

THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE. II

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Introduction

The decomposition of hydrogen peroxide by light is a reaction which is extraordinarily sensitive to the influence of catalysts, both positive and negative. Our first paper on the photolysis of hydrogen peroxide¹ discussed the inhibition of the photo-reaction by sulphuric acid, sodium chloride, acetanilide, calcium hydroxide, sodium hydroxide and barium hydroxide. It was pointed out that the same catalysts act differently toward the thermal and the light decomposition of hydrogen peroxide. For example, sodium hydroxide, which greatly increases the rate of decomposition at 80°, acts as a preservative in the photo-reaction; calcium hydroxide, which has no effect on the thermal decomposition, inhibits the photolysis. On the other hand, sulphuric acid and acetanilide inhibit both the thermal and the photo-decompositions.

We have extended the investigation of the catalysis of the photo-reaction to a number of other catalysts with the results indicated below.

Experimental Methods and Data

The apparatus used to study the catalysis of the photo-reaction was the same as described in our first paper,¹ and we also used the same methods of preparing the peroxide solution and of following the course of the reaction.

In the graphs shown below, curves marked I represent, in every case, the course of the reaction before adding the catalyst, and curves marked II, the course of the reaction after adding the catalyst. The sudden break between curves I and II represents the dilution effect of adding the catalyst, as we have previously shown.

¹ Jour. Phys. Chem., 18, 166 (1914).

Effect of Urea

Urea is without appreciable effect on the reaction. Table I and Fig. 1 show the course of the reaction. The amount of urea added was such as to make the whole solution 0.05 percent.

TABLE I

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	7.03	141	6.38
33	6.90	167	6.29
62	6.81	193	6.20
93	6.68	215	6.11
121	6.57	235	6.05
Added urea at 134			

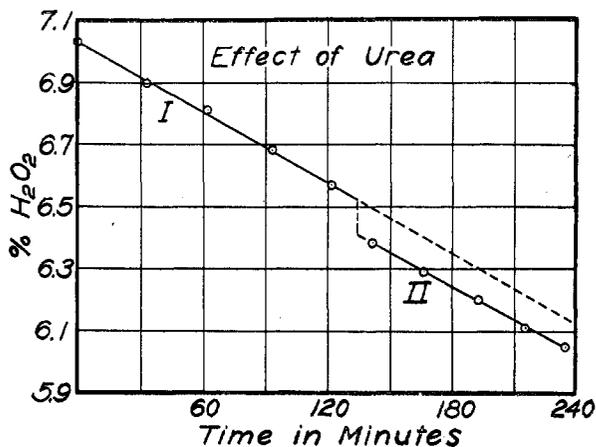


Fig. 1

Effect of Acetic Acid

Acetic acid acts as a mild preservative. Table II and Fig. 2 refer to acetic acid.

TABLE II

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	7.04	117	6.47
41	6.88	142	6.44
70	6.77	169	6.39
102	6.63	203	6.30
Added acetic acid at 110		250	6.24

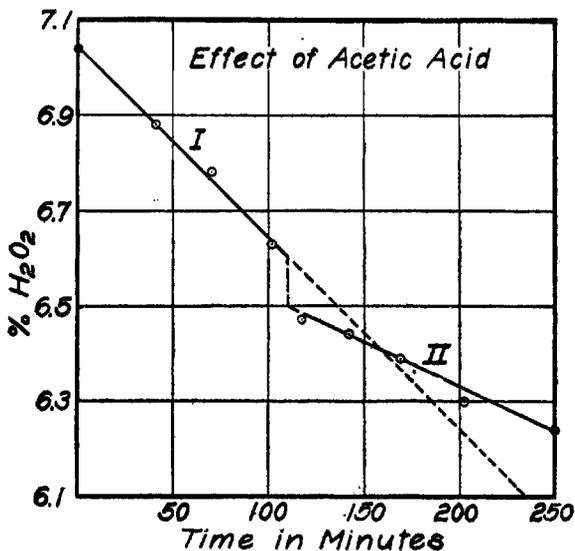


Fig. 2

Effect of Boric Acid

Boric acid has no effect on the reaction, as Table III and Fig. 3 show. The amount of boric acid added was such as to make the whole solution 0.044 percent.

TABLE III

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	4.61	120	4.24
38	4.51	146	4.16
71	4.43	187	4.06
97	4.36	221	3.97
Added the boric acid at 106			

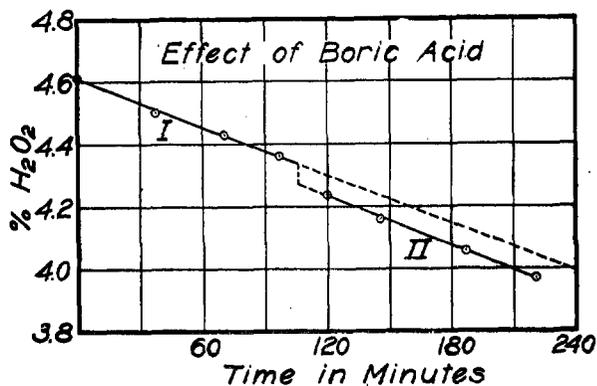


Fig. 3

Effect of Tartaric Acid

Tartaric acid is a mild preservative. In this experiment the acid was added in the solid form, and the dilution effect is therefore absent in Fig. 4. The amount of acid added was such as to make the whole solution 0.096 percent.

TABLE IV

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	4.53	120	4.26
38	4.43	163	4.225
76	4.35	199	4.20
106	4.27		
Added tartaric acid at 112			

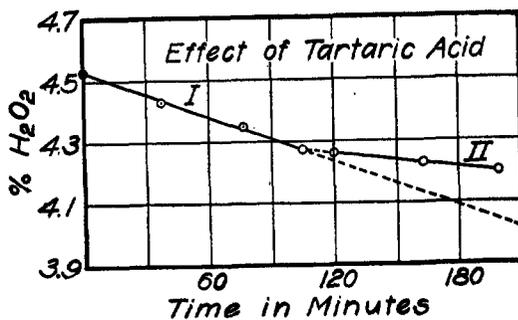


Fig. 4

Effect of Phosphoric Acid

The effect of phosphoric acid is similar to that of acetic acid and of tartaric acid, inhibiting the reaction. The amount of acid added was such as to make the whole solution 0.152 percent.

TABLE V

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	4.425	80	4.21
29	4.34	110	4.16
59	4.26	139	4.13
Added phosphoric acid at 69		171	4.10

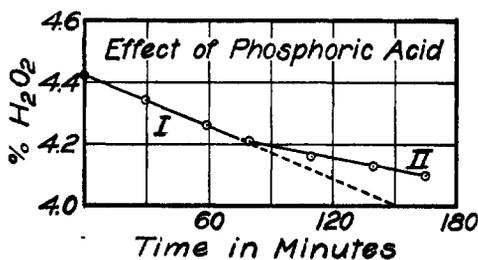


Fig. 5

Effect of Benzoic Acid

This acid is an excellent preservative. Table VI and Fig. 6 show the effect of benzoic acid on the photolysis.

TABLE VI

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	3.32	156	3.04
29	3.27	187	3.01
69	3.20	217	3.02
109	3.14	247	3.01
131	3.09		
Added benzoic acid at 146			

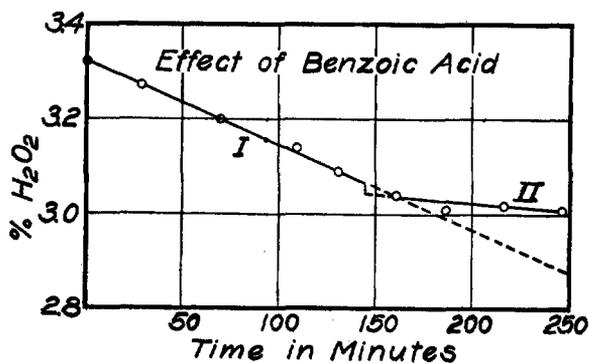


Fig. 6

Effect of Barium Chloride

The addition of this salt has no effect on the rate of the photolysis, as Table VII and Fig. 7 show. The amount of barium chloride added was such as to make the whole solution 0.037 percent.

TABLE VII

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	3.85	108	3.61
43	3.78	156	3.52
88	3.70	196	3.45
Added BaCl ₂ at 102			

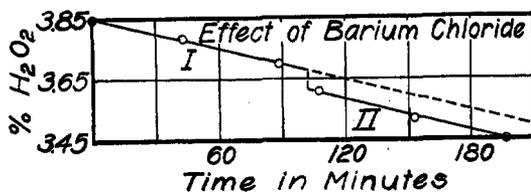


Fig. 7

Effect of Barium Nitrate

Barium nitrate increases the rate of decomposition. This is a striking fact in view of the strong preserving action

of barium hydroxide and the zero effect of barium chloride. Table VIII and Fig. 8 present the results for barium nitrate. The amount of salt added was such as to make the whole solution 0.037 percent.

TABLE VIII

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	3.77	109	3.49
41	3.69	147	3.38
80	3.62	190	3.26
Added Ba(NO ₃) ₂ at			
91			

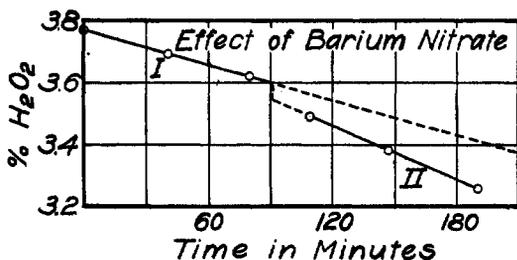


Fig. 8

Effect of Potassium Chloride

Potassium chloride, like sodium chloride, very slightly decreases the rate of photolysis. It will be seen in Table IX and Fig. 9 that for some time after the catalyst was added the rate of decomposition remained unchanged and then began to fall off very slowly. The amount of the salt added was such as to make the whole solution 0.023 percent.

TABLE IX

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	3.68	119	3.40
38	3.60	154	3.32
78	3.52	189	3.24
Added KCl at		227	3.18
92		245	3.15

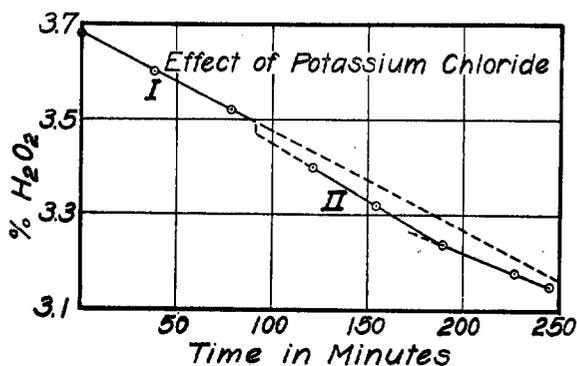


Fig. 9

Effect of Sodium Chloride

We have previously shown that sodium chloride slightly decreases the rate of photolysis of peroxide. After noting the lag in the inhibiting effect of potassium chloride, we repeated the experiment with sodium chloride, using a 0.011 percent solution instead of the 0.05 percent solution used before, and also cutting down the light intensity to that used in the potassium chloride experiment. Under these conditions we found the same lag in the inhibiting effect of sodium chloride. Table X and Fig. 10 present the results of this experiment.

TABLE X

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	3.57	94	3.27
39	3.47	130	3.17
74	3.375	159	3.13
Added NaCl at		189	3.07
83		218	3.02

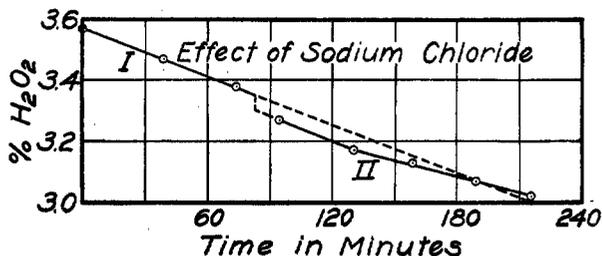


Fig. 10

Effect of Acetamide

As acetanilide has such a strong inhibiting action, acetamide naturally suggested itself as another possible catalyst. This substance has, however, practically no effect on the rate of photolysis, as Table XI and Fig. 11 show. The amount of acetamide added was such as to make the whole solution 0.037 percent.

TABLE XI

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	3.39	104	3.09
35	3.31	139	3.00
72	3.22	172	2.94
Added acetamide at 80		206	2.86

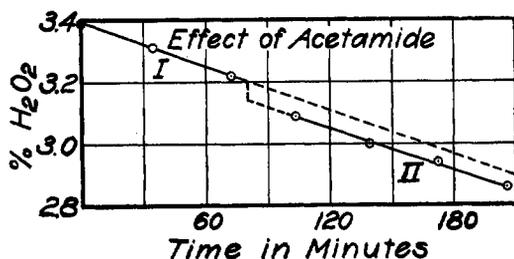


Fig. 11

Effect of Potassium Nitrate

Potassium nitrate has at first no effect on the reaction, but after it has been present for some time begins to inhibit the photolysis slightly, resembling in this behavior the action of sodium and potassium chlorides. In Table XII and Fig. 12 are given the results for potassium nitrate. The amount of nitrate added was such as to make the whole solution 0.031 percent.

TABLE XII

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	3.34	114	3.00
31	3.25	149	2.91
65	3.18	184	2.87
98	3.09	197	2.85
Added KNO ₃ at 105		227	2.81

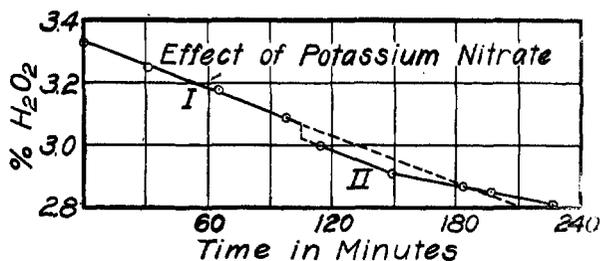


Fig. 12

Relation between the Amount of the Catalyst Added and the Magnitude of Effect Produced

The effect produced by a catalyst on the photolysis of hydrogen peroxide is not directly proportional to the amount of the catalysts used. We have tried sulphuric acid of four concentrations approximating very closely the ratios 1 : 10 : 100 : 200.¹ Table XIII and Fig. 13 show the effect of sulphuric acid 0.000175 N; Table XIV and Fig. 14 of sulphuric acid 0.00176 N; Table XV and Fig. 15 of sulphuric

TABLE XIII

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	4.90	117	4.52
35	4.81	143	4.50
62	4.74	171	4.45
89	4.68	205	4.39
Acid added at 98 Conc. 0.000175 N		229	4.34

¹ The concentrations of the acid used were exactly of these ratios, but the volume of the peroxide solution at the time of adding the acid was not the same in each case.

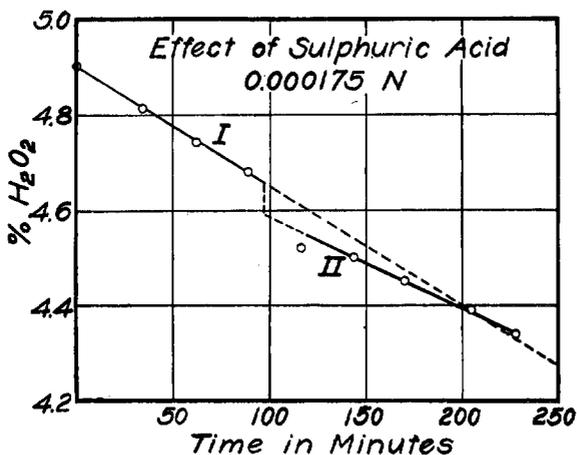


Fig. 13

acid 0.0176 N; and Table XVI and Fig. 16 of sulphuric acid 0.0349 N.

TABLE XIV

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	5.21	85	4.90
22	5.13	106	4.86
42	5.07	130	4.86
63	5.00	153	4.83
Acid added at		176	4.80
72		199	4.78
Conc. 0.00176 N		224	4.77

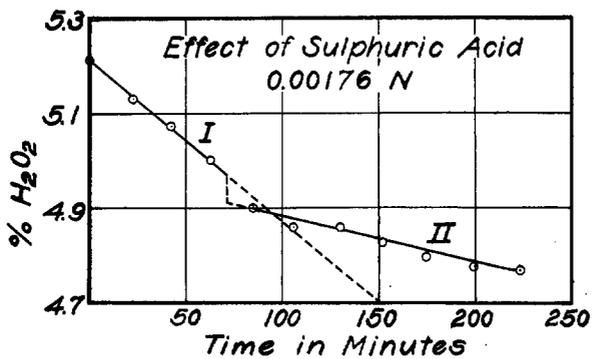


Fig. 14

TABLE XV

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	5.31	176	4.81
28	5.23	197	4.80
55	5.13	226	4.78
85	5.06	255	4.76
124	4.94		
Added acid at			
132			
Conc. 0.0176 N			

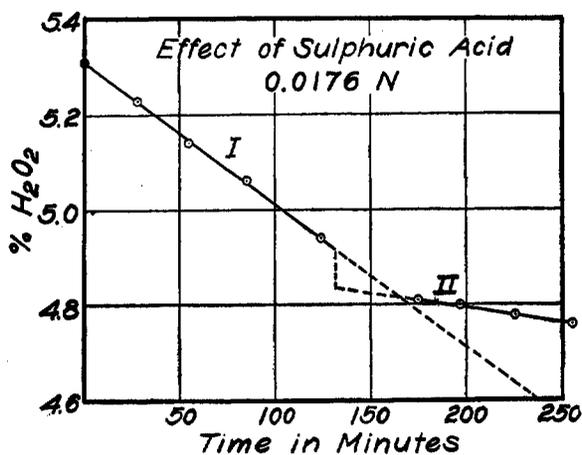


Fig. 15

TABLE XVI

Time in minutes	Percent H ₂ O ₂	Time in minutes	Percent H ₂ O ₂
0	5.19	152	4.74
36	5.10	181	4.725
71	4.99	222	4.69
119	4.88	257	4.68
Added acid at			
128			
Conc. 0.0349 N			

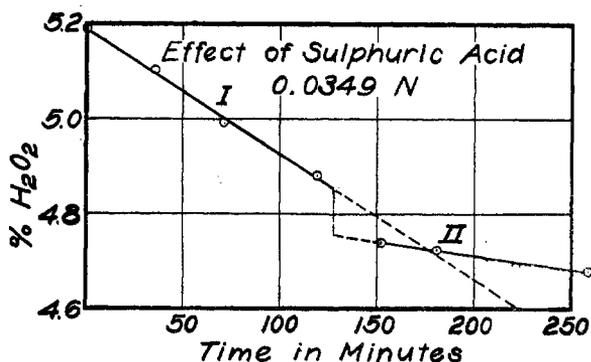


Fig. 16

The ratio of the slope of Curve II to that of Curve I will, in each case, give us a measure of the effect of the acid, since for concentrations of peroxide such as used in these experiments the rate of the decomposition is practically linear.

These ratios are as follows: for 0.00175 *N* acid, 0.76, *i. e.*, the rate after adding the acid was about 76 percent of the rate before adding the acid; for 0.00176 *N* acid, 0.30; for 0.0176 *N* acid, 0.20; for 0.0349 *N* acid, 0.22.

It will be seen that the two higher concentrations of acid have practically the same effect; the effect is a little less for the 0.0176 *N* acid, and very much less for the most dilute of the four. Judging from these results, which are, perhaps, not extensive enough to be conclusive, it appears that while the magnitude of the catalytic effect varies in the same direction as the concentration, the two are by no means directly proportional. And further, that above a certain concentration, the catalytic effect becomes nearly constant.

We have noted the same behavior in the case of the catalysis by means of sodium chloride. After changing the rate of the photolysis by adding 0.006 gram of salt, the further addition of 0.5 gram had no effect on the rate of decomposition.

The Absorption of Light by Hydrogen Peroxide Solutions

We have attempted to find a relationship between the change of light absorption in the peroxide solution upon adding

the catalyst and the effect produced. The change is too small to be measured with any certainty by the Rubens' linear thermopile. The photographic method used by Henri¹ was also tried. The results showed qualitatively that the absorption is very slightly increased by adding the catalyst, but threw no light upon the specific nature of catalytic effect.

Henri and Wurmser have noted² that the addition of an alkali to a peroxide solution increases its absorption in the ultraviolet, but found no connection between the absorption and the nature of the catalyst. It might be expected that such an increase in absorption would increase the rate of decomposition, rather than decrease it as is actually the case.

The Surface Tension of Hydrogen Peroxide Solutions

W. Spring³ has shown that the surface tension of pure hydrogen peroxide is only about 45 percent that of pure water at 10°, and that it increases very rapidly as water is added. Our own measurements indicate that the surface tension of a 5 percent solution of peroxide is slightly less than that of pure water. The change in surface tension of a hydrogen peroxide solution on adding a small amount of acid or of alkali is exceedingly small. We at first attempted to detect a difference using a stalagmometer. While this instrument would show the difference between the surface tension of pure water and peroxide solution it would not detect any change when a small amount of acid was added to the peroxide.⁴

On applying the capillary tube method, and reading the heights of the column in the capillary with an excellent cathetometer, we found that a trace of sulphuric acid would lower the surface tension slightly. A trace of alkali had but little effect, while a larger amount would very slightly increase the surface tension.

¹ *Phys. Zeit.*, 14, 515 (1913).

² *Comptes rendus*, 157, 284 (1913).

³ *Zeit. anorg. Chem.*, 8, 424 (1895).

⁴ The stalagmometers at hand have a capacity of only about 42 drops for water, and the accuracy on small changes of surface tension would naturally not be great.

W. Spring¹ compared the surface tension of an acid solution of peroxide with that of an alkaline solution of the same density, finding the surface tension of the alkaline solution to be a few percent higher than that of the acid solution.

Since both sulphuric acid and sodium hydroxide decrease the rate of photolysis of hydrogen peroxide, it does not seem that an explanation of catalytic effect is to be found in the slight changes of surface tension. Moreover, the change in the rate of photolysis of hydrogen peroxide on adding a trace of a catalyst is altogether out of proportion to the change in surface tension of the solution as a result of adding a catalyst.

The Chemical Nature of the Catalysts and their Specific Catalytic Effect

We tabulate below the various catalysts we have tried (including those for which the data were given in our previous paper) and their influence on the rate of photolysis of hydrogen peroxide.

TABLE XVII

Substance	Amount used Percent	Effect on photolysis
Acetanilide	0.04	Strong inhibition
Acetamide	0.037	Practically no effect
Urea	0.05	Practically no effect
Acetic acid		Mild inhibition
Benzoic acid		Strong inhibition
Boric acid	0.044	No effect
Tartaric acid	0.096	Mild inhibition
Phosphoric acid	0.152	Mild inhibition
Sulphuric acid	0.000875	Slight inhibition
Sulphuric acid	0.008624	Mild inhibition
Sulphuric acid	0.08624	Mild inhibition
Sulphuric acid	0.17101	Mild inhibition
Calcium hydroxide	0.002	Strong inhibition
Sodium hydroxide	0.053	Strong inhibition
Barium hydroxide	0.007	Strong inhibition
Barium chloride	0.037	No effect
Barium nitrate	0.037	Increases rate
Potassium nitrate	0.031	Very small inhibition
Potassium chloride	0.023	Very small inhibition
Sodium chloride	0.011	Very small inhibition
Sodium chloride	0.05	Mild inhibition

¹ Zeit. anorg. Chem., 10, 161 (1895).

The table clearly emphasizes the specific catalytic action of the substances used. Aside from this, there are but few regularities to be found in the table. It will be noted that all the alkalis tried inhibit the reaction; of the acids, benzoic is an excellent preservative, sulphuric, acetic, tartaric, phosphoric are mild preservatives, while boric acid is without effect; of the neutral salts, barium nitrate hastens the photolysis, barium chloride is without effect, while potassium chloride, sodium chloride and potassium nitrate have a very small inhibiting effect after they have been present in the solution for some time. Acetanilide is an excellent preservative, while urea and acetamide are without effect.

The influence of foreign substances on the *thermal* decomposition of hydrogen peroxide has been the subject of a considerable amount of investigation and a great deal of speculation. The reason for the effects has not yet been discovered. The problem is, of course, a special case of the broader phenomenon of catalysis in general, which phenomenon yet remains to be explained by any theory to which experimental data can be applied.

When more is known about catalysis in general, it may be possible to explain why sulphuric acid strongly inhibits the thermal decomposition of hydrogen peroxide, while sodium hydroxide is a strong positive catalyst for the thermal reaction. It will then remain to show why both of these substances inhibit the photolysis of hydrogen peroxide.

Summary

1. The influence of a number of inorganic and organic compounds on the rate of photolysis of hydrogen peroxide has been measured quantitatively.
2. The same catalysts do not effect the thermal decomposition and the photochemical decomposition of hydrogen peroxide in the same way.
3. There is no general relationship between the chemical nature of a compound and its catalytic effect on the photolysis of hydrogen peroxide.

4. While the magnitude of the catalytic effect and the concentration of the catalyst vary in the same direction, there is not a direct proportionality between these two quantities.

5. Neither the change in the light absorption nor the change in surface tension of a hydrogen peroxide solution brought about by the addition of a small amount of a catalyst seems adequate to explain the marked catalytic effect produced.

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