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Abstract

Full Text

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PHYSICAL CHEMISTRY

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STUDY OF THE MECHANISM OF ELECTROLYTIC FORMATION AND DECOMPOSITION OF PERCARBONATE, PERBORATE, AND PERPHOSPHATE BY THE ISOTOPIC METHOD

It was shown earlier ⁽¹⁾ that hydrogen peroxide does not participate in the anodic formation of persulfate and is not its intermediate product, and also that, during hydrolysis of persulfate, the oxygen of water does not enter into the hydrogen peroxide formed. In the present work the heavy isotope of oxygen, O^{18} , was used to study the mechanism of the anodic formation, hydrolysis, and thermal decomposition of percarbonate, perborate, and perphosphate.

Potassium percarbonate $K_2C_2O_6$ was obtained ⁽²⁾ by electrolysis of 20-30 g of K_2CO_3 in 50 ml of H_2O^{18} with a current of 1.2-2 A between platinum electrodes at a temperature from -10 to -14° in a cell. Periodically withdrawn samples of electrolyte of 1-2 ml were degassed by pumping, after which H_2SO_4 at a concentration of 1 : 3 was added to them in vacuum. After pumping off the released CO_2 , $KMnO_4$ was added to liberate peroxide oxygen. The O^{18} content in the resulting CO_2 and O_2 was determined on an MS-2 mass spectrometer. Control experiments confirmed the absence of exchange between CO_2 and the electrolyte, as well as the nonparticipation of oxygen from $KMnO_3$ in the O_2 released under the described conditions. The results of one of the experiments, as well as of an experiment on the electrolysis of $K_2CO_3^{18}$ (obtained by exchange of carbonate with H_2O^{18}) in ordinary water, are given in Table 1. The isotopic composition

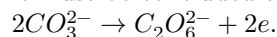
Table 1

Preparation of percarbonate

Time, min	Electrolysis of K_2CO_3 in H_2O^{18} with 1.100% O^{18} : O^{18} content, % in K_2CO_3	Electrolysis of K_2CO_3 in H_2O^{18} with 1.100% O^{18} : O^{18} content, % in $K_2C_2O_6$	Electrolysis of $K_2CO_3^{18}$ with 0.714% O^{18} in H_2O : O^{18} content, % in K_2CO_3	Electrolysis of $K_2CO_3^{18}$ with 0.714% O^{18} in H_2O : O^{18} content, % in $K_2C_2O_6$
30	0.213	0.194	0.699	0.683
60	0.249	0.204	0.665	0.674
90	0.0259	0.223	0.635	—
120	0.303	—	0.593	0.605
150	0.308	0.258	—	—

of oxygen in CO_2 and in O_2 is close to its composition in the initial carbonate. This excludes the participation of water in the formation of percarbonate. The slow increase in the fraction of O^{18} during electrolysis is caused by exchange between water and carbonate under conditions of local heating of the electrode-adjacent layers of electrolyte: after the current was switched off, the fraction of O^{18} in the peroxide O_2 did not change, while in CO_2 over 4–6 hours it increased by 0.05% at -6° and remained the same at -15° . The fraction of O^{18} in CO_2 was always somewhat higher than in O_2 . This is explained by the fact that exchange in the carbonate continues throughout the experiment, whereas in the percarbonate the isotopic composition is fixed.

oxygen by the time of its formation, after which further exchange in it ceases. If the oxygen of water participated in the formation of percarbonate, the content of O^{18} in the peroxide oxygen could not be lower than in CO_2 . Oxygen exchange between H_2O_2 and percarbonate proceeds very rapidly as a result of hydrolysis: it is completed during the time of mixing the solutions and extracting a portion of H_2O_2 with ether for isotopic analysis. This did not make it possible to use the isotope-dilution method, previously applied to persulfate ⁽¹⁾, to test the Glesthorn and Hickling mechanism ⁽³⁾ with intermediate formation of H_2O_2 . Earlier, Gaisinskii ⁽⁴⁾ showed the doubtful nature of this mechanism for the anodic formation of percarbonate and perborate. From all the data presented it must be concluded that percarbonate is formed by the reaction



Electrolytic preparation of perborate with appreciable yields occurs only in the presence of carbonate. For it, either direct formation of perborate at the anode ⁽⁵⁾, or primary formation of percarbonate, which then gives off H_2O_2 split off from it to borate ⁽⁶⁾, is assumed. To clarify this question we carried out a series of electrolyses of solutions of 4 g $Na_2B_4O_7^{18}$ + 12 g Na_2CO_3 in 100 ml H_2O^{18} (and also solutions of $Na_2B_4O_7 + Na_2CO_3^{18}$ in ordinary water) at $+10$ – 14° , with a current of 2–3 A between a Pt anode (1.9 cm²) and an Sn cathode (15 cm²), periodically determining the isotopic composition of oxygen in carbonate CO_2 and peroxide O_2 . In addition, the isotopic composition was determined of the

O_2 obtained by heating the precipitated perborate after washing it with water and drying it. The results of two such experiments are given in Table 2. In interpreting the data obtained it is necessary to bear in mind that in borax (or in metaborate) oxygen has the same isotopic composition as in water, because of very rapid exchange between them.

Table 2
Preparation of perborate

Time, min	Electrolysis of $Na_2B_4O_7^{18}$ with 1.100% O^{18} + Na_2CO_3 in H_2O^{18} with 1.100% O^{18} : in Na_2CO_3	Electrolysis of $Na_2B_4O_7^{18}$ with 1.100% O^{18} + Na_2CO_3 in H_2O^{18} with 1.100% O^{18} : in peroxide oxygen	Electrolysis of $Na_2B_4O_7^{18}$ with 1.100% O^{18} + Na_2CO_3 in H_2O^{18} with 1.100% O^{18} : in solid perborate	Electrolysis of $Na_2CO_3^{18}$ with 0.983% O^{18} + $Na_2B_4O_7$ in H_2O : in peroxide oxygen	Electrolysis of $Na_2CO_3^{18}$ with 0.983% O^{18} + $Na_2B_4O_7$ in H_2O : in peroxide oxygen
30	0.363	—	—	0.831	0.881
60	0.521	0.410	—	0.758	0.799
90	0.645	—	—	0.697	0.723
120	0.719	0.640	—	0.620	0.630
150	0.758	0.712	0.688	—	—

In all experiments, CO_2 and O_2 from the electrolyte and O_2 from perborate have close (with predominance in CO_2) and much smaller, than in water, contents of O^{18} . The latter rules out the participation of water oxygen in the formation of perborate. The accumulation of O^{18} in CO_2 and O_2 during the course of electrolysis is not connected with the presence of borax, which was confirmed by its identical increase in an experiment conducted under the same conditions but without borax. It, as in the experiments on the preparation of percarbonate, is connected with exchange in carbonate, which here proceeds more rapidly because of the considerably higher electrolysis temperature. All these data lead to the conclusion that the primary electrode process is the formation of percarbonate. From these data it also follows that the perborate obtained by electrolysis is the product of addition of H_2O_2 , and not a salt of a true peroxy acid, since in the latter case the proportion of O^{18} in its peroxide oxygen would have been intermediate between its content in water and in percarbonate: it has the structure $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, and not $NaBO_3 \cdot 4H_2O$.

Potassium perphosphate $K_4P_2O_8$ was obtained (7) by electrolysis of 30 g

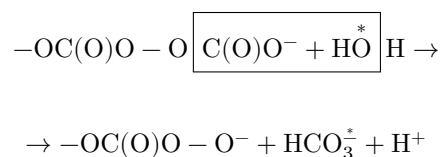
$KH_2PO_4 + 20 \text{ g } KOH + 0.036 \text{ g } K_2CrO_4 + 12 \text{ g } KF$ in 100 ml H_2O^{18} , with a current of 4 A at +10–14° for 2 h, between a Pt anode (1.9 cm²) and a cathode (145 cm²). On evaporation of the electrolyte, perphosphate separated; it was recrystallized from water and dried in vacuum. There is no exchange between it and water in 5 days at 20°, or in 6 h at 100°. Heating the perphosphate obtained gave oxygen of normal isotopic composition (0.199–0.204% O^{18}) when the water contained 1.10% O^{18} . Thus, mechanisms involving water (7) are also excluded in this case. The formation of perphosphate evidently proceeds by the reaction $2PO_4^{3-} \rightarrow P_2O_8^{4-} + 2e$.

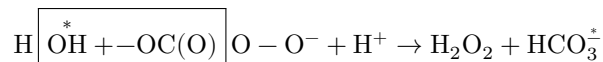
Table 3

Hydrolysis of salts of peracids

Substance	O^{18} content, percent: in the substance	O^{18} content, percent: in water	O^{18} content, percent: in H_2O_2
Potassium percarbonate	0.591	0.204	0.586
Potassium percarbonate	0.204	1.100	0.194
Sodium perborate	0.204	1.100	0.199
Sodium perborate	0.654	0.204	0.660
Potassium perphosphate	0.204	1.100	0.199

Hydrolysis of percarbonate and perborate was carried out at 20–30° in H_2O^{18} in the presence of dilute H_2SO_4 . Hydrolysis was also carried out in ordinary water on heavy salts obtained by electrolysis of $K_2CO_3^{18}$ and $Na_2CO_3^{18} + Na_2B_4O_7^{18}$. Hydrolysis of perphosphate was carried out at 60° in a saturated solution in H_2O^{18} with the addition of 1/4 by volume of H_2SO_4 . The H_2O_2 formed was distilled off in vacuum. In all experiments (Table 3) its oxygen had the same composition as the peroxide oxygen in the salt, irrespective of its composition in the water. Thus, in the hydrolysis of percarbonate, perborate, and perphosphate, the peroxide group $O-O$ passes, without being destroyed, into the H_2O_2 formed, just as was previously found (1) for the hydrolysis of persulfate. These data correspond to the mechanism



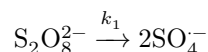


for percarbonate, and to an analogous mechanism for perphosphate. For perborate it is more correct to speak not of hydrolysis, but of cleavage of molecularly attached H_2O_2 . This process occurs rapidly, since perborate immeasurably rapidly exchanges oxygen with H_2O_2 .

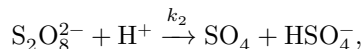
Thermal decomposition of percarbonate and perborate in H_2O^{18} gives oxygen of normal isotopic composition. This was to be expected, since in solution both split off free H_2O_2 ; the oxygen from its decomposition, as is known from other work, does not contain oxygen from water. Otherwise decomposition occurs for the more slowly hydrolyzing perphosphate in H_2O^{18} . It gives oxygen whose composition depends on the pH of the solution. Decomposition of 0.01 M $\text{K}_4\text{P}_2\text{O}_8$ in H_2O^{18} , with the addition of various amounts of H_3PO_4 or KOH , was carried out in sealed ampoules at 120°, after removal of dissolved gases by pumping. The oxygen evolved was analy-

Fig. 1. Dependence of the isotopic composition of oxygen on pH during decomposition of perphosphate and persulfate in H_2O^{18} . *I* —our data for perphosphate at 120° (a), *II* —data of Kolthoff and Miller for persulfate at 50° (b) and 90° (c).

was analyzed in a mass spectrometer. The pH was measured in the solution with a glass electrode. The dependence of the composition of oxygen on pH is represented by curve *I* in Fig. 1. At pH 5.2, 81% of it comes from perphosphate (0.283% O^{18} at 1.11% O^{18} in the water), and at pH 12.4 it comes entirely from water (1.09%). The curve has the same course as that obtained from the data of Kolthoff and Miller (⁸) for the thermal decomposition of persulfate at 50° and 90° (Fig. 1, curve *II*), but is shifted by several pH units. The similarity of the curves suggests an identical mechanism; however, the mechanism proposed by these authors for persulfate is not applicable to perphosphate. According to this mechanism, the decomposition of persulfate proceeds by two parallel paths: a slow step independent of pH,



and a catalytic slow step,



from which it follows that the ratio of the fractions of O_2 from persulfate and from water is equal to $k_2[\text{H}^+]/k_1$. According to our data for persulfate, the ratio k_2/k_1 changes over the studied pH interval by 2 orders of magnitude, instead of remaining constant.

We found that at room temperature over 8 hours there is no oxygen exchange between perphosphate and H_2O^{18} , in contrast to its very rapid exchange with percarbonate and perborate.

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

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