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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Kinetics and Mechanism of Decomposition of Peroxide Compounds in the Liquid Phase of the KOH–H_2O_2–H_2O System in Vessels Made of Various Materials

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Abstract—Decomposition kinetics of peroxide compounds in the liquid phase of the system KOH–H_2O_2–H_2O at an initial hydrogen peroxide concentration of about 14.5 M and pH 12.7 in vessels made of Pyrex glass, polyethylene terephthalate, and 12Kh18N10T steel was studied in the temperature range from –10 to +50°C. The main kinetic parameters of the processes under study were determined. The influence exerted by the material of the reaction vessel on the kinetics and mechanism of decomposition of peroxide compounds in the liquid phase of the system under study were determined.

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Inorganic peroxide compounds of alkali metals are rather widely used by modern industry as bleaching materials, agents for air regeneration in closed volumes, and sterilizing agents and disinfectants. The most widely used methods for their synthesis are based on interaction of hydrogen peroxide with the corresponding hydroxides (or their derivatives) in an aqueous or aqueous-organic medium and on dehydration of the resulting solutions or suspensions to give a solid phase [1–9]. It should be noted that most of M(OH)–H_2O_2–H_2O (where M is an alkali metal ion) systems used in various stages of chemical-technological processes to obtain peroxide compounds of alkali metals change their chemical composition in the course of time, which leads to a decrease in the content of the main substance in synthesis products. The change in the chemical composition of M(OH)–H_2O_2–H_2O systems (alkaline solutions of hydrogen peroxide) is due to decomposition of peroxide compounds in the liquid phase under the action of various factors [10]. However, there is no evidence in the scientific literature about the decomposition of concentrated hydrogen peroxide solutions in a strongly alkaline medium and about the effect of reaction vessel materials on the kinetics and mechanism of this process.

It has been found in the development of a technique for synthesis of potassium superoxide from hydrogen peroxide and potassium hydroxide [8, 9, 11, 12] that the decomposition of peroxide products in the liquid phase of the system KOH–H_2O_2–H_2O (with H_2O_2 concentration exceeding 12 M and pH > 11) can be divided with a sufficient precision into two constituents: homogeneous decomposition of H_2O_2, catalyzed by ions present in the solution under study, and heterogeneous decomposition of H_2O_2 and its derivatives at walls of reaction vessels and pipes contacting with the liquid phase [13, 14]. The heterogeneous decomposition of the H_2O_2 vapor can be neglected because of the insignificant contribution of this process to the overall decomposition of peroxide products in the systems under study.

In continuation of our previous studies in this area [13, 14], we examined the decomposition kinetics of peroxide products in the liquid phase of the system KOH–H_2O_2–H_2O, stored in vessels made of various materials, in a wide temperature range in order to determine the main kinetic parameters and possible mechanisms of the occurring processes.

EXPERIMENTAL

Experiments for analyzing the decomposition kinetics of peroxide products in the liquid phase of the system KOH–H_2O_2–H_2O, stored in vessels made of various materials, were carried out as follows. In the first stage, an alkaline solution of hydrogen peroxide was prepared. For this purpose, to a 50% H_2O_2 solution preliminarily stabilized with magnesium sulfate was added, under permanent agitation and cooling, solid 90% KOH, so that the reaction zone temperature did not exceed 20°C [5, 8, 9]. Magnesium sulfate was added to the system under study to preclude decomposition of hydrogen peroxide by metal ions present in raw materials [15, 16]. The starting components were mixed in the following molar ratios: H_2O_2 : KOH = 1.65 and H_2O_2 : $MgSO_4$ = 750. The H_2O_2 concentration at the beginning of the experiment was about 14.5 M, pH 12, for all the solutions we studied.

The given molar ratio between the starting reagents was chosen because just under these conditions the technique we suggest yields a product with the maximum content of K_2O [8, 9, 11, 12], i.e., the conditions of a real chemical-technological process were almost fully reproduced. All the substances used in the experiments were of analytically pure grade.

Then aliquot amounts of the resulting solution (500 ml) were placed in vessels made of 12Kh18N10T steel, laboratory glass, and polyethylene terephthalate (PETP). To make the experimental conditions identical, all the vessels had the same configuration (cylinder with a radius $r = 4.3$ cm). The ratio between the surface area of contact with the liquid phase of the systems under study and their volume was the same in all the experiments ($S/V \approx 0.75$ cm^{-1} = const). Before performing the main experiments, all the vessels were passivated with the solution at a temperature of 70–75°C for 24 h. Reproducible kinetic data were obtained after three preliminarily performed passivations.

In the subsequent stage, the vessels with the solutions under study were placed in a thermostat maintaining constant the required temperature to within ±0.2°C. During the entire experiment, the thermostat was kept in a dark place to preclude decomposition of peroxide products under the action of light. The decomposition kinetics of peroxide products in the liquid phase of the system KOH–H_2O_2–H_2O was studied in the temperature range from –10 to +50°C. When measuring kinetic curves at 0°C, solutions were cooled with ice; at –10°C, a cooling mixture composed of snow and potassium chloride was used.

It is known that, when kept in air, H_2O_2 solutions are concentrated because of the more intense evaporation of water (at 20°C, the vapor pressure of water is 17.5 mm Hg, and that of H_2O_2, 1.36 mm Hg) [17]. Therefore, to preclude loss of water from a solution under study and to diminish thereby the experimental error, vessels with the solution under study were closed and equipped with reflux condensers. This made it possible to reduce the loss of water through incomplete condensation during the entire experiment to 0.1 wt % in the temperature range under consideration. After certain intervals of time, we analyzed the solutions for the content of peroxide compounds by permanganatometric titration with an accuracy of ±0.01% [18] and plotted kinetic curves of decomposition of peroxide compounds in the systems under study.

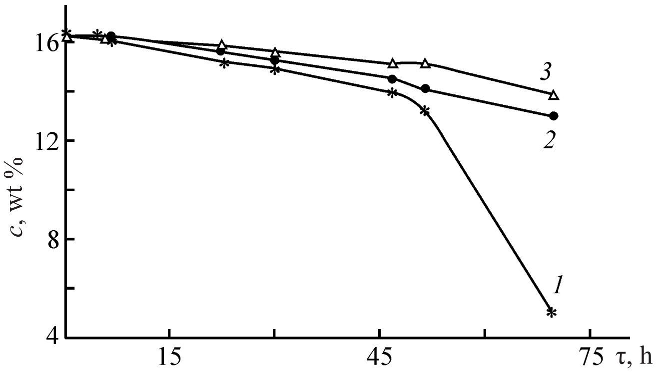

Fig. 1. Kinetics of decomposition of peroxide products in the system KOH–H_2O_2–H_2O placed in vessels made of various materials, at 0°C. (c) Content of active oxygen in the liquid phase and (τ) process duration; the same for Fig. 2.

The kinetic curves of decomposition of peroxide products in the liquid phase of the system KOH–H_2O_2–H_2O in the temperature range from –10 to +50°C are similar in shape. Therefore, Fig. 1 shows as typical results only those obtained at 0°C.

The kinetic curves were processed using the equation of a monomolecular reaction

$$\ln\frac{c_0}{c} = k(\tau - \tau_0), \tag{1}$$

where c_0 and c are the contents of active oxygen in the solution under study at instants of time τ_0 and τ, respectively.

To determine the reaction order with respect to hydrogen peroxide, we constructed plots in the coordinates log w–log $c(H_2O)$ [19]. The experimental results are satisfactorily described by the equation of a straight line whose slope to the abscissa axis is equal to the reaction order.

The activation energy E_a of the processes under study was calculated from the temperature dependence of the time during which the reaction proceeds to the same

Kinetic parameters of the decomposition of peroxide compounds in the liquid phase of the system KOH–H_2O_2–H_2O in vessels made of various materials [a]

Vessel material	T, °C	Rate constant $k \times 10^{-3}$, min^{-1}	Average temperature coefficient γ	Reaction order with respect to H_2O_2	Activation energy E_a, kJ mol^{-1}
PETP	−10	1.20	1.46	1.92	43.67
	0	2.25		1.90	
	13	3.16		1.94	
	18	3.48		1.89	
	32	7.38		1.94	
	51	12.23		1.91	
Glass	−10	1.21	1.70	1.84	39.45
	0	2.35		1.82	
	13	4.57		1.87	
	18	5.38		1.88	
	32	11.06		1.93	
	51	30.74		1.85	
Steel	−10	1.56	2.39	1.76	28.62
	0	5.29		1.79	
	13	16.61		1.80	
	18	22.27		1.74	
	32	93.34		1.75	

[a] All the kinetic parameters of decomposition of peroxide compounds in the liquid phase of the system KOH–H_2O_2–H_2O placed in a 12Kh18N10T steel vessel are presented for the first portion of the kinetic curve.

extent. This way to find the activation energy for static experimental conditions gives more accurate values of E_a [19, 20] than do calculations with reaction rate constants. We used in the calculations the equation

$$E_a = \frac{4.58 \log \frac{\tau_{T_1}}{\tau_{T_2}}}{\frac{1}{T_1} - \frac{1}{T_2}}, \tag{2}$$

where T_1 and T_2 are the experiment temperatures, and τ_{T1} and τ_{T2}, times of a 20% decomposition of peroxide compounds in the liquid phase of the system under study at temperatures T_1 and T_2, respectively.

For the temperature range under consideration, we calculated the average temperature coefficients of the decomposition reaction rates of peroxide compounds in the liquid phase of the ternary system KOH–H_2O_2–H_2O placed in vessels made of various materials, by the formula

$$\log \frac{k_{T_2}}{k_{T_1}} = \frac{\log \gamma}{10}(T_2 - T_1), \tag{3}$$

where T_1 and T_2 are the experiment temperatures, and k_{T1} and k_{T2}, reaction rate constants at temperatures of T_1 and T_2, respectively.

The table lists the main kinetic parameters of the processes under study.

It can be seen in Fig. 1 that the kinetic curves of decomposition of peroxide products in the liquid phase of the system KOH–H_2O_2–H_2O in vessels made of different materials are different. The nearly identical run of the kinetic curves for processes in glass and PETP vessels in the entire temperature range studied indicates that the peroxide products decompose by the same mechanisms. In both cases, there occurs homogeneous catalysis of peroxide compounds under the influence of hydroxide ions. The catalytic effect of alkalis consists in electrolytic dissociation of H_2O_2, formation of a free hydroxyl, and further chain decomposition of hydrogen peroxide [21]. In this case, the catalytic mechanism can be described by the following reaction equations:

$$\mathrm{OH^- + HO_2^- \rightleftarrows O_2^- + H_2O}$$

$$\mathrm{O_2^{2-} + H_2O_2 \longrightarrow O_2^- + OH^- + OH^{\bullet}}$$

$$\mathrm{OH^{\bullet} + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet}}$$

$$\begin{array}{c} O_2^- + H_2O \longrightarrow HO_2^{\bullet} + OH^- \\ 2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \\ \hline 2H_2O_2 = 2H_2O + O_2 \end{array} \quad (4)$$

The contribution of the heterogeneous component of the decomposition of H_2O_2 and its derivatives at the reaction vessel walls is considerably smaller, which is indicated by the nonsignificant discrepancy between the numerical values of the kinetic parameters of the processes under study in vessels with catalytically active (glass) and inactive walls (PETP). The data obtained are in good agreement with the results of a study in which the decomposition of aqueous solutions of hydrogen peroxide (0.2–2 wt %) was studied at pH 1–12 and temperatures of 25–90°C [22].

In the kinetic curves of decomposition of peroxide compounds in a solution placed in a vessel made of 12Kh18N10T steel, a bend is present in the entire temperature range and two portions can be clearly distinguished, with the decomposition of the peroxide products being more intense in the second portion.

Comparison of the first portion (slower reaction) of the kinetics curves obtained in an experiment in a 12Kh18N10T steel vessel with those obtained in glass and PETP vessels suggests that the rate of the process under study is higher in the metallic vessel. This fact indicates that the contribution from the heterogeneous constituent of the decomposition process of hydrogen peroxide and its derivatives is larger at the metal surface.

The presence of the bend in the kinetic curve can be attributed to a change of the decomposition mechanism of peroxide products in the system under study. It can be assumed that, after a certain interval of time, a process catalyzed by products of corrosion of the metal surface by the alkaline solution of hydrogen peroxide is added to the homogeneous constituent of the catalytic decomposition of peroxide products under the action of hydroxide ions. A fact is known that even corrosion resistant steels of the 12Kh18N10T type gradually contaminate, despite the very low corrosion rate (<0.0001 g m^{-3} h^{-1}), H_2O_2 solutions with catalytically active corrosion products. After a certain time, this leads to a substantial increase in the decomposition rate of peroxide compounds [23]. This assumption is confirmed by the fact that the color of the system under study gradually changes from light cream to yellow. The sharp increase in the decomposition rate of H_2O_2 is characteristic of homogeneous catalysis in the presence of two or more catalysts, when the total effect substantially exceeds the effect of each of the separately taken catalysts [24].

To assess the correctness of the assumption about the decomposition mechanism of hydrogen peroxide, we performed experiments with partial replacement of the solvent with benzene by the Baxendale–Nikolaev method [25] based on the ability of benzene to bind $OH^{\bullet}$ radicals, to be converted to phenol, and thereby to hinder the decomposition of peroxide products. Alkaline solutions of H_2O_2, prepared by the method described, were placed in vessels made of various materials and kinetic curves of the decomposition of peroxide products were recorded. Then, the experiment was performed under the same conditions, but with 25 ml of benzene added to each of the solutions under study. During the whole experiment, the vessels with the solutions were periodically shaken to emulsify benzene into the bulk of the liquid phase of the systems under study. The experiments were performed under conditions identical to those described above, at a temperature of 13°C. The results obtained are shown in Fig. 2.

It can be seen in Fig. 2 that introduction of benzene into alkaline solutions of hydrogen peroxide, placed in PETP and glass vessels (curves *1a* and *2a*, respectively), leads to a decrease in the decomposition rate of peroxide products in the systems under study. This means that their decomposition is catalyzed by hydroxide ions [Eq. 4)]. The behavior of the system in the 12Kh18N10T steel vessel is of different nature. In the first stage, as in

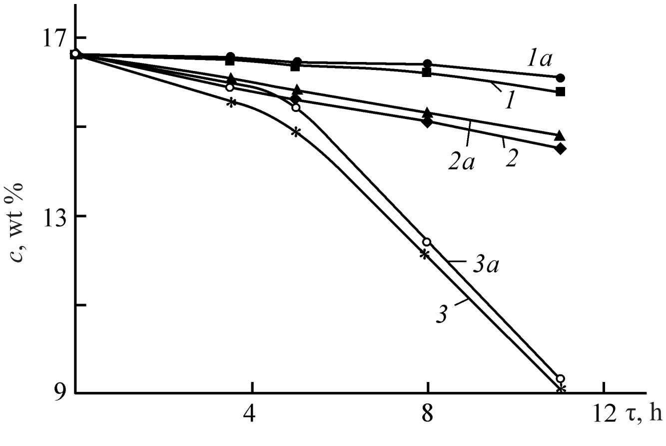

Fig. 2. Kinetics of decomposition of peroxide compounds in the system KOH–H_2O_2–H_2O placed in vessels made of various materials, at 13°C. (*1*) PETP, (*1a*) PETP + benzene, (*2*) Pyrex glass, (*2a*) Pyrex glass + benzene, (*3*) 12Kh18N10T steel, (*3a*) 12Kh18N10T steel + benzene.

experiments in glass and PETP vessels, the decomposition rate of peroxide products decreases. However, the presence of benzene in the system affects only slightly the process kinetics in the second stage, whose onset almost coincides in time in both the curves.

The experimental data obtained confirm the suggestion that the presence of the bend in the kinetic curves is due to the onset of the catalytic decomposition of peroxide products in the liquid phase of the system $KOH–H_2O–H_2O$ by metal ions delivered to the liquid phase by corrosion of the material of the vessel.

The fact that, in the second portions of the kinetic curves, the rates of the processes under consideration with and without benzene are almost the same suggests the following. In the given case, the decomposition of peroxide products in the system under study is largely determined by heterogeneous decomposition at walls and by homogeneous catalysis by corrosion products, which occurs via formation of intermediates, with the given constituent of the homogeneous decomposition of H_2O_2 being more important than the constituent associated with the presence of hydroxide ions (radical mechanism of catalysis).

Experiments aimed to verify the adequacy of the suggestion about the possible mechanism of the process under study were carried out as follows. An alkaline solution of H_2O_2 was prepared in accordance with the procedure described above and placed in a 12Kh18N10T steel vessel. After the decomposition of peroxide products was complete, we placed the remaining solution in a Pyrex glass vessel and successively (twice) added the starting alkaline solution of hydrogen peroxide and pure 50% H_2O_2 in such a way that the volume of the solution under study was 500 ml in all the experiments, and recorded kinetic curves of the primary, secondary, and tertiary reactions of decomposition of peroxide products. Under the same conditions, we recorded kinetic curves similar to those obtained in an experiment in a glass vessel. The results obtained are shown in Fig. 3.

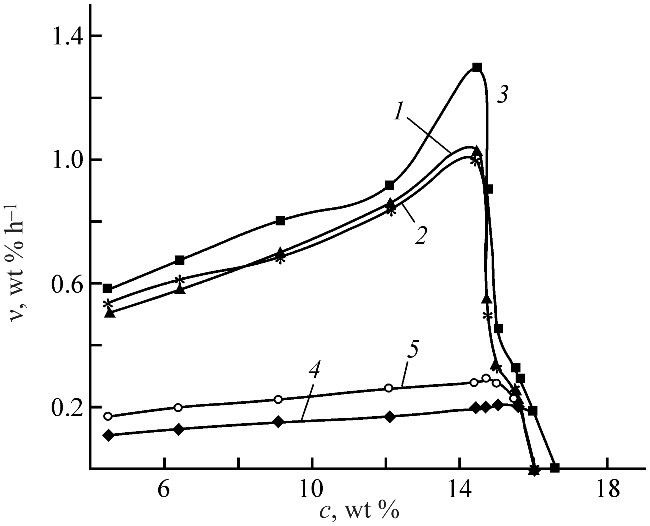

Fig. 3. Kinetics of decomposition of peroxide products in the system $KOH–H_2O_2–H_2O$ placed in vessels made of various materials, at 20°C. (*c*) Content of active oxygen in the liquid phase and (ν) release rate of active oxygen. (*1*) Pyrex glass (secondary reaction), (*2*) Pyrex glass (tertiary reaction), (*3*) 12Kh18N10T steel (primary reaction, (*4*) Pyrex glass + pure H_2O_2, and (*5*) Pyrex glass + starting alkaline solution of H_2O_2. (*1*) 12Kh18N10T steel, (*2*) Pyrex glass, and (*3*) PETP.

It follows from the position of the kinetic curves for the secondary (curve *1*) and tertiary reactions (curve *2*) between the curves characterizing the decomposition of peroxide products in the system placed in vessels made of Pyrex glass (curve *5*) and 12Kh18N10T steel (primary reaction, curve *3*) that, in the given case, the decomposition largely occurs through homogeneous catalysis under the action of products formed in corrosion of the metal by the starting solution. The higher decomposition rate of the peroxide products, compared with the decomposition of hydrogen peroxide by corrosion products (curve *4*), indicates that hydroxide ions are involved in the catalysis process, as is frequently the case in redox processes occurring in solution. The fact that the kinetic curves of the secondary and tertiary reactions are almost identical suggests that there occurs ideally reversible catalysis, in which the same insignificant amount of a catalyst can decompose an unlimited amount of a substrate.

CONCLUSIONS

(1) It was found that, in glass and polyethylene terephthalate vessels, the decomposition of peroxide products in the system $KOH–H_2O_2–H_2O$ largely occurs at an initial hydrogen peroxide concentration of about 14.5 M and pH 12.7 in the temperature range from –10 to +50°C via homogeneous catalysis under the action of hydroxide ions.

(2) In the case of a vessel made of 12Kh18N10T steel, the kinetic curves clearly show two portions in the entire temperature range. The first portion (slower reaction) is associated with the heterogeneous catalytic decomposition at reaction vessel walls and the homogeneous catalysis under the action of hydroxide ions. In the second stage

(faster reaction), to the above-mentioned factors affecting the decomposition of peroxide compounds in the system under study is added the homogeneous catalysis by corrosion products of the material of the reaction vessel, which occurs via formation of intermediate compounds.

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