

THE ROLE OF PERHYDROXYL IONS IN THE REACTIONS OF HYDROGEN PEROXIDE

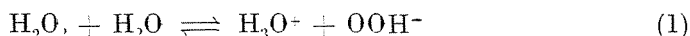
By

J. INCZÉDY and L. ERDEY

Department for General Chemistry, Technical University, Budapest

(Received April 19, 1962)

In diluted aqueous solutions, hydrogen peroxide as a weak acid protolyses according to the following equation:



At the same time hydrogen peroxide also inclines to autoprotolysis:

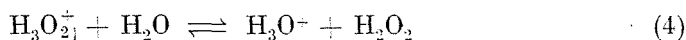


Since water is a much stronger base than hydrogen peroxide, the second reaction takes place in a diluted aqueous solution only to negligible extent compared to the first one. Autoprotolysis is only considerable in concentrated hydrogen peroxide solutions.

The dissociation constant of hydrogen peroxide in diluted aqueous solutions is:

$$K_0 = \frac{[\text{H}^+][\text{OOH}^-]}{[\text{H}_2\text{O}_2]} \quad (3)$$

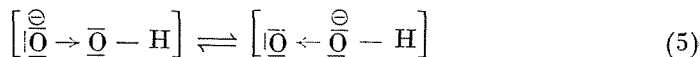
the numerical value of which, according to the good agreement measurements of JOYNER [1], KARGIN [2] as well as of EVANS and URI [3] is $1.6 \cdot 10^{-12}$ (at 20 C°). Taking the concentration of water into account, the equilibrium constant of the (1) reaction is $K_1 = 2.9 \cdot 10^{-14}$. According to EVANS and URI [3] the equilibrium constant of the reaction



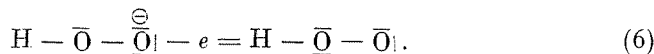
is approximately 10^3 . From these data the equilibrium constant of autoprotolysis of hydrogen peroxide is $K_2 \sim 3 \cdot 10^{-17}$.

The structure of perhydroxyl ions, formed on protolytic reactions, greatly differs from the point of view of energy, for the more saturated structure similar to a "screwed tub" of non-dissociated hydrogen peroxide molecule [4]. In the perhydroxyl ion, formed by the splitting off of a hydrogen ion the O—O

bond is loosened to a high extent, therefore, it inclines to giving off an oxygen atom, while hydroxyl ion is formed:



Raman-spectroscopic measurements of SIMON and MARCHAND [6] also proved the loosening of the O—O bond. These investigators could namely experience the 877 cm^{-1} line, corresponding to the oxygen bond of hydrogen peroxide, which disappears in alkalic solutions together with the shifting of the dissociation equilibrium of hydrogen peroxide, towards the dissociated form. Energy changes are also proved by the fact that in strongly alkalic solutions the polarographic wave of perhydroxyl ions occurs at more positive potentials than that of the non-dissociated hydrogen peroxide [7]. Against some oxidizing agents perhydroxyl ions are able to reduce, when a transitional, highly reactionable HO_2 molecule is formed, according to the following reaction:



In diluted aqueous solutions the perhydroxyl ion concentration of the solution becomes higher and higher with an increasing pH. In a solution at pH 12, nearly 50% of hydrogen peroxide is dissociated. Therefore the behaviour of perhydroxyl ions can first of all be studied by the reactions of alkalic hydrogen peroxide.

In our earlier papers [8,9] we have shown that in the decomposition of heavy metal-free solutions of diluted hydrogen peroxide, as effected by sodium hydroxide, perhydroxyl ions have an important role. The decomposition velocity of hydrogen peroxide solutions can be expressed by the following equation, according to our measurements:

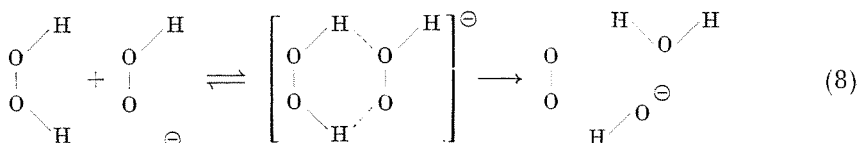
$$-\left(\frac{d [\text{H}_2\text{O}_2]_a}{dt} \right)_{T,F} = k_1 [\text{H}_2\text{O}_2] [\text{OOH}^-] \quad (7)$$

The k_1 rate constant of the reaction of second order is at 22 C° , in the presence of an $F = 150 \text{ cm}^2 \cdot \text{ml}^{-1}$ relative glass surface $6 \cdot 10^{-5}$, while at 50 C° $1.5 \cdot 10^{-3} \text{ mole}^{-1} \text{ litre} \cdot \text{sec}^{-1}$. The value of the rate constant almost increases proportionally to the square root of the glass surface. For the activation energy of the decomposition, independent of the glass surface, we found $20 \text{ kcal} \cdot \text{mole}^{-1}$.

The fact that we could quantitatively for the first time in literature, investigate the kinetics of reactions of hydrogen peroxide in alkalic solutions was partly due to our methods used for purification of solutions and vessels, partly to the experimental method that we investigated, for decomposition

rates not as a function of the alkali added, but as a function of pH of the solutions, in the presence of buffers.

Our kinetic results proved the following reaction mechanism:



according to which from the non-dissociated hydrogen peroxide and a perhydroxyl ion an instable transition complex is formed, which on the wall decom-

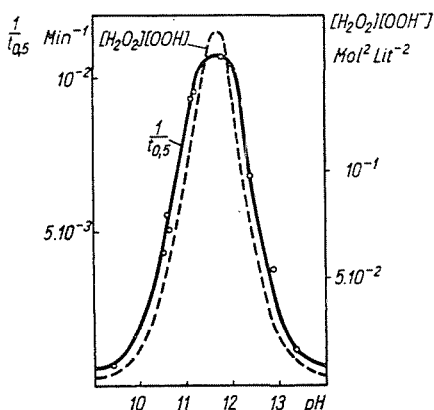


Fig. 1 Variation of the reciprocal half-life times and calculated $[H_2O_2][OOH]$ concentration products with pH, on the decomposition of heavy metal ion-free, alkalic hydrogen peroxide solutions. $[H_2O_2]_0 = 0.25 \text{ mol.lit}^{-1}$; 50°C

poses to oxygen, water and hydroxyl ions. Since the concentration of perhydroxyl ions depend on pH, the reaction (8) will take place at a maximal rate, in such a solution where the value of $[H_2O_2] \cdot [OOH^-]$ concentration product shows a maximum. Calculated values of concentration products and the corresponding reciprocal values of half-life times (the latter being proportional to the decomposition rates), as a function of pH, are shown in Fig. 1.

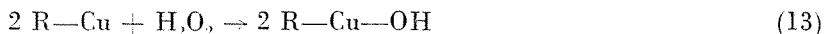
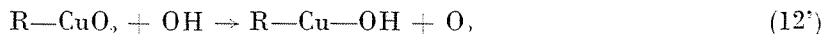
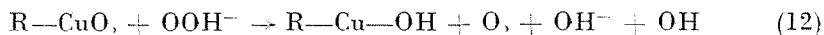
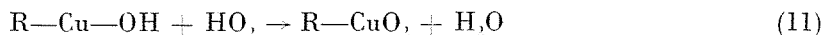
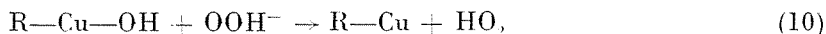
If the analytical concentration of hydrogen peroxide $[H_2O_2]_a$ and its K_0 dissociation constant are taken into consideration, equation (7) can be transformed as follows:

$$- \left(\frac{d[H_2O_2]_a}{dt} \right)_{T,F} = k_1 \frac{K_0 [H_2O_2]_a^2 [H^+]}{(K_0 + [H^+])^2} \quad (9)$$

According to this equation the decomposition rate shows a maximum at $\text{pH} = -\log K_0$ (about 11.8), which agrees well with our measurements.

At the same time ABEL [10] also found similar kinetical results. Later DORABIELSKA and KOŁODZIEJCZAK [11] proved the same mechanism with their investigations. Most recently DUKE and HAAS [12] made investigations in polyethylene vessels on the decomposition of alkalic hydrogen peroxide solutions, and had arrived at similar results. According to their investigations, however, in the presence of polyethylene surface the decomposition process is homogeneous, the rate constant is about ten fold, while the activation energy is about the tenth of the values found by us in glass, quartz or ceresined glass vessels. The role and reaction ability of cyclic transitional complex, shown in equation (8) is also proved by the most recent verification, that luminole emits a chemiluminescent light in the presence of fluorescein and hydrogen peroxide with a maximal rate at $\text{pH} \sim 12$ [13].

In the decomposition of alkalic hydrogen peroxide solutions, catalyzed by heavy metal ions, perhydroxyl ions have also an important role. According to our kinetical investigations [14], [15], decomposition of hydrogen peroxide in the presence of copper(II) ions, complex-forming citrate ions and sodium hydroxide takes place according to the following equations:



In the first (10) reaction from perhydroxyl ions the instable perhydroxyl radicals were formed, which instantly oxidize the copper(II) ions, bound in complex by citrate, to brown peroxy-copper complex. The latter compound decomposes to oxygen and copper(II) ions according to reactions (12) and (12'). The rate of the brutto process is determined by the rate of reaction (12). According to our kinetic measurements the rate of decomposition, which increases as a monotone function with the increase of pH in alkalic solutions (see Fig. 2) at constant copper(II) ion concentration, but is almost independent of the size of the wall can be described by the following equation:

$$-\left(\frac{d[\text{H}_2\text{O}_2]_a}{dt}\right) = k_2 K_0 \frac{[\text{OOH}^-]^2}{[\text{H}_2\text{O}_2]} [\text{R—CuO}_2] \quad (14)$$

As during the decomposition of a given hydrogen peroxide solution the pH is almost constant, the concentration ratio $\frac{[\text{OOH}^-]}{[\text{H}_2\text{O}_2]}$ is also constant, and the

rate of decomposition is proportional to the concentration product of peroxy-copper compound and perhydroxyl ions.

In the presence of other heavy metal ions, like iron [16, 17], cobalt [18] manganese, molybdene and chromium, the role of perhydroxyl ions is similar

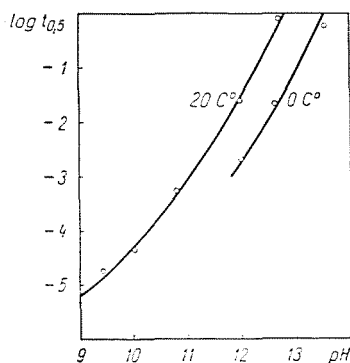
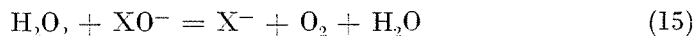


Fig. 2. Relation between $-\log t_{0.5}$ and pH in the presence of copper citrate catalyst. $[H_2O_2]_0 = 5 \cdot 10^{-2}$, $[Cu^{2+}]_0 = 2 \cdot 10^{-4}$ mol. lit $^{-1}$

to that in catalytic decomposition of hydrogen peroxide in the presence of copper.

According to our investigations [19], hypohalogenite ions, being similar in structure to perhydroxyl ions, also incline to reaction with hydrogen peroxide molecules according to the following equation:



X means a halogen in the equation. In accordance with kinetic investigations among hypiodite, hypobromite and hypochlorite ions, hypiodite reacts with perhydroxyl ions at the maximal rate. In the presence of hypiodite ions of hydrogen peroxide is a homogeneous process, seeming to be a reaction of the first order. The explanation of this is, that IO^- and HIO are always reformed because of the reoxidation of iodide ions.

In the presence of hypobromite ions the maximum rate of decomposition of hydrogen peroxide is shifted towards pH 11 as shown in Fig. 3. With the increase of hypobromite concentration, namely, rate-determining reaction (15) takes place ever more extensively over the reaction (8). If hypobromite concentration is sufficiently high, the kinetic equation can be described as follows:

$$\frac{d[H_2O_2]_a}{dt} = k_3 [H_2O_2] [BrO^-] \quad (16)$$

The reaction between hypochlorite ion and hydrogen peroxide molecule is probably slow, in the presence of hypochlorite ions, however, the decomposi-

tion of hydrogen peroxide is very fast. According to our measurements the high rate of reaction is partly due to a highly active transition product formed from the reaction of hypochloric acid molecule and hypochlorite ions, which

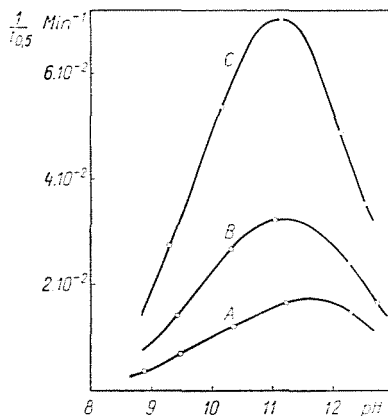


Fig. 3. Dependence of the reciprocal half-life times on the pH of the solution in reaction of hydrogen peroxide with hypobromite ions at 30° C

- A. $[\text{H}_2\text{O}_2]_0 = 0.20$; $[\text{NaOBr}]_0 = 0.10$; $[\text{Br}^-] = 0.10$ mol. litre⁻¹
 B. $[\text{H}_2\text{O}_2]_0 = 0.20$; $[\text{NaOBr}]_0 = 0.20$; $[\text{Br}^-] = 0.20$ mol. litre⁻¹
 C. $[\text{H}_2\text{O}_2]_0 = 0.40$; $[\text{NaOBr}]_0 = 0.20$; $[\text{Br}^-] = 0.20$ mol. litre⁻¹

react with hydrogen peroxide, and partly to the fact, that over pH 10 the reaction of $\text{H}_2\text{O}_2 \cdot \text{OOH}^-$ complex and hypochlorite ions accelerates the decomposition.

Table 1

Calculated composition of pure hydrogen peroxide solutions at various concentrations, and the rate of oxygen delibration

(The latter data according to the measurements of W. C. SCHUMB [21])

Concentration, weight %	0	3.4	34	65	85	100
$[\text{H}_2\text{O}]$ mol/litre	55.6	53.7	42	24	12	—
$[\text{H}_2\text{O}_2]$..	—	1	10	24	35	43
$[\text{H}_3\text{O}^+]$..	10^{-7}	$1.3 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$	$4.2 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$	—
$[\text{H}_3\text{O}_2^+]$..	—	$2 \cdot 10^{-4}$	$8.9 \cdot 10^{-10}$	$4.1 \cdot 10^{-9}$	$1.1 \cdot 10^{-8}$	$2.4 \cdot 10^7$
$[\text{OH}^-]$..	10^{-7}	$1.1 \cdot 10^{-7}$	$1.8 \cdot 10^{-9}$	$4.7 \cdot 10^{-10}$	$1.5 \cdot 10^{-10}$	—
$[\text{OOH}^-]$..	—	$1.3 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$	$4.2 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$	$2.4 \cdot 10^{-7}$
$\frac{\Delta \text{O}_2}{\Delta t}$ $\frac{\text{g} \cdot \text{litre} \cdot \text{hour}^{-1}}{(\text{50}^\circ \text{C})}$	0.0	0.023	0.095	0.121	0.116	0.080

In our opinion it is probable, that perhydroxyl ions have a big role not only in the decomposition of alkalic solutions of hydrogen peroxide, but also in pure, stabilizing agent-free more concentrated hydrogen peroxide solutions. From the equilibrium constants of reactions (1) and (2), as well as from autoprotolytic constant of water and density of hydrogen peroxide solutions, we

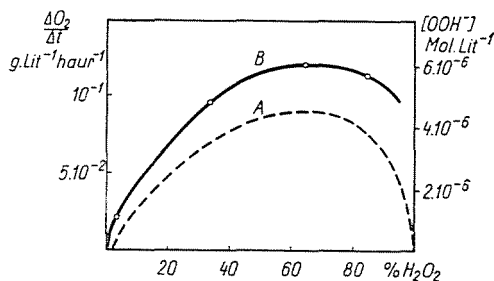


Fig. 4. A. Calculated concentration of perhydroxyl ions in hydrogen peroxide solutions of various concentrations. B. The rate of oxygen evolution at 50° C, according to the measurements of W. C. SCHUMB [21]

have calculated the concentrations of components of hydrogen peroxide solutions at various concentrations [20]. According to our results, as it is to be seen from data of Table I, the concentration of perhydroxyl ions is maximal in an about 65% hydrogen peroxide solution, in which the $\text{H}_2\text{O}_2 : \text{H}_2\text{O}$ mole ratio is close to 1 : 1. SCHUMB [21] found, that the decomposition rate of hydrogen peroxide is also maximal at 65% hydrogen peroxide concentration. The calculated perhydroxyl ion concentrations and the decomposition rates, measured by SCHUMB at 50 C°, plotted as a function of hydrogen peroxide concentration, are shown in Fig. 4. The similar shape of these curves proves our hypothesis, that, in the decomposition of more concentrated hydrogen peroxide solutions, also the perhydroxyl ions play the most important role.

Summary

In the decomposition reactions of hydrogen peroxide perhydroxyl ions, formed at protolysis have an important role. In alkalic hydrogen peroxide solutions, in which the perhydroxyl ion concentrations are considerable, the main reaction of the decomposition is the reaction between perhydroxyl ions and non-dissociated hydrogen peroxide molecules. In the presence of heavy metal ions the catalytic decomposition also involves perhydroxyl ions in a chain reaction, playing an important role in it. Finally, the similar shape of the decomposition curves of pure hydrogen peroxide solutions at various concentrations and the calculated perhydroxyl ion concentrations makes the supposition probable, that in pure, stabilizer-free hydrogen peroxide solutions in the decomposition reactions perhydroxyl ions have also an important role.

Literature

1. JOYNER, R. A.: *Z. anorg. Chem.* **77**, 103 (1912)
2. KARGIN, V. A.: *Z. anorg. Chem.* **183**, 77 (1929)
3. EVANS, M. G., URI, N.: *Trans. Faraday Soc.* **45**, 224 (1949)
4. PENNEY, W. G., SUTHERLAND, G. B.: *J. Chem. Phys.* **2**, 492 (1934)
5. SIMON, A., FEHÉR, F.: *Z. Elektrochemie* **41**, 290 (1935)
6. SIMON, A., MARCHAND, H.: *Z. anorg. Chem.* **262**, 192 (1950)
7. CHODKOWSKY, J.: *Roczniki Chem.* **27**, 309 (1953); *C. A.* **48**, 13468 (1954)
8. ERDEY, L.: *Acta Chim. Hung.* **3**, 15 (1935)
9. ERDEY, L., INCZÉDY, J.: *Acta Chim. Hung.* **7**, 93 (1955)
10. ABEL, E.: *Monatshefte* **83**, 422 (1952)
11. DORABIALSKA, A., KOŁODZIEJCZAK, K.: *Zeszyty Nauk. Politechn. Lodz. Chem.* **8**, 3 (1960)
12. DUKE, F. R., HAAS, T. W.: *J. Phys. Chem.* **65**, 304 (1961)
13. ERDEY, L., PICKERING, W., WILSON, C.: *Talanta* **9**, 371. (1962)
14. ERDEY, L., INCZÉDY, J.: *Acta Chim. Hung.* **17**, 93 (1958)
15. ERDEY, L., INCZÉDY, J.: *Mikrochim. Acta* **1959**, 438.
16. JONES, P., KITCHING, R., TOBE, M. L., WYNNE-JONES, W. F. K.: *Trans. Faraday Soc.* **55**, 79 (1959)
17. HAGGET, M. L., JONES, P., WYNNE-JONES, W. F. K.: *Trans. Faraday Soc.* **56**, 153 (1960)
18. BOBTELSKY, M., SIMCHEN, A. E.: *J. Am. Chem. Soc.* **64**, 2492 (1942)
19. ERDEY, L., INCZÉDY, J.: *Acta Chim. Hung.* **11**, 125 (1957)
20. INCZÉDY, J.: Thesis 1956. Budapest.
21. SCHUMB, W. C.: *Ind. Eng. Chem.* **41**, 992 (1949)

Prof. L. ERDEY, }
J. INCZÉDY. } Budapest XI., Gellért tér 4. Hungary