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Abstract

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INVESTIGATION OF THE MECHANISM OF ANODIC FORMATION OF OZONE FROM SULFURIC ACID SOLUTIONS

Very little is known about the mechanism of anodic ozone formation. By analogy with its formation in a silent discharge, one may assume the gross scheme $O_2 + O = O_3$ (^{1}). The participation of water is more probable

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

with possible intermediate formation of oxygen ions or radicals. Investigation of anodic voltage curves and of the state of the electrodes led a number of authors ($^{2-4}$) to the conclusion that, in anodic formation of O_2 and anodic oxidation, oxygen participates in the form of surface oxides. In particular, V. I. Veselovskii et al. (^{5}) suggest, for platinum electrodes at high overvoltages corresponding to the production of ozone, the formation of higher oxides of the peroxide type, which with water yield ozone or oxygen:

$$PtO + 2H_2O = PtO[O-O] + 4H^+ + 4e; \tag{2a}$$

$$PtO[O-O] + H_2O = PtO + O_3 + 2H^+ + 2e; \tag{2b}$$

$$PtO[O-O] = PtO + O_2. \tag{2c}$$

This scheme differs from (1) in that the oxygen evolved at the anode does not directly participate in the formation of ozone. On the other hand, we previously found (^{6}) that, during electrolysis of $KHSO_4$ solutions, the yield of persulfate decreases sharply upon addition of H_2O_2, and the latter proves to be the main source of anodic O_2. As the concentration of H_2O_2 decreases, the persulfate yield increases and, in parallel, the fraction of oxygen from water in anodic O_2 increases. This made it possible to suppose that the higher surface oxides of platinum are formed not only according to (2a) from water, but also from peroxide compounds, for example

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

and that these peroxide compounds, or their precursors in the anodic reaction, also participate in ozone formation.

To investigate anodic ozone formation we used the heavy isotope of oxygen, which we had already successfully employed earlier ([2,6–10]) for the study of anodic processes.

Electrolysis was carried out in a vessel connected to a vacuum apparatus for separation of ozone and analysis of the anodic gas. After freezing out water, the latter was passed through a trap with 5% KI, where the ozone was collected and titrated, while the oxygen was measured by volume. For isotopic analysis, the gas entered another branch of the apparatus, where, after additional drying, the ozone was frozen out, degassed by pumping, purified by distillation into another vessel, where it was thawed and decomposed by heating to 150°. The anodic oxygen and the oxygen from ozone were analyzed for O^{18} content in a mass spectrometer. The completeness of ozone decomposition was checked by control

experiments on increasing the pressure by a factor of $1^1/_2$ (with an accuracy of 5%) after heating the vessel in which the collected liquid ozone had been evaporated. The completeness of separation was also checked: ozone containing no excess O^{18} was frozen out from a mixture with O_2^{18}. To determine O^{18} in H_2SO_4 and $KHSO_4$, they were converted into $PbSO_4$, which was heated with degassed carbon at 700°. The resulting CO_2 was introduced into the mass spectrometer. The content of O^{18} in water was also determined in the form of CO_2 after exchange with steam ([11]). Heavy $H_2SO_4^{18}$ was prepared by adding anhydrous acid to H_2O^{18}. From it, $KHSO_4^{18}$ was obtained by neutralization with KOH. An electrolyte containing 4-10 g of monoperoxysulfuric acid (Caro' s acid) in 60-70 ml of 5-6.5 M H_2SO_4 solution in H_2O^{18} was prepared by dissolving 40 g of $K_2S_2O_8$ powder with 26 ml of conc. H_2SO_4 under strong cooling, after which 50 ml of cooled H_2O^{18} was added. After standing for 1 h at 20°, the liquid was filtered. Electrolysis was carried out at 20°, with a current of 4-7 A, at a voltage of 11 V, an anodic current density of 1-1.5 A/cm^2, and a volumetric current density of 0.1-0.2 A/ml. The hollow platinum anode was additionally cooled with running water. Before the experiment it was washed in nitric acid and repolarized with a current of 0.1 A/cm^2. The determination of $S_2O_8^{2-}$ and SO_5^{2-} in the electrolyte was carried out iodometrically ([12,13]). Under the experimental conditions, appreciable amounts of H_2O_2 were not formed, and ozone condensed, depending on the experimental conditions, at 2–6 mg/h with oxygen evolution of about 1 l/h. In experiments with 4.5-6.8 M H_2SO_4, during electrolysis 0.004–0.008 moles of H_2SO_5 (per 40-60 ml) were formed as a result of hydrolysis of persulfate.

During electrolysis of saturated solutions of $KHSO_4$ in H_2O^{18} or $KHSO_4^{18}$ in H_2O, as well as 2.5 M H_2SO_4 in H_2O^{18}, the ozone had the isotopic composition of the oxygen of water, while in the sulfate the oxygen composition did not change (Table 1, experiments 1-3).

Table 1

Isotopic composition of the electrolyte, oxygen, and ozone

Experiment No.	Composition of electrolyte, mol/l	Duration of electrolysis, h	At. % O^{18} above natural: in initial SO_4^{2-}	At. % O^{18} above natural: in final SO_4^{2-}	At. % O^{18} above natural: in H_2O	At. % O^{18} above natural: in O_2	At. % O^{18} above natural: in O_3	At. % O^{18} above natural: calculated O_3 by (1)
1	Saturated $KHSO_4$	4	0.85	0.85	0	0.01	0.02	0
2	Same	4	0	0	0.73	0.68	0.72	0.70
3	2.5 M H_2SO_5	1	0	–	1.24	1.20	1.18	1.21
3	2.5 M H_2SO_5	2	0	0	1.24	1.18	1.18	1.21
4	4.5 M H_2SO_4	1	0	–	0.76	0.62	0.69	0.67
4	4.5 M H_2SO_4	2	0	0.06	0.76	0.63	0.69	0.67
5	6.8 M H_2SO_4	2	0	–	1.15	0.44	0.65	0.68
5	6.8 M H_2SO_4	3	0	0.28	1.15	0.54	0.75	0.73
6	5.5 M H_2SO_4 + 9.9 g H_2SO_5	1.5	0	–	1.18	0.25	0.59	0.60

Experiment No.	Composition of electrolyte, mol/l	Duration of electrolysis, h	At. % O^{18} above natural: in initial SO_4^{2-}	At. % O^{18} above natural: in final SO_4^{2-}	At. % O^{18} above natural: in H_2O	At. % O^{18} above natural: in O_2	At. % O^{18} above natural: in O_3	At. % O^{18} above natural: calculated O_3 by (1)
6	5.5 M H_2SO_4 + 9.9 g H_2SO_5	3.0	0	–	1.18	0.42	0.59	0.60
7	6.0 M H_2SO_4 + 8.7 g H_2SO_5	2	0	0.09	1.18	0.50	–	–
7	6.0 M H_2SO_4 + 8.7 g H_2SO_5	3	0	0.12	1.18	0.41	0.66	0.67
7	6.0 M H_2SO_4 + 8.7 g H_2SO_5	4	0	0.17	1.18	0.37	0.66	0.64
8	2.5 M H_2SO_4 + 5.8 g H_2O_2	1	0	0.03	1.00	0.28	0.52	0.52
9	2.6 M H_2SO_4 + 3 g H_2O_2	0.5	0	0.01	0.80	0.36	0.52	0.51

It was found earlier (^{6,8}) that oxygen from water does not enter the simultaneously formed persulfate. These data exclude the participation of persulfate (or its possible precursors) in ozone formation. In agreement with this, the addition of persulfate to the electrolyte does not increase the ozone yield (^{1}).

In the electrolysis of more concentrated H_2SO_4 in H_2O^{18}, the anodic oxygen is diluted with sulfate oxygen to a greater extent, the higher the acid concentration, while ozone has an isotopic composition intermediate between O_2 and water. A. N. Frumkin[2] found the same intermediate composition in the electrolysis of an $HClO_4$ solution. With increasing acid concentration, the fraction of O^{18} in it that passes from the water increases. This is caused not by exchange, which under these conditions proceeds very slowly[14], but by the hydrolysis of persulfate, in which, as we found earlier[10], oxygen from water enters the sulfate formed. This hydrolysis is favored by the high acid concentration. As a result of it, light H_2SO_5 is formed, the anodic decomposition of which dilutes $O_2{}^{18}$ with light oxygen. In experiments 4 and 5 with 4.5 and 6.8 M H_2SO_4, the content of O^{18} in ozone is equal to that calculated from (1). For a more reliable verification of this equation, we increased the difference between the isotopic composition of the anodic oxygen and that of water by carrying out electrolysis with additions of Caro' s acid (experiments 6 and 7) or hydrogen peroxide (experiments 8 and 9). In the experiments with H_2O_2, its constant concentration of about 2% was maintained by adding 80% H_2O_2 dropwise to the electrolyte. It is evident from Table 1 that in all experiments the 1 : 2 ratio of oxygen from water and from anodic O_2 in the ozone formed is observed with good accuracy.

From the experiments described it follows that the formation of ozone and persulfate are two independent parallel processes and that ozone is formed according to the schematic stoichiometric equation (1). Taking into account the electrochemical and other data mentioned above, one must consider that in this process oxygen actually participates in the form of higher surface oxides, according to equation (2b), but these oxides are formed not only from water according to (2a), but in the presence of peroxy compounds also (and even predominantly) with the participation of the latter, for example according to (3) in the case of the presence of H_2O_2. From these same oxides, according to (2c), anodic O_2 of the same isotopic composition as theirs is formed.

As indicated above, steps (3) and (2c) also explain the predominance of oxygen from H_2O_2 in the anodic O_2 obtained in the electrolysis of sulfate or sulfuric acid solutions in the presence of hydrogen peroxide. Apparently, our results can be explained only by such a mechanism.

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