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Abstract

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ISOTOPIC STUDY OF THE MECHANISM OF REACTIONS OF DECOMPOSITION OF PEROXOMONOSULFURIC ACID

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To study the reactions of formation and decomposition of peroxomonosulfuric acid (Caro' s acid) ([1–5]), we used a heavy isotope of oxygen. Peroxomonosulfuric acid was prepared by mixing equimolecular amounts of freshly distilled chlorosulfonic acid (fraction 150–152°) and crystalline 99–100% hydrogen peroxide, with cooling, followed by dissolution of the H_2SO_5 crystals in water ([6,7]). The yield was 80–85% of theoretical. Qualitative analysis did not reveal traces of H_2O_2 or $H_2S_2O_8$. $H_2O_2^{18}$ was prepared by the ethylanthraquinone method ([8]), and $K_2S_2O_8^{18}$ by electrolysis of $KHSO_4^{18}$ ([9]). H_2SO_5 and $H_2S_2O_8$ were analyzed iodometrically ([10]); H_2O_2 was determined quantitatively by permanganate titration, and qualitatively by means of Ti^{4+} in H_2SO_4. Isotopic analysis of oxygen and CO_2 was carried out on an MX 13-0.2 mass spectrometer with the participation of V. G. Golovaty. Oxygen was liberated from H_2O_2 with permanganate; from H_2SO_5, by heating the acidified solution to 100°; and from $K_2S_2O_8$, by heating the salt to 300°. The oxygen of sulfate was converted to CO_2 by heating lead sulfate with dehydrated platinized carbon at 700°. The O^{18} content is everywhere given in atomic percent above natural abundance.

Table 1

Anodic decomposition of peroxomonosulfuric acid

Time, min	Decomposed H_2SO_5, mM	Volume* H_2, ml	Volume* O_2, ml	$H_2S_2O_8$ formed, mM	O^{18} content, % H_2O	O^{18} content, % final SO_4^{2-}	O^{18} content, % O_2	Current consumption, % (1a)	Current consumption, % (2)–(7)
15**	50	–	–	–	2.79	0.11	0.69	–	–
35	19.5	810	600	1.13	2.12	0.09	0.57	75	96
40	22.2	795	593	1.22	1.15	0.10	0.58	75	90
135	40	2720	1572	10.3	1.07	0.09	0.73	58	91

* Gas volumes are reduced to normal conditions.
** Electrolysis was carried out in an undivided cell.

Anodic decomposition of peroxomonosulfuric acid

In the anodic compartment of an electrolyzer with separated anodic and cathodic spaces, 1–2 M H_2SO_5 in H_2O^{18} was placed. The catholyte was 1–2 M H_2SO_4. Electrolysis was carried out on a platinum anode at 20°, with an anodic current density of 0.5–1.3 A/cm^2 and a volume current density of 0.08–0.22 A/cm^2. The gases liberated at the electrodes were collected in measuring vessels. From the volume of hydrogen, the amount of electricity passed through the electrolyte was calculated. After the experiment, the remaining H_2SO_5 and the $H_2S_2O_8$ formed were determined in the anolyte. The SO_4^{2-} ions formed during decomposition of H_2SO_5 were precipitated with $Pb(NO_3)_2$ (Table 1).

For the anodic decomposition of peroxomonosulfuric acid, equations ([1–3]) have been proposed:

$$H_2SO_5 + O \rightarrow H_2SO_4 + O_2 \tag{1}$$

or

$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + O_2 + 2H^+ + 2e. \tag{1a}$$

However, for the evolution of anodic oxygen according to (1a), only 58-75% (59-78% allowing for the $H_2S_2O_8$ formed) of the current actually expended is required. In addition, this oxygen should consist half of

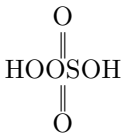
from the oxygen of water and H_2SO_5. In fact, in different experiments it contained from 25 to 70% oxygen from water. This indicates that the anodic decomposition of H_2SO_5 is not associated with the evolution of oxygen from water by a single mechanism, as follows from equations (1) and (1a). Apparently, the evolution of oxygen from peroxomonosulfuric acid and from water are two independent parallel processes.

The anodic decomposition of water is a two-electron process:

$$H_2O \rightarrow O + 2e + 2H^+, \tag{2}$$

proceeding, evidently, like other anodic reactions, with the participation of surface oxides of platinum [11].

The isotopic composition of the sulfate after the experiment shows that, in the anodic decomposition of



the O—O bond is broken, and not the O—S bond, since in the latter case one oxygen atom from water would enter the sulfate formed, and SO_4^{2-} would contain 25% O^{18} from the initial water.

Apparently, the evolution of oxygen from peroxomonosulfuric acid occurs by a one-electron discharge of HSO_5^- with simultaneous formation of SO_4^-, i.e., by homolytic cleavage of the O—O bond in H_2SO_5:

$$HSO_5^- - e \rightarrow H^+ + O + SO_4^-. \tag{3}$$

Thus, during electrolysis of aqueous solutions of peroxomonosulfuric acid, anodic oxygen is evolved mainly by the parallel reactions (2) and (3).

The amount of light oxygen from H_2SO_5, calculated from the isotopic composition of the anodic oxygen, in all experiments exceeded by 50–70 ml the volume of oxygen evolved from the decomposed H_2SO_5. Apparently, this difference is associated with the participation in the evolution of light oxygen of SO_4^- radical ions formed according to (3), which partially dimerize:

$$2SO_4^- \rightarrow S_2O_8^{2-}, \tag{4}$$

The persulfate formed hydrolyzes

$$S_2O_8^{2-} + H_2O \rightarrow SO_5^{2-} + SO_4^{2-} + 2H^+, \tag{5}$$

and H_2SO_5 decomposes electrochemically, evolving the above-indicated amount of light oxygen, which leads to consumption of up to one third of the sulfate radical ions formed according to (3). The persulfate remaining in solution, determined analytically, corresponds to recombination of up to one half of the SO_4^- formed. In total, according to (4), from 1/3 to 2/3 of all SO_4^- react, and about 40% of the current passed is consumed for the evolution of all light oxygen.

For the remaining sulfate radical ions one may assume interaction with water according to the equation:

$$\overline{SO}_4 \cdot + H_2O \rightarrow SO_4^{2-} + \cdot OH + H^+ \tag{6}$$

and oxygen evolution from water by:

$$\cdot OH \rightarrow O + e + H^+ \tag{7}$$

or

$$2 \cdot OH \rightarrow \tfrac{1}{2}O_2 + H_2O. \tag{8}$$

A choice between (7) and (8) is impossible, since the total current consumption, equal to approximately 60%, for (2) and (7), and for (2) and (8), and the isotopic composition of the evolved oxygen are the same. The sum of the electricity expended on reactions (2)–(7) satisfactorily coincides with the amount of electricity that actually passed through the electrolytic cell.

Cathodic decomposition of peroxomonosulfuric acid. The cathodic decomposition of H_2SO_5 was studied in the same electrolyzer after reversing the sign of the charge on the electrodes. In 30 min, at a cathodic current density of 0.8 A/cm^2, 3.5 g of H_2SO_5 decomposed. After the experiment, the sulfate contained 0.02-0.03% O^{18}, with 1.2% in the initial water, which, within the experimental error, indicated the absence of incorporation of water oxygen into the sulfate formed, i.e., cleavage of the O–O bond in H_2SO_5. Apparently, cathodic decomposition of H_2SO_5 proceeds by a mechanism analogous to the electroreduction of persulfate ([12],[13])

$$H_2SO_5 + 2e \rightarrow OH^- + HSO_4^-. \tag{9}$$

Thermal decomposition of peroxomonosulfuric acid. A solution of light H_2SO_5 in water containing 2.23% O^{18} was boiled for 60-90 min in a previously evacuated and sealed ampoule. Under these conditions H_2SO_5 decomposed completely with formation of O_2, H_2O_2, and H_2SO_4. The acidity of the solution after the experiment was 2-2.5 N. Under these conditions exchange of H_2SO_4 with water is negligible ([14]). O_2 and H_2O_2 proved to be light, while the sulfate contained 0.54-0.59% O^{18}, i.e., 1/4 of that in the initial water.

The data obtained show that thermal decomposition of H_2SO_5 in an acid medium, unlike electrochemical decomposition, proceeds with cleavage of the S–O bond, separation of the peroxide group, and incorporation of one oxygen atom from water into the sulfate formed, as had also been assumed earlier ([9],[15]).

Decomposition of peroxomonosulfuric acid in alkaline and acidic solutions. To a 0.015-1.75 M solution of H_2SO_5 in H_2O^{18}, the calculated amount of NaOH solution was added in vacuo. The oxygen evolved was collected in evacuated flasks. After the experiment was completed, the alkalinity of the solution and the isotopic composition of the sulfate from decomposition of H_2SO_5 were determined; in experiments in which decomposition was not carried to completion, the isotopic composition of the residue of peroxomonosulfuric acid was also determined.

Table 2

Alkaline decomposition of H_2SO_5 in H_2O^{18}

Exp. No.	Time, min	Alkalinity, g-equiv./l	Initial H_2SO_5 conc., mmol/l	Additives	H_2O	Final SO_4^{2-}	O_2	Final H_2SO_5
1	5	–	1750		1.20	–	0.01	–
1	60	0.7	–		–	–	0.20	0.03
2	5	–	960		1.20	–	0.05	–
2	10	2.5	–		–	–	0.11	0.02
3	24 h	1.9	610		2.79	0.02	0.40	–
4	»	1.9	610	Bohemian glass	2.79	–	0.42	–
5	»	1.9	610	Ag^+ < 0.01 N	2.79	0.08	0.53	–
6	5	–	75		2.20	–	1.02	–
6	190	3	–		–	0.05	1.16	–
7	24 h	1.6	13		2.79	–	1.49	–
8	»	1.6	13	Ag^+ < 0.01 N	2.79	–	1.34	–

As can be seen from Table 2, in more concentrated alkaline solutions of peroxomonosulfuric acid (0.1-1.75 M), oxygen is evolved at first only from H_2SO_5, and then, as it decomposes, oxygen from water becomes admixed. If a more dilute solution (0.01-0.1 M) is subjected to decomposition, oxygen is evolved immediately, consisting half of the oxygen of water and half of the oxygen of peroxomonosulfuric acid.

The isotopic composition of the sulfate (experiments Nos. 3, 5, 6) indicates that decomposition of H_2SO_5 proceeds at the O–O bond, and not the S–O bond, and therefore the evolution of oxygen from H_2SO_5 cannot be explained analogously to the thermal decomposition of peroxomonosulfuric acid in an acid solution. The subsequent incorporation of oxygen from water into the evolved O_2 is not associated with the entry of O^{18} into H_2SO_5 by exchange or by its formation, since the isotopic composition of peroxomonosulfuric acid does not change during the experiment (experiments Nos. 1,

2). From experiments Nos. 4, 5, and 8 it follows that the isotopic composition of the evolved O_2 does not change upon addition of silica gel or silver cations, which are active catalysts for the decomposition of peroxide products.

The mechanism proposed by Ball and Edwards [16], on the basis of a study of the kinetics of the spontaneous decomposition of H_2SO_5, is not consistent with the isotopic data. We believe that the difference in the isotopic composition of the evolved oxygen as a function of acid concentration is associated with a change in the reaction mechanism on going from concentrated to dilute solutions. Apparently, in concentrated solutions the evolution of oxygen proceeds according to

$$(HSO_5^-,\ SO_5^{2-}) \rightarrow O_2 + 2SO_4^{2-} + H^+,$$

whereas in dilute solutions it proceeds according to

$$(HSO_5^-,\ {}^-OH) + SO_5^{2-} \rightarrow O_2 + 2SO_4^{2-} + H_2O.$$

The data presented are insufficient for a detailed specification of these reactions.

Decomposition of peroxomonosulfuric acid in the presence of hydrogen peroxide and persulfate. A solution of persulfate or hydrogen peroxide was added in vacuo to a solution of peroxomonosulfuric acid, the label being introduced in some experiments into the water and in others into the peroxide compounds. The experiments were carried out in acidic and alkaline media (0.001–3 N). It was found that, upon interaction of hydrogen peroxide with H_2SO_5 in an acidic medium, oxygen was evolved from the hydrogen peroxide over the course of 1–4 days. The sulfate from the decomposition of H_2SO_5 contained no oxygen from the water. Apparently, the evolution of O_2 proceeds through the intermediate formation of a complex

$$\mathrm{H}\cdots\mathrm{O}-\mathrm{O}\cdots\mathrm{H}$$

$$\mathrm{H}-\mathrm{O}\cdots\mathrm{O}-\mathrm{SO_3H}$$

the composition of which agrees with the equimolecularity of this reaction found in [5].

In alkaline solution, up to 20% of oxygen from H_2SO_5 was admixed with the oxygen of H_2O_2, which can be explained by the parallel occurrence of an independent decomposition of H_2SO_5 according to the mechanism described above. In a mixture of peroxomonosulfuric acid with persulfate, oxygen was evolved mainly from H_2SO_5, to which, in acidic medium, peroxomonosulfuric acid formed by hydrolysis of $S_2O_8^{2-}$ was admixed with time. In alkaline solution, up to 40% oxygen from water was already found in O_2, which indicates the occurrence, to a considerable extent, of parallel reactions of alkaline decomposition of SO_5^{2-} and $S_2O_8^{2-}$.

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