

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE UNIVERSITY OF WISCONSIN.]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN CERTAIN NONAQUEOUS SOLUTIONS.

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The fact that aqueous solutions of hydrogen peroxide are extremely sensitive to the presence of foreign substances was recognized by Thenard,¹ who reached the conclusion that all substances exert some effect on this substance, some, like the acids, increasing its stability, others, like the finely divided metals and certain metallic oxides, tending to decompose it.

Concerning the stability of nonaqueous solutions of hydrogen peroxide towards foreign substances comparatively little is known. The metallic oxides, such as manganese dioxide and lead dioxide readily decompose ethereal solutions of the peroxide. To the knowledge of the authors, however, no data exist showing whether such soluble salts as the alkali iodides, which readily decompose hydrogen peroxide,² will show a similar action towards nonaqueous solutions of this substance.

Experimental.

In a series of experiments carried out by A. Brann,³ it was found that ethereal solutions of the peroxide show absolutely no reaction when the following organic acids are dissolved in them: malic, picric, sulfanilic, citric, anthranilic, cinnamic, salicylic, gallic, camphoric, succinic, anisic, pyrogallic, benzoic, oxalic, mono- and trichloroacetic, and stearic. The following are also without influence: acetamide, acetanilide, diphenyl amine, alloxan, *p*-toluidine, phenyl hydrazine, aniline, urethane, naphthalene, β -naphthylamine, nickel bromide, and the cobalt, calcium and cadmium salts of abietic acid. The following salts are soluble in ether, but they are decomposed when added to an ethereal solution of hydrogen peroxide, the decomposition being accompanied with the formation of a precipitate: cadmium iodide, ferric chloride, cupric chloride, copper oleate, and the abietates of silver, nickel, copper and manganese. The only ether soluble substance found that decomposed the ethereal solution of the peroxide catalytically, and without forming a precipitate, is lithium iodide. In this case the evolution of oxygen is copious.

Inasmuch as hydrogen peroxide is soluble in many other organic solvents,⁴ and since many of these solvents dissolve some of the inorganic salts very readily, it was of interest to compare the activity of certain salts in nonaqueous and aqueous solutions of hydrogen peroxide. The following solvents were used: amyl acetate, amyl alcohol, isobutyl alcohol, and

¹ *Ann. chim. phys.*, **9**, 314 (1818).

² Walton, *Z. physik. Chem.*, **47**, 2 (1904).

³ Dissertation, Wisconsin, 1914.

⁴ Walton and Lewis, *THIS JOURNAL*, **38**, 633 (1916).

quinoline. By shaking with the proper amounts of "perhydrol," solutions of the above were obtained, having concentrations of hydrogen peroxide varying from 1 to 3%. They also contained, of course, a small amount of water. In making an experiment, from 0.05 to 0.1 g. of the substance to be tested was dissolved in 5 cc. of the pure solvent. This was then added to the peroxide solution. If no gas was evolved the solution was carefully warmed. Table I gives the salts used and their behavior in the different solutions.

TABLE I.

The catalytic action of various inorganic salts on aqueous and certain nonaqueous solutions of hydrogen peroxide. D = vigorous decomposition; *d* = slight decomposition; N = no decomposition; *p* = precipitate formed.

	Water.	Amyl acetate.	Quinoline.	Isobutyl alcohol.	Amyl alcohol.
Cobalt acetate.....	D	D	..	D — <i>p</i>	D
Copper acetate.....	<i>p</i>	D — <i>p</i>	D	D — <i>p</i>	D — <i>p</i>
Lead acetate.....	D	D	D	D	D
Manganese acetate.....	D	D	D	D — <i>p</i>	D — <i>p</i>
Nickel acetate.....	D	D	..	D	D — <i>p</i>
Silver acetate.....	D	D	..	D	D
Cupric chloride.....	D	D	D	D — <i>p</i>	D
Ferric chloride.....	D	..	D	D — <i>p</i>	..
Manganese chloride.....	<i>d</i>	..	D
Mercuric chloride.....	N	..	N	N	..
Ammonium iodide.....	D	D	D	D	D
Cadmium iodide.....	D	D	..	D	D
Calcium iodide.....	D	..	D	D	D
Cuprous iodide.....	..	D	D	D	D
Lithium iodide.....	D	D	D	D	D
Manganese iodide.....	D	D — <i>p</i>	D	D	D
Mercuric iodide.....	..	N	N	N	N
Mercurous iodide.....	N	<i>d</i>	D
Potassium iodide.....	D	<i>d</i>
Sodium iodide.....	D	D	D	D	D
Strontium iodide.....	D	D	D	D	D
Lead nitrate.....	<i>d</i>	..	D	..	<i>d</i>
Mercuric nitrate.....	<i>d</i>	N	N	N	N
Silver nitrate.....	<i>d</i>	<i>d</i>	N	<i>d</i>	<i>d</i>
Cuprous cyanide.....	..	D	D	D	D
Mercuric cyanide.....	<i>d</i>	N	N	N	N
Mercuric bromide.....	N	N	N	N	N

The experiments show that in general those substances that act as catalyzers to hydrogen peroxide in aqueous solution are similarly active when the peroxide is dissolved in nonaqueous solvents.

The great solubility of hydrogen peroxide in quinoline is evidenced by

the fact that at 0° for certain concentrations the partition coefficient¹ $\frac{\text{H}_2\text{O}_2 \text{ in water}}{\text{H}_2\text{O}_2 \text{ in quinoline}}$ may be as low as 0.276.

An investigation of the rate of decomposition of a peroxide solution in quinoline was undertaken. Manganese acetate was used as a catalyzer. To find out whether or not the catalytic decomposition of hydrogen peroxide in quinoline solution is quantitative, a solution of peroxide in quinoline was prepared and two 25 cc. portions placed in flasks. To one flask manganese acetate dissolved in quinoline was added, to the other an aqueous solution of potassium iodide and the solutions allowed to stand until no further decomposition took place. The volumes of oxygen liberated in each case were the same, 42.7 cc.

Proof that the amount of oxygen does not vary to any great extent with the amount of catalyzer is shown by the following data, the experiments being carried out in a manner similar to those just described:

Gram of manganese acetate per 26 cc. of solution.....	0.1	0.1	0.05	0.05
Oxygen evolved at 0° and 760 mm.....	34.80	34.75	35.00	34.70

A series of measurements of the velocity of decomposition of hydrogen peroxide in quinoline solution at 25° , using manganese acetate as a catalyzer was carried out.

Reagents.

Quinoline. The synthetic product was used. This was redistilled, the portion coming over between 234° and 236° being employed in the experiments.

Manganese acetate. The purest preparation of a standard make was used. It contains one molecule of water of crystallization.

The hydrogen peroxide was Merck's "Perhydrol."

The quinoline-peroxide solution was prepared by dissolving 6 cc. of 15% hydrogen peroxide in 250 cc. of the quinoline. This gave a solution that contains about 2.5% of water.

Procedure.

In carrying out an experiment 25 cc. of this solution were placed in a flask (Fig. 1) and 1 cc. of a quinoline solution of manganese acetate placed in the capsule A. The reaction flask was then put in a thermostat kept at 25° ; it was connected with a gas buret and its contents allowed to come to the temperature of the bath. By turning the rod B, the capsule was dropped into the quinoline solution. The flask was then shaken, and

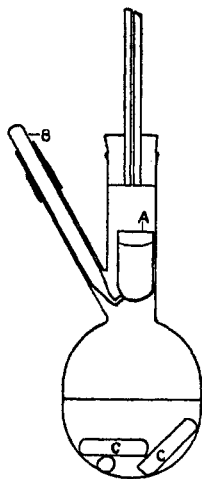


Fig. 1.

¹ Walton and Lewis, *loc. cit.*

the velocity of the decomposition of the peroxide determined by reading the volumes of oxygen in the gas burets. A number of pieces of glass rod, C, placed in the flask, increased the efficiency of the shaking apparatus.

In the following tables, t = time in minutes; x = vol. dry oxygen evolved at 0° and 760 mm.; A = total vol. oxygen evolved; C = g. catalyzer in 26 cc. of solution; K_1 = velocity constant for a monomolecular reaction; K_2 = velocity constant for a bimolecular reaction.

TABLE II.

A = 41.2.		C = 0.005.	
t.	x.	K_1 .	K_2 .
3.4	9.3	0.0692	0.001865
4.9	11.8	0.0693	0.001778
6.6	14.3	0.0649	0.001770
9.2	18.0	0.0626	0.001825
11.7	20.7	0.0598	0.001845
18.9	25.7	0.0506	0.001805
22.5	27.4	0.0487	0.001787
27.3	29.5	0.0461	0.001830
30.8	30.2	0.0431	0.001752
32.1	31.2	0.0384	0.001884

Average $K_2 = 0.001814$

TABLE III.

A = 35.0.		C = 0.005.	
t.	x.	K_1 .	K_2 .
3.2	6.9	0.0686	0.002193
4.7	9.7	0.0690	0.002331
6.2	12.2	0.0691	0.002466
9.2	16.5	0.0692	0.002770
10.7	18.2	0.0685	0.002893
12.7	20.3	0.0682	0.003107
14.7	22.2	0.0684	0.003371
17.7	24.5	0.0679	0.003766
20.7	26.5	0.0683	0.004302
24.7	28.5	0.0681	0.005071

Average $K_1 = 0.0685$

The constants in Table II show clearly that under the conditions of the experiment the hydrogen peroxide decomposes according to the second order of reaction, and not according to the first order, as in aqueous solutions of this concentration.

This may also be shown as follows: Let C_1, C_2, C_3 , represent solutions of hydrogen peroxide of different concentrations, and $\theta_1, \theta_2, \theta_3$, the time necessary for decomposing 50% of these solutions, respectively.

For a monomolecular reaction $\theta_1 = \theta_2 = \theta_3$, for a bimolecular reaction $\theta_1, \theta_2, \theta_3$, vary inversely as the concentration, that is

$$\theta.C = \text{const.} = k.$$

In the following table, concentrations and corresponding values of θ both expressed as cubic centimeters of oxygen evolved, are given:

C.....	41.2	30.9	20.6
θ	11.6	15.5	22.3
$\theta.C$	478.0	479.0	459.0

The constancy of the value $\theta.C$ is a further proof that this reaction is bimolecular.

A repetition of this experiment gave a value of $K_2 = 0.001968$, as against 0.001814 for the results given in Table II. The experiment was repeated, using a freshly prepared solution of peroxide in quinoline. The value of K_2 this time was 0.001546. It was suspected that this difference might be due to different amounts of water in the quinoline, caused by different

conditions of pressure, etc., when purifying this substance. To eliminate this variable the quinoline was saturated with water at 25°, and the water-saturated quinoline used in all subsequent experiments.

The experiment just described was repeated, the conditions being identical with the exception that water-saturated quinoline was used. The results are recorded in Table III.

An inspection of the values computed for K_1 and K_2 shows that the reaction is now monomolecular. Apart from the constancy of their constants this is shown by the fact that the time necessary to decompose 50% of a quinoline-peroxide solution is independent of the concentration of the peroxide. This is shown by the following data:

C.....	35	30	20	15
θ	10	10	10.2	10.2
$\theta.C$	350	300	204	153

The change from a bi- to a monomolecular reaction is of interest, and brings to mind the investigations of Dyer and Dale¹ and Bassett,² who showed that when hydrogen peroxide solutions of a greater concentration than 1/9 mol per liter are decomposed by colloidal platinum the reaction is bimolecular, whereas in dilute solutions it decomposes according to the first order. In this investigation there is, however, no change of concentration. The change of the reaction from a bi- to a monomolecular reaction is obviously brought about by saturating the quinoline with water.

Experiments similar to those described were carried out with different amounts of catalyzer. The following results were obtained:

	(1)	(2)	(3)	(4)	(5)	(6)
Gram manganese acetate per 26 cc. of solution.....	0.005	0.005	0.0025	0.0025	0.00125	0.00125
Time required to decompose 50% of the H ₂ O ₂ (minutes).	10.2	10.1	22.9	22.1	109.5	121.5

Decreasing the concentration of the catalyzer by 50% approximately decreases the speed of the reaction by the same amount. When the concentration is further decreased, however, the reaction is much slower, as is shown by comparison of Experiments 3 and 4 with 5 and 6. This is due primarily to a side reaction, in which some of the hydrogen peroxide is used up in oxidizing the quinoline. A quinoline-hydrogen peroxide solution can be kept for several days without any appreciable change. Addition of enough catalyzer to decompose the peroxide in a few minutes yields practically all the oxygen; if a small amount of catalyzer is added however, so that the experiment runs for two or three hours, only a part of the oxygen (about 75%) will be evolved; the rest is used up in oxidizing the quinoline. The manganese acetate not only catalyzes the peroxide

¹ *Proc. Chem. Soc.*, 29, 55 (1913).

² *Ibid.*, 29-30, 56 (1913).

decomposition, but it also catalyzes the oxidation of the quinoline by the peroxide.

In order to study the relation between the conductivity and the effect of the different concentrations of catalyzer, conductivity measurements were made at 25° with quinoline saturated with conductivity water at 25°, then with manganese acetate dissolved in 26 cc. portions of the solution in the concentrations in which it was used as a catalyzer in the experiments described. The results obtained are tabulated below:

Gram of manganese acetate per 26 cc.	0.00	0.00125	0.0025	0.005
Specific conductivity	2.3×10^{-6}	3.4×10^{-6}	3.75×10^{-6}	5.2×10^{-6}

From these data it is evident that there is no simple relation between the conductivity of the solutions of manganese acetate in water-saturated quinoline and the velocity with which the peroxide solutions are decomposed in the presence of the corresponding amounts of manganese acetate.

Summary.

The results of this investigation may be briefly summarized as follows:

1. A number of compounds that decompose aqueous solutions of hydrogen peroxide catalytically are also active as catalyzers towards solutions of hydrogen peroxide in amyl alcohol, amyl acetate, isobutyl alcohol and quinoline.
2. Hydrogen peroxide in quinoline solution is decomposed quantitatively by manganese acetate. If the manganese acetate is present in so small a concentration that the reaction is slow, a side reaction, *viz.*, the oxidation of the quinoline by the hydrogen peroxide, is also appreciably catalyzed by the manganese acetate.
3. A solution of hydrogen peroxide in quinoline containing about 2% of water, when decomposed catalytically by manganese acetate, follows the second order of reaction. If the quinoline is saturated with water the reaction is monomolecular.
4. In solutions containing the catalyzer in high concentrations the velocity of reaction is approximately doubled by doubling the concentration of the catalyzer.

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STUDIES IN DIALYSIS. I. THE DIALYSIS OF A COLLOIDAL SOLUTION OF HYDROUS CHROMIC OXIDE IN CHROMIC CHLORIDE.¹

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In an effort to prepare the red form of colloidal chromic oxide² by pass-

¹ Presented at the Spring Meeting of the American Chemical Society, 1916.

² Woudstra, *Z. Chem. Ind. Kolloide*, 5, 33 (1909).