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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE MECHANISM OF OZONE FORMATION DURING THE ELECTROLYSIS OF CONCENTRATED PERCHLORIC ACID SOLUTIONS

(Presented by Academician A. N. Frumkin, 26 XI 1960)

Comparatively few works have been devoted to elucidating the mechanism of anodic ozone formation ($^{1-4}$). This is explained by the fact that this process is complicated by oxidation of the electrodes, anodic evolution of oxygen, formation of peracids, and other processes occurring at the potentials of ozone evolution.

In the present communication the results are set forth of an investigation of the mechanism of anodic formation of ozone from concentrated solutions of perchloric acid at low temperature by the tracer-atom method in combination with the method of recording polarization curves.

As in the study (^{5}) carried out at room temperature, solutions of perchloric acid labeled with the heavy isotope of oxygen, or ordinary perchloric acid in water enriched in O^{18}, were subjected to electrolysis; samples of the evolved oxygen and ozone were collected at different potentials, and their isotopic composition was determined by the mass-spectrometric method.

Fig. 1. Cell for electrolysis of perchloric acid at low temperature: 1 —anode; 2 —diaphragm; 3 —cathode; 4 —capillary for the thermocouple; 5 —stopcock for measuring the anode potential relative to hydrogen electrode 6; 7 —ground joint

Fig. 2. Schematic of the system for taking samples of ozone and oxygen

Figure 2: Fig. 2. Schematic of the system for taking samples of ozone and oxygen

for attaching the trap-collector

The use of perchloric acid as the electrolyte seemed to us more appropriate in the present case than the use of sulfuric acid, since complications associated with the formation of peracids and with oxygen exchange between water and acid were excluded; the absence of such exchange under the conditions of electrolysis of $HClO_4$ solutions was shown in work (^{5}).

Electrolysis was carried out in the cell shown in Fig. 1. The anode was a platinum plate with an area from 0.5 to 20 cm^2, depending on the required current density. A platinum mesh was used as the cathode. The anodic and cathodic spaces were separated by a porous diaphragm of glass cloth, made in the form of a cylinder, inside which the cathode was placed. A low temperature at the anode was created by immersing the cell in a cooling mixture of methanol and solid carbon dioxide. The temperature was measured with an iron-constantan thermocouple placed in a thin jacket that was in contact with the anode. The construction of the cell

made it possible, in addition to recording polarization curves, to collect samples of the gas evolved at the anode at various potentials. Before the start of electrolysis, the anode was treated with sulfuric and warm nitric acids, washed twice with distilled water, and then the anode was polarized with a current from 10^{-6} to 10^{-4} A for 30 min.

After 1.5-2 hours of electrolysis at the specified temperature, during which saturation of the electrolyte with the gas evolved at the anode was practically attained, liquefaction of the latter was begun in a receiver-trap (Fig. 2) made of molybdenum glass. The liquefaction temperature was achieved by immersing the receiver-trap in a copper block 6 cooled with liquid nitrogen. Special ampoules for taking samples for mass-spectrometric analysis were sealed in advance to the tube of the receiver. During liquefaction of the gas, in order to regulate the pressure in the receiver, branch tube 9 remained unsealed and was closed with a drop of water. At the end of electrolysis the stopcocks of the receiver 1 and 2 were closed, the current was switched off, branch tube 9, after drying, was quickly sealed, the copper block 6 was completely immersed in liquid nitrogen, and the receiver-trap was connected by means of ground joint 7 to a vacuum apparatus for pumping off oxygen.

Fig. 2. Schematic of the system for taking samples of ozone and oxygen

Before sampling oxygen, the space up to stopcock 1 (Fig. 2) was evacuated and then filled with oxygen evaporating from the trap. After this, ampoules 4 were sealed off for the mass-spectrometric determination of the isotopic com-

Fig. 3. Anodic polarization curves of a platinum electrode in perchloric acid at −40°. 1 −6.3 N; 2 −7.1 N; 3 −10 N

Figure 3: Fig. 3. Anodic polarization curves of a platinum electrode in perchloric acid at −40°. 1 −6.3 N; 2 −7.1 N; 3 −10 N

position of oxygen. Next, ampoules were filled with ozone; for this purpose, after the system had been pumped out for 1.5 hours, the temperature of the copper block was raised and, while cooling the ampoules with liquid nitrogen, ozone was transferred into ampoules 10. Then the ampoules were sealed off and heated first to room temperature and then in a drying oven to 150–200° in order to decompose the ozone to oxygen, from whose isotopic composition the composition of the ozone was determined.

Fig. 3. Anodic polarization curves of a platinum electrode in perchloric acid at −40°. 1 −6.3 N; 2 −7.1 N; 3 −10 N

Some of the results obtained in the work are presented in Fig. 3 in the form of polarization curves recorded at a temperature of −40°, and in Table 1. The notation $HClO_4^{18}/H_2O$ in Table 1 means that a solution of labeled perchloric acid in ordinary water was studied, while $HClO_4/H_2O^{18}$ denotes a solution of ordinary perchloric acid in labeled water. The same table gives data on the isotopic composition of the starting materials ($HClO_4^{18}$ and H_2O^{18}) and of the reaction products evolved at the anode (O_2 and O_3).

As can be seen from Fig. 3, the polarization curves recorded at low temperature are similar in shape to the curves obtained earlier ($^{5-9}$) at room temperature. The sections of sharp rise in overvoltage in the case of low temperature are shifted toward lower current densities and more positive potentials; the dependence of overvoltage on acid concentration observed at room temperature is preserved. On the basis of these data it may be assumed that the mechanism of oxygen evolution does not change when the temperature is lowered. Indeed,

Table 1

Composition and concentration of electrolyte	T-ra at anode, °C	Current density, A/cm	Oxygen source	Enrichment, %	Fraction of water participation in the formation process: oxygen n_k	Fraction of water participation in the formation process: ozone n_o	N
$5.8N$ $HClO_4^{18}/H_2O$	40	$2.2 \cdot 10^{-2}$	$HClO_4^{18}$	0.399	–	–	0.35
$5.8N$ $HClO_4^{18}/H_2O$	40	$2.2 \cdot 10^{-2}$	O_2	0.059	0.85	–	0.35
$5.8N$ $HClO_4^{18}/H_2O$	40	$2.2 \cdot 10^{-2}$	O_3	0.038	–	0.90	0.35
$HClO_4/H_2O^{18}$	40	$1.2 \cdot 10^{-1}$	H_2O^{18}	0.742	–	–	0.50
$HClO_4/H_2O^{18}$	40	$1.2 \cdot 10^{-1}$	O_2	0.680	0.91	–	0.50
$HClO_4/H_2O^{18}$	40	$1.2 \cdot 10^{-1}$	O_3	0.710	–	0.95	0.50
$6.3N$ $HClO_4^{18}/H_2O$	40	$2 \cdot 10^{-2}$	$HClO_4^{18}$	1.780	–	–	0.39
$6.3N$ $HClO_4^{18}/H_2O$	40	$2 \cdot 10^{-2}$	O_2	0.482	0.73	–	0.39
$6.3N$ $HClO_4^{18}/H_2O$	40	$2 \cdot 10^{-2}$	O_3	0.296	–	0.83	0.39
$HClO_4/H_2O^{18}$	50	$2 \cdot 10^{-2}$	H_2O^{18}	0.738	–	–	0.48
$HClO_4/H_2O^{18}$	50	$2 \cdot 10^{-2}$	O_2	0.519	0.70	–	0.48
$HClO_4/H_2O^{18}$	50	$2 \cdot 10^{-2}$	O_3	0.624	–	0.84	0.48
$7.1N$ $HClO_4^{18}/H_2O$	40	$2 \cdot 10^{-2}$	$HClO_4^{18}$	1.780	–	–	0.30
$7.1N$ $HClO_4^{18}/H_2O$	40	$2 \cdot 10^{-2}$	O_2	0.46	0.74	–	0.30
$7.1N$ $HClO_4^{18}/H_2O$	40	$2 \cdot 10^{-2}$	O_3	0.32	–	0.82	0.30
$HClO_4/H_2O^{18}$	50	$2 \cdot 10^{-2}$	H_2O^{18}	2.481	–	–	0.41
$HClO_4/H_2O^{18}$	50	$2 \cdot 10^{-2}$	O_2	1.193	0.48	–	0.41
$HClO_4/H_2O^{18}$	50	$2 \cdot 10^{-2}$	O_3	1.723	–	0.69	0.41
$8.6N$ $HClO_4^{18}/H_2O$	50	10^{-2}	$HClO_4^{18}$	1.78	–	–	0.37
$8.6N$ $HClO_4^{18}/H_2O$	50	10^{-2}	O_2	1.005	0.44	–	0.37
$8.6N$ $HClO_4^{18}/H_2O$	50	10^{-2}	O_3	0.633	–	0.64	0.37
$HClO_4/H_2O^{18}$	50	$5 \cdot 10^{-2}$	H_2O^{18}	0.455	–	–	0.51
$HClO_4/H_2O^{18}$	50	$5 \cdot 10^{-2}$	O_2	0.148	0.32	–	0.51
$HClO_4/H_2O^{18}$	50	$5 \cdot 10^{-2}$	O_3	0.305	–	0.67	0.51
$10N$ $HClO_4^{18}/H_2O$	40	$2 \cdot 10^{-2}$	$HClO_4^{18}$	0.569	–	–	0.35
$10N$ $HClO_4^{18}/H_2O$	40	$2 \cdot 10^{-2}$	O_2	0.413	0.27	–	0.35
$10N$ $HClO_4^{18}/H_2O$	40	$2 \cdot 10^{-2}$	O_3	0.270	–	0.53	0.35
$HClO_4/H_2O^{18}$	50	$2 \cdot 10^{-2}$	H_2O^{18}	4.36	–	–	0.38

Composition and concentration of electrolyte	T-ra at anode, °C	Current density, A/cm	Oxygen source	Enrichment, %	Fraction of water participation in the formation process: oxygen n_k	Fraction of water participation in the formation process: ozone n_o	N
$HClO_4/H_2O^{\underline{18}}$	50	$2 \cdot 10^{-2}$	O_2	1.235	0.28	–	0.38
$HClO_4/H_2O^{\underline{18}}$	50	$2 \cdot 10^{-2}$	O_3	2.411	–	0.55	0.38

As can be seen from Table 1, the oxygen evolved at low temperature, in the case of the use of $HClO_4^{18}$, is enriched in the heavy isotope of oxygen, which indicates participation of the acid anion in the process of its formation(5).

It might have been expected that parallel samples of oxygen and ozone would have a similar isotopic composition, which would indicate an analogy in the mechanism of their formation. However, although the acid anion participates both in the process of oxygen formation and in that of ozone formation, there is a stage that distinguishes this process from the anodic formation of oxygen (see Table 1).

From the data on the isotopic composition of oxygen and ozone, the fractions of water participation in the process of formation of ozone n_o and oxygen n_k from water oxygen and anion oxygen were calculated. For solutions of ordinary perchloric acid in labeled water, n_o and n_k were calculated as the ratio of the excess content of O^{18} in the evolved oxygen and ozone to that in the initial solution for H_2O^{18}. For solutions with labeled acid, the fractions of participation of the acid anion in these processes were calculated in the same way, while n_o and n_k represent the difference between 1 and the corresponding fraction of participation of the acid anion. As can be seen from Table 1, the fractions of water participation in the process of ozone formation n_o are always greater than the fractions of water participation in the process of oxygen formation n_k.

On the basis of these data, it seems possible to assume that the chemisorbed oxygen present on the anode during the formation

ozone is diluted with oxygen from the water. Table 1 gives the values

$$Q = \frac{n_0 - n_k}{1 - n_k},$$

which express, as is easy to see, the fraction of participation of water in the formation of ozone from oxygen and water, under the stated assumption, i.e., schematically according to the reaction $(1-Q)O + QH_2O \to \frac{1}{3}O_3$. The value $Q = 1/3$ would have been obtained if ozone were evolved by the mechanism of electrochemical desorption according to the scheme:

$$\mathrm{PtO}|nO|_{\mathrm{ads}} + \mathrm{H_2O} - 2e \to \mathrm{PtO}|(n-2)O|_{\mathrm{ads}} + \mathrm{O_3} + 2\mathrm{H}^+, \qquad (1)$$

while oxygen would be formed by the direct decomposition of surface platinum oxides.

The experimental values obtained for Q somewhat exceed 1/3. Experiments carried out with H_2O^{18} give on average $Q = 0.45 \pm 0.05$; experiments carried out with $HClO_4{}^{18}$, $Q = 0.36 \pm 0.05$; the overall mean is $Q = 0.4 \pm 0.05$ (besides those listed in Table 1, another 15 experiments were performed and taken into account in finding the mean value).

Taking into account the appreciable scatter of the experimental data, one may adopt scheme (1) as a first approximation.

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