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# PHYSICAL CHEMISTRY

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TYURIKOV

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**Abstract**

**Full Text**

PHYSICAL CHEMISTRY

V. Ya. CHERNYKH, S. Ya. PSHEZHETSKII, and G. S. TYURIKOV

## KINETICS OF THE DECOMPOSITION OF HYDROGEN PEROXIDE UNDER THE ACTION OF GAMMA RADIATION

*(Presented by Academician V. A. Kargin, February 16, 1957)*

The kinetics of the decomposition reaction of hydrogen peroxide in aqueous solutions under the action of ionizing radiation has been investigated in a number of works (<sup>1</sup>). However, the results obtained in these works are in many respects contradictory. This applies to the dependence of the reaction rate on the concentration of H<sub>2</sub>O<sub>2</sub>, the radiation intensity, and also to the reaction yields per absorbed radiation energy. The lack of agreement among the results of different studies is apparently due in large measure to the fact that the measurements were carried out in different and narrow intervals of H<sub>2</sub>O<sub>2</sub> concentrations, chiefly in dilute solutions.

It was of interest to determine to what extent the actual kinetic regularities depend on the concentration range in which the measurements are made; in particular, it was important to investigate the kinetics of this reaction in concentrated solutions.

In order to clarify the specific features of the radiation reaction, it was of interest to compare it with the kinetic regularities of the thermal and photochemical reactions, determined in the same concentration range.

We investigated the kinetics of H<sub>2</sub>O<sub>2</sub> decomposition in aqueous solutions over a wide concentration range, from 2 to 92 mole % H<sub>2</sub>O<sub>2</sub>, under the action of gamma radiation, as well as certain kinetic regularities of the thermal and photochemical reactions in the same concentration range.

The source of gamma radiation was Co<sup>60</sup>, with an activity of 80 curies; the source of ultraviolet radiation was a PRK-2 mercury lamp. As the initial solution we used a 92.23 mole % solution of hydrogen peroxide, obtained by triple distillation; its specific electrical conductivity was  $7.3 \cdot 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ .

The rate of the hydrogen peroxide decomposition reaction was measured volumetrically from the rate of evolution of oxygen from the solution. The rate of the radiation or photochemical reaction was determined as the difference between the measured rate and the rate of the thermal reaction.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The energy of radiation absorbed by the solution was measured by means of a dosimetric reaction—the oxidation of divalent iron to trivalent iron in solutions of 0.8 N H<sub>2</sub>SO<sub>4</sub>. In the calculations it was assumed that, per 100 eV of absorbed energy, 15.5 equivalents of divalent iron are oxidized.

The radiation intensity was varied by changing the distance of the apparatus from the radiation source.

**Kinetics of the reaction initiated by gamma radiation.** The dependence of the reaction rate on the concentration of the solution was measured in the range from 1.78 to 92.23 mole % H<sub>2</sub>O<sub>2</sub>.

The intensity of the  $\gamma$ -radiation was varied from  $0.26 \cdot 10^{18}$  to  $1.84 \cdot 10^{18}$  eV/1·sec; the temperature was varied from  $-30$  to  $50^\circ$ . The dependence of the reaction rate on the H<sub>2</sub>O<sub>2</sub> concentration is shown in Fig. 1, from which

it is seen that the reaction rate, as a function of the concentration of H<sub>2</sub>O<sub>2</sub>, passes through a maximum at all temperatures.

Measurements of the dependence of the reaction rate on the radiation intensity showed that the reaction rate is proportional to the square root of the radiation intensity for all investigated concentrations, from 1.78 to 92.23 mole % H<sub>2</sub>O<sub>2</sub>.

The dependence of the reaction rate on temperature was investigated at  $50$ ;  $30$ ;  $10$ ;  $1$ ;  $-4$ ;  $-11$ ;  $-21^\circ$ . The decomposition of a 92.33% H<sub>2</sub>O<sub>2</sub> solution at  $-30^\circ$  was also investigated.

Fig. 1

Fig. 2

Fig. 1. Dependence of the rate of the radiation reaction on the composition of the solution and temperature.

Absorbed radiation energy  $1.84 \cdot 10^{18}$  eV/1·sec

Fig. 2. Dependence of the rate of thermal decomposition of H<sub>2</sub>O<sub>2</sub> on the concentration of the solution and temperature

For all solutions there is a linear dependence  $\lg W \left( \frac{1}{T} \right)$ . However, the straight line has a break at a temperature of  $\sim 10^\circ$ . In the temperature region from  $-21^\circ$  to  $10^\circ$  the average value of the activation energy is  $6.5 \pm 1.0$  kcal/mole. Above  $10^\circ$  the average value of the activation energy is  $2.8 \pm 1.0$  kcal/mole.

Fig. 3

Figure 3: Fig. 3

Figure 4 graph: plots for determining  $K$  from equation (2).

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As experiments with stirring of the solution showed, above  $10^\circ$  the rate of oxygen evolution increases upon stirring. Below  $10^\circ$  stirring does not affect the reaction rate. This shows that above  $10^\circ$  diffusion is superimposed on the reaction rate, and it is the cause of the apparent decrease in the activation energy.

The reaction yields per absorbed energy depend on concentration and temperature and lie within the range from 21 (at  $-4^\circ$ ) to 230 (at  $50^\circ$ ) peroxide molecules per 100 eV of absorbed gamma-radiation energy. Such yields characterize a chain process.

Fig. 3. Dependence of the rate of decomposition of  $\text{H}_2\text{O}_2$  by ultraviolet irradiation on concentration at a temperature of  $30^\circ$ .  $I$  —photochemical reaction,  $II$  —thermal reaction in the same vessel

**Kinetics of the thermal reaction.** Measurement of the rate of the thermal reaction was carried out in the same concentration interval at  $10$ ;  $30$  and  $50^\circ$ . Below  $10^\circ$  the reaction rate was small and difficult to measure. The results of the measurements are given in Fig. 2. As is seen in the figure, the dependence of the reaction rate on the  $\text{H}_2\text{O}_2$  concentration has the same character. In absolute magnitude, the rate of thermal decomposition at  $30$ – $50^\circ$  is approximately an order of magnitude lower than the rate of radiation decomposition.

The average value of the activation energy of the thermal reaction is  $12.6 \pm 1.5$  kcal/mole. The activation energy for very small and very large concentrations is somewhat lower than this value.

**Kinetics of the decomposition of hydrogen peroxide under the action of ultraviolet radiation.** Concent-

the rational dependence of the reaction rate under the action of ultraviolet light was investigated in the same concentration range. The dependence of the reaction rate on the concentration of  $\text{H}_2\text{O}_2$  was measured at  $30^\circ$ . The results of these measurements are given in Fig. 3. The curve  $\lg W \left(\frac{1}{T}\right)$  has a break at approximately  $10^\circ$ .

In the interval  $1$ – $10^\circ$  the value of the activation energy is  $7.3$  kcal/mole, and in the interval  $10$ – $50^\circ$  it is  $4.0 \pm 1.0$  kcal/mole.

Stirring the solution leads to elimination of the break in the curve  $\lg W \left(\frac{1}{T}\right)$ . In this case the activation energy in the interval  $1$ – $10^\circ$  is  $8.9$  kcal/mole,

**Fig. 4.** Plots for determining  $K$  from equation (2)

and in the interval 10–50° it is  $7.9 \pm 1.5$  kcal/mole, i.e., it has practically the same value for both temperature intervals. This value is close to the activation energy of the reaction proceeding under the action of gamma radiation.

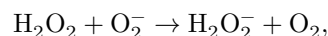
**Kinetic equation and probable reaction mechanism.** The identical character of the dependence of the reaction rate on concentration in radiation-, photo-, and thermally initiated reactions, as well as the closeness of the activation energies in radiation and photodecomposition, indicates that the basic reaction mechanism does not depend on the nature of the initiation. This is due to the fact that the decomposition of hydrogen peroxide is a chain process.

Comparison shows that the dependence of the rate of the decomposition reaction on the  $\text{H}_2\text{O}_2$  concentration is analogous to the dependence of the specific electrical conductivity of peroxide solutions on its concentration <sup>(2)</sup>. The parallel course of these dependences indicates that ions play a major role in the process of hydrogen peroxide decomposition. This is confirmed by a number of studies that have established the participation of ions in the process of photochemical and thermal decomposition of hydrogen peroxide in aqueous solutions.

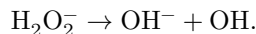
The elementary stages of the process that are apparently of greatest importance are the following:

		Rate constants of reactions
(1)	$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$	$K_1$
(2)	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$K_2$
(3)	$\text{H}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{OH}$	$K_3$
(3')	$\text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{O}_2^-$	$K_3 - K_3'$
(4)	$\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \text{HO}^- + \text{OH} + \text{O}_2$	$K_4$
(5)	$\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$K_5$

Since the  $\text{HO}_2$  radical is inactive, the decomposition of hydrogen peroxide by reaction (3') should proceed slowly. In aqueous solutions dissociation of  $\text{HO}_2$  occurs according to reaction (3). There can then occur a charge-transfer process:



which leads to dissociation of hydrogen peroxide:



Reaction (3) and both of these processes should proceed rapidly, since transfer of a proton or electron should occur without substantial ener-

...kinetic difficulties. This mechanism was considered by Weiss <sup>(3)</sup> as applied to the decomposition of peroxide in the presence of the ion  $\text{Fe}^{++}$ , and by Kornfeld <sup>(4)</sup> for the photodecomposition of  $\text{H}_2\text{O}_2$ , and was substantiated by V. N. Kondrat'ev <sup>(5)</sup>.

In dilute solutions, the formation of active centers may also occur as a result of the radiolysis of water.

Taking into account the bimolecular character of reaction (3), it may be assumed that its rate is determined by a second-order equation:

$$W_3 = K_3[\text{HO}_2][\text{H}_2\text{O}]. \quad (1)$$

Starting from the reaction mechanism written above and applying the method of stationary concentrations of intermediate products, we obtain the following approximate equation for the reaction rate:

$$W = -\frac{d[\text{H}_2\text{O}_2]}{dt} \simeq K\sqrt{J} \sqrt{[\text{H}_2\text{O}_2][\text{H}_2\text{O}]}, \quad (2)$$

where

$$K = 2\sqrt{\frac{K_1K_2K_3}{K_5}}.$$

As indicated, the reaction rate is proportional to  $\sqrt{J}$ , as required by equation (2).

In the graph of Fig. 4, data are given which illustrate the fulfillment of equation (2) for the radiation reaction. Satisfactory agreement with experiment is also found for the photo- and thermal decomposition over the entire range of concentrations and for all temperatures at which the measurements were made.

It may be assumed that, in a number of cases, the rate equations for the radiation decomposition reaction of  $\text{H}_2\text{O}_2$  obtained in other works represent approximations to the actual kinetic law of the reaction in various narrow concentration intervals—dilute solutions of  $\text{H}_2\text{O}_2$ .

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

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