[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL COOPERATION, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Mechanism of Decomposition of Hydrogen Peroxide Solutions with Manganese Dioxide. I

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Introduction

Quantitative data on the catalytic decomposition of hydrogen peroxide with manganese dioxide[1] are meager. Altschuler, Konovalova and Petin[2] have carried out an extensive kinetic study, and have correlated their results by use of the Langmuir equations, assuming that decomposition took place by simple surface catalysis. Miscellaneous unsubstantiated statements can be found in the literature[3,4] suggesting that catalysis takes place by successive oxidation and reduction of manganese.

The object of the work described in this paper was to clarify the mechanism by which manganese dioxide catalyzes the decomposition of aqueous hydrogen peroxide.

The peroxide used throughout this work was obtained by vacuum distillation of a commercial 48% solution of hydrogen peroxide.

Conditions Necessary for Catalysis

Qualitative Behavior.—When dilute potassium permanganate was added slowly to hydrogen peroxide, the first portions were decolorized completely and no catalytic decomposition occurred. On continued addition, a brownish colloid appeared and catalytic decomposition became evident. Filtration of the partly decomposed solution through a 1-micron porcelain filter yielded a brown deposit on the filter, and a clear filtrate in which the undecomposed peroxide was stable.

Similar behavior was observed when manganous salts and alkali were added to peroxide. Apparently unlimited quantities of manganous sulfate could be added without inducing catalysis. However, when base was added also, the colloid appeared and decomposition started.

Quantitative Relations.—To establish a criterion for the point at which the colloid formed and catalysis started, a series of measurements of the relative quantities of manganese sulfate–potassium hydroxide, and potassium permanganate–potassium hydroxide required to initiate catalysis in peroxide solutions of various concentrations was made. The points of incipient catalysis were determined visually, with a reproducibility of 10–15%, by observation of the appearance of the colloid and onset of catalysis. Attempts to increase precision by conductometric, Redox electrode and glass electrode measurements were unsuccessful.

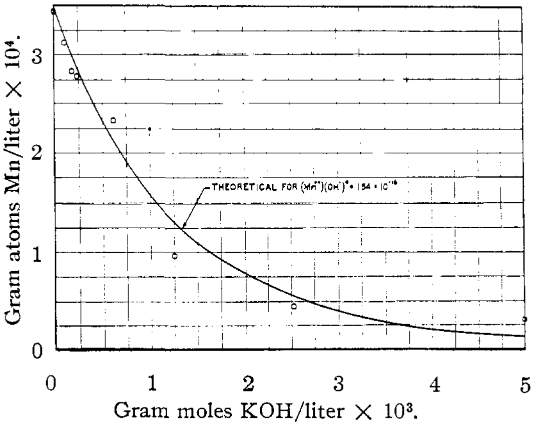

Fig. 1.—Concentration of manganese required for catalysis, in the addition of $KMnO_4$ and KOH to 18% H_2O_2.

In Fig. 1, the results of tests in which potassium permanganate and potassium hydroxide were added to hydrogen peroxide of 18 ± 1 weight per cent. are presented. The results of tests in which manganous sulfate and potassium hydroxide were added to solutions of various peroxide concentrations are given in Table I.

TABLE I

H_2O_2–$MnSO_4$–KOH CATALYSIS POINTS

Wt. % H_2O_2	Mg. atoms K/l.	Mg. atoms Mn/l.
24.4	0.657	4.66
32.3	1.11	2.45
33.5	2.02	1.32
17.5	6.54	0.033
6.12	0.22	6.65
17.3	3.23	0.157
17.0	2.11	.318
14.9	1.10	1.59
6.35	0.286	6.52
6.09	.374	6.65
29.7	2.33	1.68
33.6	1.34	5.02
57.0	1.86	2.66
59.3	0.664	11.5

A similar series of measurements was made to determine the effect of sodium pyrophosphate, which forms insoluble manganous salts, on the

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[1] The composition of the oxide formed in neutral or slightly basic hydrogen peroxide solutions is indefinite. Various compositions are reported in the literature, an average figure being $MnO_{1.88}$. For convenience in writing equations, the catalytic oxide is written as manganese dioxide, although it is actually a hydrated oxide, in which the manganese has a valence between 3 and 4.

[2] Altschuler, Konovalova and Petin, *J. Phys. Chem., U. S. S. R.*, 907–915 (1939).

[3] D. Kausch, "Das Wasserstoff Superoxyd," W. Knapp, Halle, Germany, 1938.

[4] W. Machu, "Wasserstoff Peroxyd und Die Perverbindungen," J. Springer, Vienna, 1937.

quantity of potassium permanganate required for catalysis in hydrogen peroxide of 34 ± 1 weight per cent. The results are presented in Fig. 3. In these experiments, a white inactive curd of manganous pyrophosphate appeared when the first portions of permanganate were added to the solution of pyrophosphate in peroxide. On continued addition, the colloid appeared and catalysis started. Addition of more pyrophosphate to this solution would result in disappearance of the brown colloid and cessation of catalysis.

In all these experiments, the formation of the active colloid was reversible; *i.e.*, addition of a trace of free acid, or of more peroxide of the same concentration, to a solution containing a trace of colloid would cause disappearance of the colloid and cessation of catalysis.

Interpretation of Results.—The initial reaction of permanganate with peroxide is undoubtedly complete reduction to manganous ion, with the necessary acid being provided in these experiments by the natural acidity of hydrogen peroxide.

A number of hypotheses as to the phenomena occurring at the point of formation of the manganese dioxide colloid are possible. These will first be stated, and then discussed in relation to the data. The equilibrium constants quoted were calculated from standard free energy data.

Hypothesis 1.—Reduction of permanganate takes place in two steps

$$2MnO_4^- + 3H_2O_2 + 2H^+ \longrightarrow 2MnO_2 + 4H_2O + 3O_2 \quad (1)$$
$$K_1 = 10^{100}$$
$$MnO_2 + H_2O_2 + 2H^+ \longrightarrow Mn^{++} + 2H_2O + O_2 \quad (2)$$
$$K_2 = 4 \times 10^{20}$$

Reaction (1) continues, but reaction (2) reaches equilibrium. Consequently, manganese dioxide persists when more permanganate is added, or, in cases where manganous sulfate and base were added, manganous ion is oxidized to manganese dioxide by reversal of (2).

Hypothesis 2.—Reactions (1) and (2) both continue, but at certain relative concentrations, the following reaction becomes thermodynamically possible, and manganese dioxide is regenerated.

$$Mn^{++} + H_2O_2 \longrightarrow MnO_2 + 2H^+ \quad (3)$$
$$K_3 = 1.3 \times 10^{16}$$

Hypothesis 3.—Divalent manganese is oxidized only when present as manganous hydroxide.

Hypothesis 4.—No definite thermodynamic equilibrium is reached, but the relative rates of reactions consuming and producing manganese dioxide, such as (2) and (3), become such that the solid becomes a kinetically stable form. This is unlikely, because the net result of such reactions would be the decomposition of peroxide, whereas no increase in decomposition rate is observed when manganous sulfate is added to neutral peroxide solutions.

It is evident that any of hypotheses 1–3 requires constancy of the ionic product $(Mn^{++})\cdot(OH^-)^2$ at the point of catalysis, in peroxide of a given concentration. Its numerical value, however, is different for each hypothesis.

As a preliminary test of the data, a line has been drawn on Fig. 1, showing the relation between the quantities of potassium hydroxide and permanganate to be expected, if the ionic product $(Mn^{++})(OH^-)^2$ were constant at the point of incipient catalysis. The value 1.54×10^{-16} was chosen arbitrarily as that fitting the data best.

The theoretical relative quantities of base and permanganate were calculated by solving the following system of equations for (Mn^{++}) at various assumed values of (K^+)

$$(H^+)(OH^-) = K_w(H_2O) \quad (a)$$
$$(H^+)(HO_2^-) = K_p(H_2O_2) \quad (b)$$
$$2(Mn^{++}) + (H^+) + (K^+) = (OH^-) + (HO_2^-) \quad (c)$$
$$(Mn^{++})(OH^-)^2 = 1.54 \times 10^{-16} = K_m \quad (d)$$

In the entire absence of data, all ion activity coefficients were arbitrarily taken as unity. The activities of water and peroxide were assumed proportional to their partial pressures. These were calculated from the vapor-liquid equilibrium and total pressure data of peroxide solutions at 30° of Giguère and Maass.[5] The theoretical curve fits the data reasonably well. The value of the ionic product is considerably different from the literature values of $0.7 - 2.7 \times 10^{-14}$ given for the solubility product of manganous hydroxide in water.

From the data of Table I, the ionic products have been calculated, and are plotted against peroxide concentration in Fig. 2. The calculation was made by solving equations (a), (b) and (c) for (OH^-). The best line through these points extrapolates to an ionic product, at zero per cent. peroxide, within the range of literature values for the solubility product of manganous hydroxide. The theoretical values of the ionic product corresponding to the other hypotheses are far different, as shown in Fig. 2. The fall in the product with increasing peroxide concentration is probably due to ion activity abnormalities.

It was concluded from these data that the point at which colloidal manganese dioxide would form and catalytic decomposition would proceed in peroxide solutions probably coincided with the point at which the solution became saturated with manganous hydroxide.

The effect of sodium pyrophosphate on the quantity of permanganate required to initiate catalysis is shown in Fig. 3. The presence of the pyrophosphate results in reduction of permanganate by peroxide to insoluble, inactive manganous phosphates. The deviation of the slope of the line from the theoretical value of 2.00, corresponding to formation of $Mn_2P_2O_7$, may be due to partial hydrolysis of the pyrophosphate, and formation of compounds such as $Mn(H_2PO_4)_2$.

The foregoing facts are all consistent with the view that the catalytic action of manganese dioxide is the result of a cycle involving its reduction to manganous hydroxide and subsequent reoxida-

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(5) P. A. Giguère and D. Maass, *Can. J. Res.*, **18B**, 181 (1940).

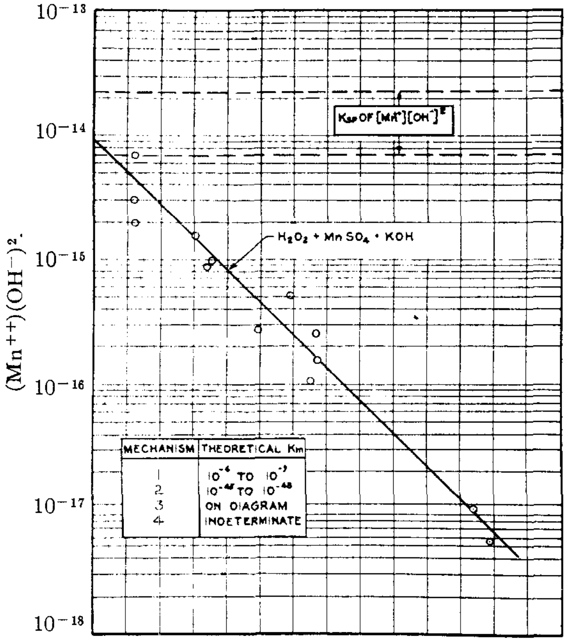

Fig. 2.—Comparison of experimental and theoretical values of ionic product $(Mn^{++})(OH^-)^2$ at point of catalysis.

tion, hydrogen peroxide acting alternately as an oxidizing and reducing agent. Any factor which prevents formation of manganous hydroxide (dilution, addition of acid, or addition of a salt to form a manganous compound more insoluble than the hydroxide) prevents the reoxidation step from taking place. Consequently, any manganese dioxide present in such a system will be reduced until the solution is again saturated with manganous hydroxide.

Radioactive Tracer Studies

If catalysis proceeds by oxidation and reduction of manganese, it would be expected that, in a peroxide solution initially containing radioactive manganese dioxide and normal manganous ion, the radioactive manganese would be distributed throughout the colloidal and soluble phases in a constant ratio to normal manganese. Since the concentration of soluble manganese decreases as peroxide decomposes, no radioactive manganese would enter the soluble state in the absence of such a mechanism.

Polissar[6] has studied exchange reactions of a number of manganese compounds and has reported no exchange between manganese dioxide and manganous ion in neutral or slightly basic aqueous solutions.

A radioactive manganese isotope, having a half life of 6.8 days, was furnished as manganous nitrate solution by the M.I.T. Radioactivity Center. This material disintegrates according to the equation

$$Mn^{52} \longrightarrow Cr^{52} + e^+$$

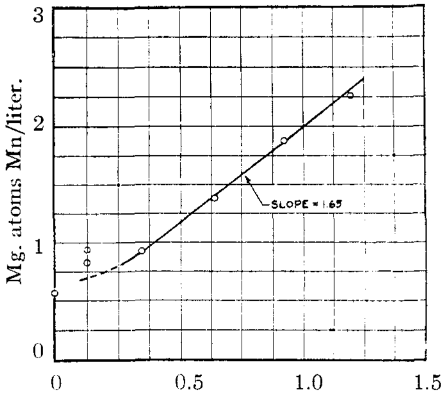

Fig. 3.—Effect of $Na_4P_2O_7$ on quantity of $KMnO_4$ to initiate catalysis in 33–35% H_2O_2.

The sample was adjusted to a manganese molality of 0.0064 and a *p*H of 2.75. The only appreciable impurity was sodium nitrate. All the samples on which activity determinations were to be made were brought into solution with acid peroxide, adjusted to a standard volume, and the activity measured with a Geiger counter. As a standard, a portion of the original manganous nitrate solution was diluted to the same volume and same approximate activity and measured similarly.

A sample of radioactive manganese dioxide colloid was prepared by adding 7.00 cc. of the standard 0.00664 manganous nitrate solution to a solution of 30 cc. of 17% H_2O_2 and 10.5 cc. of 0.01 *N* sodium hydroxide, and allowing the peroxide to decompose completely. A test of a solution prepared in this manner failed to reveal any trace of manganese in the filtrate from a 1-micron porcelain filter.

A second solution was then prepared by mixing 75 cc. of 32% peroxide, 25 cc. of non-radioactive 0.00664 *M* manganous nitrate solution and 20 cc. of 0.01 *N* sodium hydroxide. A small quantity of manganese dioxide formed in this solution and catalytic decomposition started. The solution containing the radioactive manganese dioxide colloid, described above, was then added. The mixture was cooled in an ice-bath to prevent excessively rapid decomposition and allowed to stand until the hydrogen peroxide had decomposed completely. After forty-eight hours, the colloid was filtered on a 1-micron porcelain filter, the filtrate was made up to 250 cc., and its activity measured. The residue was dissolved in acid peroxide, made up to 100 cc., and measured similarly.

The distribution of radioactive manganese in two duplicate tests made in this manner is reported in Table II, as Tests A-1 and A-2.

To determine the distribution of total manga-

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(6) M. J. Polissar, THIS JOURNAL, **58**, 1372 (1936).

nese between colloid and solution, Tests B-1 and B-2 were made. These were identical in all respects with A-1 and A-2, except that radioactive manganese was used throughout. The results are reported in Table II.

Table II

	A-1	A-2	B-1	B-2
Rad. Mn in colloid	0.0235	0.0244	0.122	0.126
Rad. Mn in filtrate	.0174	.0167	.097	.097
Total Rad. Mn (anal.)	.0409	.0411	.219	.223
Total Rad. Mn added	.0465	.0465	.212	.212
Total Mn added	.212	.212	.212	.212

The material balances on radioactive manganese close well for the B series, but less satisfactorily (15% difference) for the A series. It is thought that this might be due to nonlinearity of the counter. In spite of this, however, the results are unambiguous.

Since the A runs are chemically identical with the B runs, it can be assumed that the distribution of total manganese between colloid and filtrate is the same in both. Averaging the results, the ratio of radioactive to total manganese is 0.194 in the colloid and 0.176 in the filtrate. The radioactive manganese, originally present only as colloid, has become almost homogeneously distributed with the total manganese. The figures indicate that the colloid still holds a little excess radioactive manganese, but the accuracy does not warrant a definite statement.

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Summary

A study has been made of the catalytic decomposition of hydrogen peroxide with oxides of manganese, formed *in situ* from permanganate or manganous salts and alkali. The use of radioactive tracers indicates that catalysis takes place by alternate reduction and oxidation of manganese. Determination of the conditions under which catalysis occurs shows that the oxidation step of the cycle does not take place unless the solution is saturated with manganous hydroxide. A probable mechanism is

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\begin{array}{c}
MnO_2 + H_2O_2 + 2H^+ \longrightarrow Mn^{++} + 2H_2O + O_2 \\
Mn^{++} + 2H_2O_2 \rightleftarrows Mn(OH)_2 + 2H^+ \\
Mn(OH)_2 + H_2O_2 \longrightarrow MnO_2 + 2H_2O \\
\hline
2H_2O_2 \longrightarrow 2H_2O + O_2
\end{array}
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[Contribution from the Division of Industrial Cooperation, Massachusetts Institute of Technology]

Mechanism of Decomposition of Hydrogen Peroxide Solutions with Manganese Dioxide. II

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Introduction

The results presented in the first article of this series indicated that catalysis of hydrogen peroxide decomposition took place by successive oxidation and reduction of manganese and that no catalysis occurred until the solution was saturated with manganous hydroxide.

Because macroscopic manganese dioxide surfaces cause decomposition even when the bulk of the peroxide solution contains no manganese, and because accumulation of manganous ions in such a solution is quite slow, it appeared advisable to investigate further the decomposition at such surfaces to determine whether the same type of mechanism was operating.

This work was carried out to obtain information on conditions existing at manganese dioxide–hydrogen peroxide interfaces—in particular, to determine whether the solution was saturated with manganous hydroxide.

Electrode Potential Measurements

Experimental.—A stick of porous electrolytic manganese (99.9%) was coated with manganese dioxide by allowing it to stand in 30 weight per cent. hydrogen peroxide for twenty-four hours. Its electrode potential in peroxide solutions was then measured against a saturated calomel electrode, using a conventional circuit. In each test, readings were taken for thirty to sixty minutes, in which time the potentials approached constant values. Errors caused by decomposition of peroxide during the test were small, as renewal of the solution induced only slight additional change in potential. The concentrations of peroxide, of manganous ion and of hydrogen ion were varied systematically, by adjustment with manganous nitrate, nitric acid, and sodium hydroxide.

For comparison, similar measurements were made on electrodes of bright platinum.

Results and Discussion.—The potentials of the platinum and manganese dioxide electrodes are plotted in Figs. 1–3 *vs.* concentrations of hydrogen ion, peroxide and manganous ion.

It was hoped that the relative degrees of polarization of the several electronic reactions probably occurring at the electrode surface would be such that the measured potentials would correspond to one particular reaction, and thus furnish information on conditions existing at the electrode surface.

The following electronic reactions were considered as possibly controlling the potential