposition of hydrogen peroxide is not accompanied by rupture of the O—O bond, and that the peroxide group passes, without being destroyed, from H_2O_2 into the anodic oxygen. This confirms the peroxide nature of the surface oxides of platinum formed during the discharge of H_2O_2 in accordance with stoichiometric equation (3).

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

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