This investigation was carried out with the aid of a National Research Fellowship in the Chemical Laboratory of Princeton University.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

# THE INHIBITION OF THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTIONS. II

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Received February 21, 1923

In a preceding paper[1] an attempt was made to correlate the inhibitory action of a number of typical organic compounds with selective light absorption. The present investigation was instigated in order to study inhibition by some common inorganic acids, bases and salts, and to explain, if possible, the stabilizing action of organic compounds which obviously do not act by selective light absorption, and which include among their number two classes, the alcohols and amines.

With the exception of the nitrates,[2] which exhibit weak absorption throughout the ultraviolet, all the solutions studied were practically diactinic to the incident radiation; that is, all light absorption was due entirely to the hydrogen peroxide and not to the inhibitors.[3] Selective light absorption by inhibitors may be immediately ruled out as a cause.

The apparatus and experimental procedure were practically identical with those described in Part I[1] to which the reader is referred. There also will be found a complete definition of "inhibition constant" and a detailed account of experimental errors.

The materials used were the purest obtainable and were always tested for common impurities. The volatile acids were redistilled, and the salts were in a few cases recrystallized.

The inhibitory actions of the substances employed were compared by means of the inhibition constants. Bases were found to be excellent inhibitors, acids good, and neutral chlorides and bromides fair. No other inorganic compounds tried were found to inhibit. As was expected, inhibition was found to be independent of incident wave length. All measurements were made at a temperature of 25° unless otherwise stated. Many of the inhibitors have been previously studied by Henri and Wurm-

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[1] Anderson and Taylor, THIS JOURNAL, **45**, 650 (1923).

[2] Winther, Baggesgaard-Rasmussen and Schreiner, *Z. wiss. Phot.*, **22**, 33 (1922). Hartley, *J. Chem. Soc.*, **83**, 221 (1903); **81**, 571 (1902).

[3] Miller, *Phil. Trans.*, **152**, 861 (1863). Martens, *Drude's Ann.*, **6**, 603 (1901). Houston, *Proc. Roy. Soc. Edinburgh*, **32**, 40 (1912). Retschinsky, *Ann. Physik*, **42**, 1580 (1913). Brannigan and Macbeth, *J. Chem. Soc.*, **109**, 1277 (1916). Wright, *ibid.*, **103**, 528 (1913). Henri and Wurmser, *Compt. rend.*, **156**, 1012 (1913).

ser[4] and Mathews and Curtis.[5] For convenience, the substances are grouped as Acids and Salts, Bases, and Haloids.

## Acids and Salts

TABLE I

SUMMARY OF INHIBITION CONSTANTS FOR ACIDS AND SALTS AND NEUTRAL SALT ACTION

| Acid | Acid normality | Salt | Salt normality | $K$[a] | % acid ionized |
|---|---|---|---|---|---|
| $HClO_4$ | 0.005 | ..... | 0.00 | 30 | 99 |
| ... | .00 | $KClO_4$ | .10 | 100 | .. |
| $HClO_4$ | .005 | $KClO_4$ | .10 | 40 | .. |
| $HNO_3$ | .005 | ..... | .00 | 30 | 97 |
| ... | .00 | $HNO_3$ | .005 | 100 | .. |
| ... | .00 | $NaNO_3$ | .005 | 100 | .. |
| ... | .00 | $Ba(NO_3)_2$ | .005 | 110 | .. |
| $H_2SO_4$ | .0005 | ..... | .00 | 65 | .. |
| ... | .00 | $Na_2SO_4$ | 1.00 | 100 | .. |
| $H_2SO_4$ | .0005 | $Na_2SO_4$ | 1.00 | 100 | .. |
| $H_2SO_4$ | .005 | .... | 0.00 | 35 | 85 |
| ... | .00 | $Na_2SO_4$ | 3.00 | 100 | .. |
| $H_2SO_4$ | .005 | $Na_2SO_4$ | 1.00 | 75 | .. |
| $H_2SO_4$ | .005 | $Na_2SO_4$ | 2.00 | 100 | .. |
| ... | .00 | $K_2SO_4$ | 1.50 | 100 | .. |
| $H_2SO_4$ | .005 | $K_2SO_4$ | 1.50 | 100 | .. |
| ... | .00 | $MgSO_4$ | 2.00 | 100 | .. |
| $H_2SO_4$ | .005 | $MgSO_4$ | 2.00 | 100 | .. |
| $H_2SO_4$ | .005 | $MgSO_4$ | 1.00 | 70 | .. |
| ... | .00 | $(NH_4)_2SO_4$ | 3.00 | 100 | .. |
| $H_3PO_4$ | .005 | ..... | .00 | 40 | 70 |
| $H_3BO_3$ | .005 | ..... | .00 | 100 | 0.05 |
| $H_3BO_3$ | .10 | ..... | .00 | 100 | .. |

[a] $K$ is the "inhibition constant" of hydrogen peroxide solutions containing the stated compounds at the designated concentrations.
$K$ = velocity constant (for first order) of decomposition of $H_2O_2$ with inhibitor × 100/velocity constant of uninhibited solution of $H_2O_2$ under like conditions.
$K$ for *un*inhibited solutions equals 100.

The strong acids were good inhibitors, whereas their neutral salts, even at high concentrations, had no detectable effect upon the decomposition of the peroxide. The procedure whereby a neutral salt of common ion was added to the acid solution of peroxide has unfortunately been largely limited to that of sulfate, due to experimental difficulties in the cases of nitrate and phosphate.

Sodium sulfate 3 $N$ has absolutely no effect on the photochemical decomposition of hydrogen peroxide. Sulfuric acid 0.005 $N$ slowed the rate of decomposition down to 35% of that of the uninhibited solution. The addition of sufficient anhydrous sodium sulfate to make the solution 1 $N$ with respect to sodium sulfate increased the rate of decomposition to

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[4] Henri and Wurmser, *Compt. rend.*, **157**, 284 (1913).

[5] Mathews and Curtis, *J. Phys. Chem.*, **18**, 178, 521 (1914).

75% of that of the uninhibited solution, and the addition of more salt to a concentration of 2 *N* entirely destroyed the inhibitory power of the sulfuric acid. Other neutral sulfates had a similar effect. Perchlorates and perchloric acid behaved like the sulfates.

It was impossible to apply the tests to the nitrates for these reasons: (1) nitrates in greater than extremely dilute solution react readily with permanganate; (2) aqueous solutions of nitrates, and particularly nitric acid, in more than very dilute solutions are reduced to nitrites by ultraviolet light;[6] nitrous acid reacts with permanganate; (3) nitrous acid is oxidized by 3% hydrogen peroxide to a pernitric acid which is readily hydrolyzed to nitric acid and hydrogen peroxide, the net result of completing the cycle being the loss of about 1 molecule of hydrogen peroxide.[7]

Table I shows that for comparable concentrations of acid, 0.005 *N*, there is a relationship between inhibition and extent of dissociation. Perchloric acid, practically 100% dissociated, is a good inhibitor, whereas boric acid, nearly undissociated, does not inhibit. Neutral salt action by which the dissociation of the acid is repressed by common ion effect is additional evidence of a parallelism between inhibition and dissociation. It appears that inhibition by acids is a function of the hydrogen-ion concentration. This postulates that organic acids if present in the peroxide solution in sufficient quantity should inhibit even in the wave lengths of light that they do not selectively absorb. This has been found to be correct in the case of acetic acid.

## Bases, Including Ammonium Derivatives

Of the non-light absorbing compounds, the hydroxides are by far the best inhibitors for the photochemical decomposition of hydrogen peroxide. This fact has perplexed several investigators, for the alkali hydroxides are accelerators for the thermal decomposition.

None of the neutral salts employed affects the rate of decomposition of the hydrogen peroxide. The addition of neutral salts of a common ion repressed the dissociation of the hydroxide and decreased the inhibitory effect in a manner analogous to that of the acids. It is concluded, therefore, that in this case inhibition is a function of the hydroxide-ion concentration.

The inhibitory power of amines is due most probably to the action of the hydroxide-ion concentration produced when an amine is dissolved in water. The behavior of alcohols is not understood.

The extent of inhibition by hydrogen and hydroxide ions was found to

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[6] Berthelot and Gaudechon, *Compt. rend.*, **152,** 522 (1911). Warburg, *Sitzb. preuss. Akad. Wiss. Berlin.*, **1918,** p. 1228. Moore and Webster, *Proc. Roy. Soc.*, **90B,** 158 (1919). Lombard, *Compt. rend.*, **150,** 227 (1910).

[7] Raschig, *Z. angew. Chem.*, **17,** 1419 (1904); *Ber.*, **40,** 4585 (1907). D'Ans, *Z. Elektrochem.*, **17,** 850 (1911). Trifonow, *Z. anorg. Chem.*, **124,** 123 (1922).

be independent of the wave length of the incident radiation. This behavior is in distinct contrast to that of the light-absorbing compounds where inhibition is dependent upon wave length.

TABLE II

SUMMARY OF INHIBITION CONSTANTS FOR BASES AND NEUTRAL SALT ACTION

| Substance | Normality of base | Common ion salt | Normality of salt | *K* |
|---|---|---|---|---|
| NaOH | 0.005 | ..... | 0.00 | 0 |
| NaOH[a] | .001 | ..... | .00 | 2 |
| NaOH | .001 | $Na_2SO_4$ | 1.00 | 10 |
| NaOH | .001 | $Na_2SO_4$ | 2.00 | 30 |
| NaOH | .001 | $Na_2SO_4$ | 3.00 | 70 |
| NaOH | .0005 | ..... | 0.00 | 14 |
| NaOH | .0005 | $Na_2SO_4$ | 2.00 | 60 |
| NaOH | .0005 | $Na_2SO_4$ | 3.00 | 100 |
| KOH | .005 | ..... | 0.00 | 0 |
| KOH | 0005 | ..... | .00 | 16 |
| KOH | .0005 | $K_2SO_4$ | 1.50 | 70 |
| $Ba(OH)_2$ | .005 | ..... | 0.00 | 0 |
| $NH_4OH$ | (.005 $NH_3$) | ..... | .00 | 10 |
| $NH_4OH$ | (.005 $NH_3$) | $(NH_4)_2SO_4$ | 3.00 | 60 |
| $C_2H_5NH_3OH$ | (.005 $C_2H_5NH_2$) | ..... | 0.00 | 5 |
| $C_6H_5CH_2NH_3OH$ | (.005 $C_6H_5CH_2NH_2$) | ..... | .00 | 8 |

[a] The NaOH used for the more dilute solutions was prepared free from carbon dioxide according to the method of Cornog, THIS JOURNAL, **43**, 2573 (1921), and standardized against 0.1 *N* HCl.

The effect of temperature on inhibition is of importance when considering an explanation to account for the stabilizing action of these ions. The inhibition constants of some acids and bases were determined, therefore, at two temperatures, 2° and 25°.

TABLE III

EFFECT OF TEMPERATURE ON THE INHIBITION BY ACIDS AND BASES

| Substance | Normality | Inhibition constant at 2° | Inhibition constant at 25° |
|---|---|---|---|
| | 0.025 | 22 | 20 |
| | .050 | 14 | 15 |
| $HClO_4$ | .002 | | 39 |
| | .002 | 40 | 43 |
| NaOH | .0005 | 16 | 14 |
| | .0005 | 15 | 18 |

The results at the two temperatures are, within experimental error, identical. The temperature coefficient for 10° for the uninhibited peroxide was found to be 1.43, agreeing well with the value obtained by Mathews and Curtis.[5]

## Haloids

The chlorides and bromides of the alkali and alkaline earth metals were found to be fair inhibitors, the chlorides being slightly better than the bromides. The results in Tables IV and V clearly indicate that the concentration of the chloride or bromide ions is the contributing factor, there being in this case, as in that of the acids, a correspondence between inhibition and ionization. Sodium fluoride was found to accelerate the decomposition slightly. Hydrochloric acid in comparable concentrations was a better inhibitor than any of the other acids, the inhibition probably being due to a combined effect of hydrogen and chloride ions.

TABLE IV

SUMMARY OF INHIBITION CONSTANTS FOR HALOIDS AT DIFFERENT CONCENTRATIONS

| Substance | 0.005 $N$ | 0.002 $N$ | 0.001 $N$ | 0.0005 $N$ |
|---|---|---|---|---|
| HCl | 20 | .. | ... | ... |
| NaF | 120 | .. | ... | ... |
| $NH_4Cl$ | 35 | .. | ... | 100 |
| NaCl | 40 | 70 | 80 | 100 |
| KCl | 40 | 75 | 85 | 100 |
| $MgCl_2$ | 50 | 75 | ... | 100 |
| $BaCl_2$[a] | 40 | .. | ... | ... |
| $NH_4Br$ | 55 | 80 | ... | 100 |
| KBr | 60 | 85 | 100 | 100 |
| $BaBr_2$ | 60 | .. | ... | ... |

[a] When barium salts were employed, phosphoric acid was used during the titration in place of sulfuric acid.

TABLE V

EFFECT OF COMMON CATION SULFATES ON HALOID SALTS

| Substance 0.005 $N$ | Inhibition constants | | | |
|---|---|---|---|---|
| | 0.00 $N$ | 1.00 $N$ | 2.00 $N$ | 3.00 $N$ sulfate |
| $NH_4Cl$ | 35 | .. | 45 | 55 |
| NaCl | 40 | 50 | 75 | 100 |
| KCl | 40 | 60 | 70[a] | ... |
| $MgCl_2$ | 50 | .. | 75 | ... |
| $NH_4Br$ | 55 | 60 | ... | 85 |
| KBr | 60 | 85 | 100[a] | ... |

[a] 1.5 $N$ $K_2SO_4$ used.

Walton[8] and Schöne[9] found that chlorides were slowly decomposed by aqueous solutions of hydrogen peroxide with the formation of hypochlorites. Auger[10] and Sperber[11] report, however, that hydrogen peroxide reacts slightly with all the halogen acids and salts with the liberation of the free halogen itself. Accordingly, solutions of hydrogen peroxide were prepared approximately 0.000,000,5 $N$ with respect to chlorine and bromine. In as much as both chlorine and bromine, even at this dilution, react quite rapidly with hydrogen peroxide (or water) when illuminated with ultraviolet radiation, the velocity constants for the decomposition of the hy-

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[8] Walton, *Z. physik. Chem.*, **47**, 185 (1904).

[9] Schöne, *Ann.*, **195**, 228 (1879).

[10] Auger, *Compt. rend.*, **152**, 712 (1911).

[11] Sperber, *Schweiz. Apoth. Ztg.*, **52**, 2, 245 (1914).

drogen peroxide were determined from the very beginning of illumination and compared with those of a peroxide solution without inhibitor, determined under like conditions. The results are incorporated in Table VI.

TABLE VI

VELOCITY CONSTANTS FOR PEROXIDE SOLUTIONS 0.000,000,5 $N$ WITH CHLORINE AND BROMINE

| Time from beginning Min. | Vel. const. $H_2O_2$ without inhibitor | Vel. const. $H_2O_2$ with chlorine | Vel. const. $H_2O_2$ with bromine |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 17 | 0.00203 | 0.00125 | 0.00167 |
| 37 | .00267 | .00200 | .00226 |
| 59 | .00273 | .00271 | .00269 |
| 80 | .00268 | .00265 | .00271 |

The apparent transitory inhibition by chlorine and bromine may be due to selective light absorption,[12] as aqueous solutions of chlorine and bromine transmit poorly in the ultraviolet. The action of continuously liberated chlorine and bromine from chlorides and bromides respectively may account in part for the inhibitory power of these ions, but a complete solution of the problem of inhibition appears to be much more complex.

Any theory to account for the inhibitive action by hydrogen, hydroxide, chloride and bromide ions must be in accord with the following facts.

(1) The ratio of inhibitive efficiency of hydroxide to hydrogen ions is about 1 to 25, that is, 1 hydroxide ion inhibits as much as 25 hydrogen ions. (2) Hydroxide ions *in*crease the concentration of peroxide ions in the solution by the formation of ionized peroxide salts. Hydrogen ions *de*crease the ionic dissociation of the hydrogen peroxide by common ion effect. (3) Inhibition has a zero temperature coefficient. (4) Inhibition is dependent on the concentration of hydrogen peroxide in solutions employed, 0.1 $N$ to 6.0 $N$, and of wave length of incident radiation. (5) One $h\nu$ may decompose as many as 80 molecules of hydrogen peroxide.[13] (6) Chloride ions are better inhibitors than bromide ions. (7) Alkali and alkaline earth cations, sulfate, perchlorate and nitrate ions and the undissoiated molecules of acids, bases and salts do *not* inhibit.

A qualitative approximation to a theory to account for the above facts may be made by assuming that it is the hydrogen peroxide ion ($OOH^-$) that is activated and decomposed. The mechanism of this may be demonstrated by the following equations.

$$H_2O_2 \rightleftarrows H^+ + OOH^- \qquad K_1 = \frac{C_{H^+} \times C_{OOH^-}}{C_{H_2O_2}} \tag{1}$$

$$* + OOH^- \rightleftarrows OOH^{-*} \tag{2}$$

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[12] Peskoff, *Z. wiss. Phot.*, **18,** 235 (1919).

[13] Kornfeld, *ibid.*, **21,** 66 (1921).

$$OOH^{-*} \rightleftharpoons OH^- + O + {}^* \quad K_3 = \frac{C_{OH^-} \times C_O}{C_{OOH^{-*}}} \tag{3}$$

$$O + O \rightleftharpoons O_2 \tag{4}$$

$$H^+ + OH^- \rightleftharpoons H_2O \tag{5}$$

* Indicates absorbed radiation.

The ionic dissociation represented in Equation 1 is actually realized, for hydrogen peroxide in aqueous solution is a very weak acid, 15 molecules in every 100,000 being ionized.[14] The extent of ionic dissociation of the peroxide is practically independent of temperature, wave length of incident radiation and, within wide limits, of concentration. The addition of sodium or ammonium sulfate, even in high concentrations, has no detectable effect on the rate of photochemical decomposition, although these compounds develop extensive compound formation with hydrogen peroxide in solution, and may even be obtained in a fairly stable, crystalline form.[15] These facts are consistent with an ionization hypothesis.

The assumption in Equation 3 of the liberation of momentarily atomic oxygen is not without some justification. Rideal[16] states that the ultraviolet atomic oxygen bands in the regions 2300 and 3400 Å. are observed in the decomposition of many oxygen-containing compounds. In addition, it may be concluded from the investigation of Curtis[17] on the oxidizing power of dilute solutions of hydrogen peroxide in the dark and in ultraviolet light that atomic oxygen is liberated.

The reaction represented by Equation 3 will proceed smoothly, for the products of dissociation are continually removed, the atomic oxygen practically instantaneously according to Equation 4, the hydroxide ion by Equation 5, the necessary hydrogen ion being supplied by the ionization of the hydrogen peroxide.

In view of the preceding assumptions, hydrogen ions inhibit by repression of the ionic dissociation of the hydrogen peroxide, a diminution in peroxide-ion concentration in (1) having a corresponding effect on (3) as there would be fewer peroxide ions to be activated at any one time.

The addition of an alkali to a hydrogen peroxide solution results in the formation of some alkali hydrogen peroxide.[18] $H^+ + Na^+ + OH^- + OOH^- \rightleftharpoons Na^+ + OOH^- + H_2O$. The solution contains, therefore, an increased number of peroxide ions, fewer hydrogen ions, and, due to the alkali and to hydrolysis, a considerable concentration of hydroxide ions.

[14] Joyner, *Z. anorg. Chem.*, **77,** 103 (1912). Lewis and Randall, THIS JOURNAL, **36,** 1987 (1914).

[15] Tanatar, *Z. anorg. Chem.*, **28,** 255 (1901). Jones, Barnes and Hyde, *Am. Chem. J.*, **27,** 22 (1902). Jones and Carroll, *ibid.*, **28,** 284 (1902). Willstätter, *Ber.*, **36,** 1828 (1903).

[16] Rideal, "Ozone," Van Nostrand Co., New York, **1920,** p. 11.

[17] Curtis, THIS JOURNAL, **42,** 720 (1920).

[18] Calvert, *Z. physik. Chem.*, **38,** 513 (1901). De Forcrand, *Compt. rend.*, **130,** 1555 (1900).

The assumption that the peroxide ion alone absorbs the activating energy is in accord with the observation of Henri and Wurmser[4] that the addition of a very small quantity of alkali to a peroxide solution increased its absorption. The increase in concentration of activatable peroxide ions is more than overbalanced by that of the hydroxide ions. As a result, the dissociation of the activated peroxide ions (3) is repressed, the absorbed energy probably being radiated at some other wave length, such as in the infra-red.

A few words may be written about the acceleration of the thermal decomposition of hydrogen peroxide. Sodium hydroxide is an excellent inhibitor for the photochemical decomposition, and a correspondingly excellent accelerator for the thermal decomposition. The photochemical inhibition and the thermal acceleration carried on simultaneously have been found experimentally to be independent of each other. It has been shown that the photochemical inhibition is a function of the hydroxide-ion concentration. The thermal acceleration, on the contrary appears to be independent of the hydroxide-ion concentration. Thus, a saturated solution of calcium hydroxide, yielding a high hydroxide-ion concentration, is an excellent inhibitor for the photochemical decomposition,[5] but has no influence upon the thermal decomposition.[19] Since the thermal acceleration cannot be due to sodium or hydroxide ions, it seems most probable that the medium of decomposition is a thermally unstable peroxide salt.

## Summary

1. The inhibition of the photochemical decomposition of hydrogen peroxide solutions by common inorganic acids, bases and salts has been studied. Bases were found to be excellent inhibitors, acids good, and neutral chlorides and bromides fair. No other inorganic compounds tried were found to inhibit.
2. The inhibition was shown by neutral salt action to be a function of the concentration of hydrogen, hydroxide, chloride and bromide ions.
3. The facts with which any theory of mechanism must accord have been outlined.
4. A qualitative approximation to a theory of mechanism, based on the ionization of the hydrogen peroxide, has been described.

We desire to place on record our indebtedness to E. I. du Pont de Nemours and Company, for a Du Pont Fellowship which enabled one of us (W. T. A.) to pursue this study.

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[19] Walton and Judd, *Z. physik. Chem.*, **83,** 315 (1913).