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Abstract

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ISOTOPIC STUDY OF THE MECHANISM OF ELECTROLYTIC FORMATION AND HYDROLYSIS OF PERSULFATE

The various mechanisms that have been proposed for the anodic formation of persulfates during the electrolysis of sulfates may be assigned to two types. According to the widely held views ([1,11]), persulfate is formed by direct recombination of discharging sulfate ions (or bisulfate ions), for example,

$2SO_4^{--} \to S_2O_8^{--} + 2e$,

or in two steps:

$SO_4^{--} \to SO_4^{-} + e; \quad 2SO_4^{-} \to S_2O_8^{--}$.

According to other proposals ([2,3]), at the anode or in the near-anode layer of the electrolyte the primary products formed are products of water oxidation (H_2O_2, OH, OH^-, surface oxides, etc.), which then oxidize sulfate by transfer of electrons or oxygen atoms. In particular, the mechanism of Glestoun and Hickling ([3]), with intermediate formation of hydrogen peroxide, has gained wide acceptance:

$$2HO^- \to H_2O_2 + 2e; \quad 2SO_4^{--} + H_2O_2 \to S_2O_8^{--} + 2OH^-.$$

These authors extend it to processes of anodic oxidation in general. Most of the other proposed mechanisms belong to one of the two types, with different degrees of detail in the intermediate stages.

A. N. Frumkin and co-workers ([4]) found that during the electrolysis of a solution of K_2SO_4 in H_2O^{18}, in an acidic, neutral, or weakly alkaline medium, the oxygen of the persulfate obtained is free of excess heavy oxygen. This makes it possible to exclude from consideration all mechanisms in which the participation of water oxygen in persulfate formation is assumed.

We used the heavy isotope of oxygen to clarify the possible participation of hydrogen peroxide in the anodic formation of persulfate and to study the mechanism of its hydrolysis. From earlier data ([4,5,10]) it is known that H_2O_2 and $K_2S_2O_8$ do not exchange oxygen with water.

Fig. 1. Dependence of the persulfate yield on the concentration of hydrogen peroxide. 1—without addition of H_2O_2; 2a and 2b—with initial H_2O_2 contents of 12 and 20 g/liter; 3a and 3b—decrease in the H_2O_2 content in the electrolyte in the same experiments

Figure 1: Fig. 1. Dependence of the persulfate yield on the concentration of hydrogen peroxide. 1—without addition of H_2O_2; 2a and 2b—with initial H_2O_2 contents of 12 and 20 g/liter; 3a and 3b—decrease in the H_2O_2 content in the electrolyte in the same experiments

Solutions of 40 g of $KHSO_4$ in 200 ml of water were subjected to electrolysis with a current of 3 A between platinum electrodes at 10–15°. To take samples of anodic oxygen and to improve mixing of the electrolyte, a wire anode of 0.8 cm^2 was placed in an open-bottom tube between two vertical cathode plates. The content of O^{18} was determined with an MS-2 mass spectrometer: in anodic oxygen directly, and in water—by a method developed in our laboratory ([6]), in the form of CO_2 after its exchange with vapors of the water under investigation. Sulfate was precipitated as $PbSO_4$, which was converted into CO_2 by ignition with dehydrated hydrogen charcoal. Oxygen was liberated from persulfate by heating. For isotopic analysis of hydrogen peroxide, it was decomposed with a solution of $KMnO_4$ directly in the electrolyte after its degassing by pumping, or, at low concentrations, after extraction with ether. All these procedures were checked by control experiments. Hydrogen peroxide was determined by titration with permanganate, and persulfate iodometrically in the presence of Cu^{++} as catalyst ([7]). During electrolysis no significant quantities of Caro' s acid were formed. The results of the final experiments are reported below.

1. In experiments without the use of isotopic indicators, to the electrolyte do-

10–20 g/liter of H_2O_2 was added. In this case the yield of persulfate fell sharply in comparison with the experiment without addition of H_2O_2 (curve 1) and then increased as the undecomposed residue of H_2O_2 decreased. In Fig. 1, curves 2 show the increase in the concentration of $K_2S_2O_8$, while curves 3 show the decrease in the concentration of H_2O_2 in the electrolyte in two experiments, *a* and *b*, with initial H_2O_2 contents of 12 and 20 g/liter. Electrolysis in all three experiments was carried out until solid $K_2S_2O_8$ precipitated. From these data it is evident that both anodic processes—the decomposition of H_2O_2 and the formation of $K_2S_2O_8$—apparently proceed independently of one another, with a large predominance of the former if the H_2O_2 concentration is sufficiently high, so that the presence of peroxide interferes with the formation of persulfate. This in itself casts doubt on the theory of the intermediate formation of hydrogen peroxide. Qualitatively the same results and the same conclusions were obtained by Gaisinskii (8) in the formation of percarbonate by electrolysis of K_2CO_3 in the presence of H_2O_2.

Fig. 1. Dependence of the persulfate yield on the concentration of hydrogen

peroxide.

1—without addition of H_2O_2; 2a and 2b—with initial H_2O_2 contents of 12 and 20 g/liter; 3a and 3b—decrease in the H_2O_2 content in the electrolyte in the same experiments

Table 1

Isotopic composition of the anodic oxygen during electrolysis of $KHSO_4 + H_2O_2$ in H_2O^{18} with 0.890% O^{18}

Time, min.	10	30	60	90	120
H_2O_2, g/liter	21.9	16.2	8.9	4.1	1.46
O^{18} in H_2O_2, %	0.309	0.353	0.495	0.679	0.851

The independence of the two anodic processes is confirmed by the following experiments on the electrolysis of a solution of $KHSO_4 + H_2O_2$ in H_2O^{18} with isotopic analysis of the anodic oxygen (Table 1). In it the O^{18} content at the beginning was close to that which the peroxide had (natural: 0.20%), and gradually approached its content in water in accordance with the curves in Fig. 1. From these data it is also evident that the anodic oxidation of hydrogen peroxide takes place without participation of the oxygen of water.

Table 2

O^{18} content in H_2O_2 during electrolysis of $KHSO_4 + H_2O_2$ in H_2O^{18}

Experiment No.	Cathodic current density, A/cm^2	H_2O_2 concentration, g/liter	O^{18} in H_2O_2, %	O^{18} in water, %
I	0.05	0.26	0.459	0.831
I	0.05	0.13	0.635	0.831
II	0.10	0.78	0.209	0.745
II	0.10	0.26	0.243	0.745
II	0.10	0.13	0.455	0.745
III	0.17	0.42	0.229	1.100
III	0.17	0.26	0.288	1.100
III	0.17	0.07	0.401	1.100
IV	0.75	0.49	0.199	0.920
IV	0.75	0.26	0.204	0.920
V	1.00	1.05	0.209	0.920

Experiment No.	Cathodic current density, A/cm^2	H_2O_2 concentration, g/liter	O^{18} in H_2O_2, %	O^{18} in water, %
V	1.00	0.42	0.213	0.920
V	1.00	0.16	0.213	0.920

2. For final direct proof that hydrogen peroxide does not participate in the anodic formation of persulfate, we used the isotope dilution method. In experiments analogous to those just described, isotopic analysis was performed on the residue of H_2O_2 in the electrolyte after it had fallen below 1 g/liter. If H_2O_2 were formed at the anode from water, it would have to contain an excess of O^{18} and introduce it into the residue of the H_2O_2 added beforehand, mixing with the latter. At a cathodic current density of 0.05-0.17 A/cm^2 we did in fact find in the residue of H_2O_2 several times more

increased content of O^{18}, which was the greater the lower the current density (Table 2). It was caused by cathodic formation of peroxide by the Brutto reaction $O_2 + 2H^+ + 2e \rightarrow H_2O_2$, which is unrelated to the anodic process and, as is known, proceeds with a better yield the lower the cathodic current density. Indeed, when we increased the current density to 0.75—1.0 A/cm^2, even the last residues of H_2O_2 contained no excess O^{18}, whereas according to the mechanism of Gleyston and Hickling the O^{18} content in them should have approached its content in water.

Table 3

Hydrolysis of persulfate in the presence of $HClO_4$ at 70° (content of O^{18} in percent)

Water	$K_2S_2O_8$	H_2O_2	$KHSO_4$
1.096	0.204	0.204	1.093
1.096	0.204	0.207	1.088
0.204	0.733	0.736	0.313
0.204	0.741	0.730	0.224

From all these data it is clear that hydrogen peroxide cannot be an intermediate product in the formation of persulfate at the anode. Apparently, neither can OH radicals be such products (according to the scheme $2SO_4^- + 2OH \rightarrow S_2O_8^{--} + 2OH^-$), since they rapidly exchange oxygen with water (^{9}) and easily recombine to H_2O_2.

3. A mixture of 1.5—4 g $K_2S_2O_8$ with 1—3 g of 70% $HClO_4$ or 50% H_2SO_4 was subjected to hydrolysis at 70°, by passing water vapor through it at a

> pressure of 30 mm Hg. The isotopic composition of oxygen from H_2O_2 in the distillate and of bisulfate in the residue was determined as indicated above. In experiments with $K_2S_2O_8 + H_2O^{18}$ and $K_2S_2O_8^{18} + H_2O$ (the heavy persulfate was obtained by electrolysis of $KHSO_4^{18}$, prepared from $H_2SO_4 + H_2O^{18}$), the hydrogen peroxide had the composition of the water, as is evident from Table 3. The same result was given by hydrolysis under conditions of heating a solution of $K_2S_2O_8$ with acid without distillation of the peroxide. Thus, all the oxygen of the peroxide originates from the oxygen of the persulfate without participation of the oxygen of water. These data agree with earlier studies on the decomposition of H_2O_2 and several other peroxides in water with a different isotopic composition of oxygen ([11]). In all cases it was found that the peroxide bridge is not ruptured and that the oxygen of water is not incorporated into the decomposition products of these peroxides (other peroxide compounds or O_2). This was found, in particular, by Banton and Llewellyn ([10]) for the decomposition of Caro’ s acid.

Comparison of these data with ours shows that in the sequence of transformations
$S_2O_8^{--} \rightarrow SO_5^{--} \rightarrow H_2O_2 \rightarrow O_2$
the peroxide group –O–O–passes, without rupture, from persulfate into the final product of its decomposition–oxygen. Since, under the conditions of our experiments, persulfate hydrolysis proceeds with the intermediate formation of Caro’ s acid ([12]), its simplest mechanism is as follows:

$$^{-}OS(O_2)OO\boxed{S(O_2)O^{-} + HO}H = {}^{-}OS(O_2)OO^{-} + H^{+} + H\overset{*}{O}S(O_2)O^{-}$$

$$H\boxed{\overset{*}{O}H + {}^{-}OS(O_2)}OO^{-} + H^{+} = H_2O_2 + H\overset{*}{O}S(O_2)O^{-}.$$

According to this mechanism, bisulfate should contain 3/4 of its oxygen from persulfate and 1/4 from water. The oxygen from persulfate decomposition had an isotopic composition corresponding to this scheme, but in the bisulfate its composition was close to that of water (Table 3), evidently because of fairly rapid exchange between HSO_4^-, or the H_2SO_4 formed from it, and water. In order to eliminate this side exchange as far as possible, we carried out experiments with addition of $Pb(ClO_4)_2$, so that the sulfate formed immediately precipitated as $PbSO_4$. This greatly decreased the exchange, but did not eliminate it completely. In two experiments at 70° and an initial content of 1.17% O^{18} in the water, the sulfate contained 0.412% (with an experiment duration of 1 hour) and 0.492% (2 hours) O^{18}, instead of the 0.44% required by the scheme, or somewhat less, taking into account the initial–

initial dilution with light water introduced with $HClO_4$. When the hydrolysis temperature was increased to 100°, the O^{18} content increased to 0.635%. These data undoubtedly indicate that a significant amount of O^{18} is introduced into the bisulfate formed by secondary exchange. They are consistent with the scheme presented, although they do not provide its final quantitative confirmation.

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