

# THE DETERMINATION OF THE RATE CONSTANTS OF THE SIMPLE REACTIONS OF HYDROGEN ATOMS

COMMUNICATION 1. THE RATE CONSTANT FOR THE RECOMBINATION OF  $\text{H} + \text{H} + \text{H}_2 \rightarrow 2\text{H}_2$   
AND THE RATE CONSTANT FOR THE REACTION  $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2$

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The rate constant of the reaction which produces the radical  $\text{HO}_2$  from hydrogen atoms and oxygen molecules in the triple collision  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ , where M is a molecule of hydrogen, has been determined previously by other authors [1-3]. The three values of the constant which were obtained do not agree among themselves; the minimum value [1] differs from the maximum [2] by two orders of magnitude. The rate constant for hydrogen-atom recombination in a triple collision also has been determined previously by a number of authors [1,4-6]. These values are in good agreement with one another. The present work was begun for the purpose of measuring the rate constant of the reaction  $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2$ , based on a method which we suggested for the measurement of the rate constants of reactions of atoms and radicals [7].

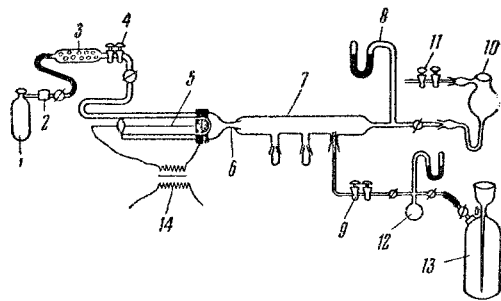


Fig. 1. Scheme of apparatus: 1) hydrogen cylinder; 2) special valve; 3)  $\text{CaCl}_2$  tube; 4), 9), 11) stopcock valve; 5) ozonizer-type tube; 6) nozzle; 7) reaction vessel; 8) manometer for measuring pressure in reaction vessel; 10) removable trap; 12) calibrated vessel from which  $\text{O}_2$  is supplied to reaction vessel; 13) gas-meter for  $\text{O}_2$ .

## EXPERIMENTAL

The experiments were carried out in a flow system in the glass vacuum apparatus which is shown schematically in Fig. 1. The source of hydrogen atoms was a silent discharge in an apparatus like an ozonizer. A high-voltage transformer of 40,000 volts was used for the discharge. The ozonizer was connected to the reaction vessel by a fine nozzle. The nozzle between the discharge zone and the reaction vessel guaranteed the impossibility of the diffusion of  $\text{O}_2$  molecules into the discharge zone when oxygen molecules were admitted to the jet which contained the hydrogen atoms. The reaction vessel had a diameter of 20 mm and a length of 1.2 m. The electrolytically produced molecular hydrogen used for these experiments was kept in an ordinary cylinder. The cylinder was connected to the apparatus with a special valve similar to the valves used in aqualungs for underwater swimming; it made possible a constant atmospheric pressure of hydrogen. A calcium chloride tube was placed between the valve and the glass part of the apparatus for the removal of the water vapor and oil which escaped with the hydrogen from the cylinder. A removable trap, cooled with liquid nitrogen, was placed at the end of the reaction tube. The gas stream and the vacuum were produced by an oil forepump.

In order to extract a greater number of hydrogen atoms into the reaction vessel, the walls of the nozzle were covered with phosphoric acid. We began with the idea that the formation of  $\text{HO}_2$  (by the interaction of H and  $\text{O}_2$ ) is a trimolecular reaction. Because Hudson and Foner [8] did not observe  $\text{HO}_2$  at low pressures, but did observe  $\text{HO}_2$  mass spectrometrically (by the reaction of  $\text{H} + \text{O}_2$ ) at pressures of about 20 mm, the present experiments were carried out at a pressure of 60 mm. The principal pressure in the reaction vessel was created by the hydrogen. The temperature was room temperature. The admission of molecular oxygen to the reaction vessel led to the formation of hydrogen peroxide which, after freezing, was observed in the trap cooled with liquid nitrogen. The quantity of peroxide was determined by titration with a solution of potassium permanganate (0.05 N) in an acidic medium. The minimum

determinable quantity of peroxide by this method is  $3 \cdot 10^{-7}$  moles. About  $(6-7) \cdot 10^{-6}$  moles of  $\text{H}_2\text{O}_2$  was ordinarily observed after the reaction.

Preliminary experiments (without the addition of  $\text{O}_2$ ) were carried out for various pressures of hydrogen in the discharge. These experiments showed that hydrogen peroxide was not formed in the absence of  $\text{O}_2$ ; however, the

Length of reaction vessel, cm	Quantity of peroxide in 20 min, $\text{M} \cdot 10^{-6}$
40	5.0
120	4.8
440	5.1

formation of water was observed, this being dependent on a small impurity of oxygen in the hydrogen. It was important to prove that the formation of hydrogen peroxide under these conditions was associated with the radical  $\text{HO}_2$  because we had observed hydrogen peroxide during earlier investigations in which a discharge tube was used at pressures of about 6 mm for the reaction  $\text{H} + \text{O}_2$  [9]. However, another mechanism for the formation of hydrogen peroxide – not involving  $\text{HO}_2$  – occurs when the reaction is carried out at a low pressure [9] and at a temperature of approximately  $100^\circ$ . It was found [9] that the principal reaction between  $\text{H}$  and  $\text{O}_2$  was the reaction occurring on the surface with the formation of  $\text{OH}$  and  $\text{O}$ , and

not with the formation of  $\text{HO}_2$ . The formation of the hydrogen peroxide then occurred on the cold walls of the trap cooled in liquid nitrogen. So, if the formation of peroxide in the present experiments was associated with a surface reaction, a decrease of the pressure should favor the formation of  $\text{H}_2\text{O}_2$ , since the diffusion of hydrogen atoms to the wall would be facilitated.

Experiments were carried out at a low pressure, and experiments were also run relating the dependence of the peroxide yield to the length of the reaction vessel. Experiments carried out at a pressure of 10 mm under conditions otherwise the same as those of experiments at 60 mm, yielded practically no hydrogen peroxide. The participation of a third particle (molecule of  $\text{H}_2$ ) in the mechanism for the formation of  $\text{H}_2\text{O}_2$  was definitely shown by the decrease of the formation of hydrogen peroxide when the pressure was lowered. The experiments relating the dependence of the rate of formation of peroxide to the length of the reaction vessel are cited in the table.

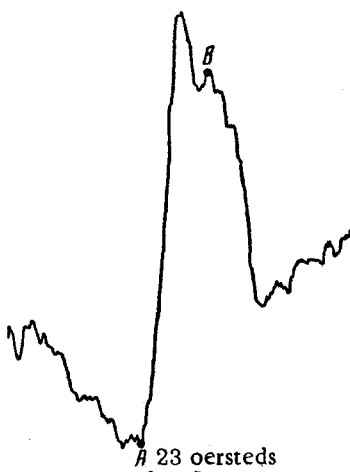


Fig. 2. The EPR spectrum of the  $\text{HO}_2$  radical at the temperature of liquid nitrogen in the solid state as frozen from the gaseous state.

The table shows that there is no dependence of the rate of formation of  $\text{H}_2\text{O}_2$  on the distance of the cold walls of the trap from the place where  $\text{H}$  mixes with  $\text{O}_2$ . This means that the formation of  $\text{H}_2\text{O}_2$  is not associated with the cold walls, but occurs in the gas space. From these experiments one can draw conclusions about the mechanism of the  $\text{HO}_2$  reaction under these conditions. The influence of the third body indicates that the principal reaction is the reaction  $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2$ .

Since the formation of  $\text{H}_2\text{O}_2$  is completed within a distance of 40 cm from the point of mixing of  $\text{H}$  with  $\text{O}_2$  at a stream velocity of 90 cm/sec, it may be concluded that the  $\text{HO}_2$  radical rather rapidly is transformed into  $\text{H}_2\text{O}_2$  by the reaction  $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ .

The formation of  $\text{H}_2\text{O}_2$  by the reaction  $\text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$  is excluded by the low temperature. We attempted to condense the  $\text{HO}_2$  radical in a trap cooled with liquid nitrogen, and placed at a distance of 4 cm from the mixing point of  $\text{H}$  with  $\text{O}_2$ . This experiment was successful. A photograph of the EPR spectrum of the frozen condensate is shown in Fig. 2.\* As is apparent from Fig. 2, the signal has an unsymmetrical form; the  $g$  factor is close to the  $g$  factor of diphenylpicrylhydrazyl. The total width of the signal was 23-26 oersteds. The signal disappeared when the condensate melted. An attempt to freeze out  $\text{HO}_2$  at a distance of 1 meter from the point of mixing of  $\text{H}$  with  $\text{O}_2$  was unsuccessful, in agreement with the data of the table, which indicates that the  $\text{HO}_2$  is already converted to  $\text{H}_2\text{O}_2$  at a distance of 40 cm. The spectrum of the condensate frozen during an experiment carried out without the addition of  $\text{O}_2$  (a blank experiment) was made. Practically no signal was obtained in this case. There is thus no doubt of the correctness of the suggested mechanism for the interaction of  $\text{H}$  with  $\text{O}_2$  according to the equation  $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2$ .

The rate constant for the reaction  $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2$  was measured by the method suggested earlier [7].

\* The EPR spectrum of the  $\text{HO}_2$  radical was taken by G. A. Kapralova with an IKhF-2 spectrometer.

For the determination of the rate constant of the reaction  $H + O_2 + H_2$  it was necessary to measure the rate of accumulation of the primary product, and its dependence on the rate of addition of molecular oxygen. The primary product of this reaction is the  $HO_2$  radical, whose concentration we were not able to measure directly. However, under the conditions of our experiment, the  $HO_2$  radical is transformed into peroxide through the interaction of two  $HO_2$  radicals.

The dependence of the final concentration of the primary product  $(H_2O_2)_K$  on the initial concentration of oxygen  $(O_2)_0$ , was determined on the basis of the following scheme:



where  $k_H'''$  is the rate constant for the disappearance of the hydrogen atoms.

From the conditions of the stoichiometry, the final concentration of hydrogen peroxide  $(H_2O_2)_K$ , which was experimentally measured, could be expressed in the following way:

$$(H_2O_2)_K = (O_2)_0 - (O_2)_K, \quad (4)$$

where  $(O_2)_K$  is the final concentration of molecular oxygen.

Let us write the following equation on the basis of the mechanism:

$$\frac{d(H)}{dt} = -k(H)(O_2)(H_2) - k_H'''(H)^2(H_2) \quad (5)$$

$$\frac{d(O_2)}{dt} = -k(H)(O_2)(H_2). \quad (6)$$

Dividing (5) by (6) we obtained:

$$\frac{d(H)}{d(O_2)} = 1 + \frac{k_H'''(H)}{k(O_2)}. \quad (7)$$

The solution of the differential equation (7) leads to the following dependence of  $(H)$  on  $(O_2)$ :

$$(H) = \frac{k}{k - k_H'''}(O_2) + C(O_2)^{\frac{k_H'''}{k}}, \quad (8)$$

where  $C$  is the integration constant which is determined from the boundary conditions: when  $(H) = (H)_0$ ;  $(O_2) = (O_2)_0$ , where  $(H)_0$  is the initial concentration of the hydrogen atoms.

Under the conditions of our experiment, the concentrations  $(H_2O_2)$  and  $(O_2)$  will cease to change, that is, will become the final concentrations when all of the atoms of hydrogen have been used up. The justification for this condition:  $(H_2O_2) = (H_2O_2)_K$  and  $(O_2) = (O_2)_K$ , when  $(H) = 0$ , is clear from the table, since the quantity of peroxide remains constant when the reaction zone is lengthened.

Using the condition:  $(O_2) = (O_2)_K$ , when  $(H) = 0$ , and changing  $(O_2)_K$  to  $(O_2)_0 - (H_2O_2)_K$ , we obtain from Eq.(8):

$$\frac{k}{k - k_H'''} [(O_2)_0 - (H_2O_2)_K] + \left[ (H)_0 - \frac{k}{k - k_H'''}(O_2)_0 \right] \left[ 1 - \frac{(H_2O_2)_K}{(O_2)_0} \right]^{\frac{k_H'''}{k}} = 0.$$

Since  $\frac{(H_2O_2)_K}{(O_2)_0} \ll 1$ , the quantity  $\left[ 1 - \frac{(H_2O_2)_K}{(O_2)_0} \right]^{\frac{k_H'''}{k}}$  can be expanded as a series.

Limiting ourselves to the first two members of the series, we obtain the equation

$$\frac{1}{(H_2O_2)_K} = \frac{1}{(H)_0} + \frac{k_H'''}{k(O_2)_0}. \quad (9)$$

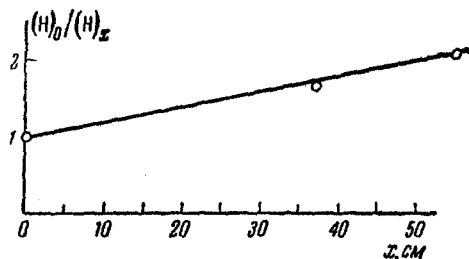


Fig. 3. The dependence of the relative concentration of hydrogen atoms  $(H)_0/(H)_x$  on the distance  $x$ .

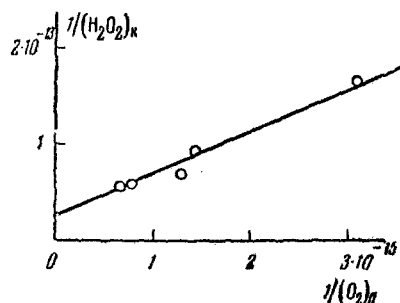


Fig. 4. The dependence of the reciprocal value of the final concentration of hydrogen peroxide  $1/(H_2O_2)_x$  on the reciprocal value of the initial concentration of oxygen molecules  $1/(O_2)_0$ .

where  $(H)_x$  is the concentration of H atoms at the distance  $x$ ;  $k_H$  is the rate constant for the linear disappearance of H;  $w$  is the linear stream velocity.

By measuring the dependence of  $(H)_0/(H)_x$  on  $x$ , and constructing the graph, one can determine whether it is the quadratic recombination of the H atoms which predominates.

If the points on the graph of the dependence of  $(H)_0/(H)_x$  on  $x$  fall on a straight line which intercepts the ordinate axis at unity, then the quadratic recombination is predominant. Figure 3 shows the straight line obtained from the experimental points for experiments done at room temperature with  $p_{H_2} = 60$  mm and  $w = 90$  cm/sec. The concentration of hydrogen atoms in various positions in the reaction vessel along the stream path was measured by the maximum yield of hydrogen peroxide for the introduction of molecular oxygen into those positions of the reaction vessel.

The experimental points taken over a large range of values of  $x$  (55 cm) fall closely on a straight line intercepting the ordinate axis at unity. However, a straight line which begins at the origin is also obtained for the coordinates  $\log [(H)_0/(H)_x]$ ,  $x$ . In order to choose which law is obeyed during the disappearance of the hydrogen atoms, it is necessary to turn to a theoretical examination of the various cases of the ratios of the linear and quadratic disappearance constants which were determined earlier [10]. In one case, when the linear disappearance was small in absolute value and the quadratic disappearance exceeded the linear by three or four times, a straight line was obtained in the coordinates  $(H)_0/(H)_x$ ,  $x$  and a curve (nearly a straight line) was obtained in the coordinates  $\log [(H)_0/(H)_x]$ ,  $x$ . Our experimental data approach this situation. Consequently, the predominating disappearance is a quadratic one and, therefore, the value  $k_H'''(H)_0$  is determined from the graph of Fig. 3, according to the equation

$$k_H'''(H)_0 = \frac{w \lg \beta}{(H_2)} \quad (13)$$

The following value of this quantity was obtained:

$$k_H'''(H)_0 = 9 \cdot 10^{-19} \text{ cm}^3 \cdot \text{sec}^{-1} \cdot \text{molecules}^{-1}.$$

The equation (9) is the equation of a straight line in the coordinates  $1/(H_2O_2)_K$ ,  $1/(O_2)_0$ . The constant  $k$  can be directly determined from the tangent of the angle of inclination according to the equation

$$k = \frac{k_H'''}{\lg \alpha} \quad (10)$$

In order to determine  $k$ , it is necessary to measure the dependence of  $(H_2O_2)_K$  on  $(O_2)_0$ , and also to know the rate constant for the disappearance of the hydrogen atoms, and that it has been found that this disappearance follows the termolecular law  $H + H + H_2 \rightarrow H_2 + H_2$ , i.e., is quadratic. We could have made use of the data of other authors on the rate constant for the recombination of hydrogen atoms. However, it was important for us to measure the rate constant for the disappearance of hydrogen atoms under the conditions of our experiments. For the measurement of the rate constant for the disappearance of hydrogen atoms, we used the method for the measurement of rate constants of the disappearance of atoms and radicals which we had published earlier [10]. Based on this method, the change in the concentration of hydrogen atoms as a function of the length of the reaction vessel for the case of a predominantly quadratic disappearance may be written in the form

$$\frac{(H)_0}{(H)_x} = 1 + \frac{x k_H'''(H)_0(H_2)}{w}, \quad (11)$$

and for the case of a predominantly linear disappearance,

$$\lg \frac{(H)_0}{(H)_x} = \frac{k_H x}{w} 0.43, \quad (12)$$

The value used for the initial concentration of hydrogen atoms  $(H)_0$  was  $1.72 \cdot 10^{13}$  molecules/cm<sup>3</sup> in measuring the dependence of  $(H)_0/(H)_x$  on  $x$ . It follows from this that  $k_H''' = 5.2 \cdot 10^{-32}$  cm<sup>6</sup> · sec<sup>-1</sup> · molecules<sup>-2</sup>.

This value of  $k_H'''$  is in good agreement with the values of other authors: Farkas and Sachsse [1],  $k_H''' = 9.3 \cdot 10^{-32}$ ; Smallwood [4],  $4.65 \cdot 10^{-32}$ ; Steiner [5],  $3.5 \cdot 10^{-32}$ ; Amdur [6],  $3.3 \cdot 10^{-32}$  (in cm<sup>6</sup> · sec<sup>-1</sup> · molecules<sup>-2</sup>).

We measured the dependence of  $(H_2O_2)_K$  on  $(O_2)_0$  for the determination of the rate constant of the reaction  $H + O_2 + H_2 \rightarrow HO_2 + H_2$ . The experimental data collected at room temperature for  $p_{H_2} = 60$  mm and  $w = 90$  m/sec are given in Fig. 4. From the tangent of the angle of inclination of the straight line (Fig. 4), and the value  $k_H''' = 5.2 \cdot 10^{-32}$ , the value of the termolecular rate constant for the reaction  $H + O_2 + H_2 \rightarrow HO_2 + H_2$  according to Eq. (10) is

$$k = 1.2 \cdot 10^{-33} \text{ cm}^6 \cdot \text{sec}^{-1} \cdot \text{molecules}^{-2}.$$

This rate constant agrees with the data of Nalbandyan and Voevodskii [3] ( $2.4 \cdot 10^{-33}$ ); it is by one order of magnitude larger than the data of Farkas and Sachsse [1], and is by one order of magnitude smaller than the data of Cook and Bates [2].

In conclusion, the authors express their gratitude to G. A. Kapralova for the determination of the EPR spectrum of the  $HO_2$  radical.

#### SUMMARY

1. The rate constant of the termolecular process for the formation of  $HO_2$  by the reaction of hydrogen atoms with molecular oxygen at room temperature was measured.
2. The rate constant for the recombination of hydrogen atoms in triple collisions was measured.
3. The EPR spectrum of the  $HO_2$  radical was determined at the temperature of liquid nitrogen as frozen from the gas phase.
4. The great activity of the  $HO_2$  radical toward conversion to  $H_2O_2$  was observed.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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