[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 144]

PROMOTER ACTION IN HOMOGENEOUS CATALYSIS. IV. DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM DICHROMATE ACCELERATED BY MANGANESE SALTS

BY ALFRED C. ROBERTSON[1]

RECEIVED MARCH 14, 1927 PUBLISHED JULY 5, 1927

Previous studies have shown that the promotion effect noticed when two catalysts act simultaneously can be explained simply upon the basis of a change in the path of the related reactions which together produce the resultant catalytic effect, and that it is not necessary to introduce the conception of activation discussed by Pease and Taylor.[2] This change in the path was first demonstrated when it was shown that the copper which promoted the catalytic decomposition of hydrogen peroxide by ferric salts[3] appeared as a new molecular species, namely, cupric acid. In a later study it was possible to show that the intermediate due to the catalyst decreased in concentration during promotion.[4] This was in the system where the decomposition of hydrogen peroxide by potassium dichromate was accelerated by the presence of cobalt salts. While in this case it was not possible to identify the intermediate due to the promoter, nor to follow the formation of this substance and to show the dependence of its formation upon the disappearance of some of the intermediate due to the catalyst, nevertheless it was shown that the shape of the promotion curve followed closely an equation which had been derived governing this effect. This agreement with theory showed that catalysis obeys the law of mass action as well as do other reactions.[4]

Other promoters have been found for this reaction, so the studies were extended further to test the hypothesis. The system chosen was the one where manganous chloride acts as a promoter for potassium dichromate in decomposing hydrogen peroxide. Although the experimental results are not altogether free from complications, the interpretation of the data forms an interesting addition to and confirmation of the earlier work.

Experimental Methods

The method of experimentation[5] is practically the same as that used in previous studies.

A special reaction flask containing the solution of hydrogen peroxide is held in the thermostat by means of a suitable clamping device. This flask is connected by small-bore glass tubing to a gas buret maintained at the same temperature as the thermostat.

---

[1] National Research Fellow in Chemistry.

[2] Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

[3] Robertson, THIS JOURNAL, **47**, 1305 (1925).

[4] Robertson, *ibid.*, **48**, 2072 (1926).

[5] Walton, *Z. physik. Chem.*, **47**, 188 (1904).

When thermal equilibrium is attained, a capsule containing the catalyst is dropped into the flask which is then shaken vigorously, and readings of the amount of gas evolved are made at convenient intervals. The method has proved rapid and accurate. The thermostat, which has been improved by the addition of an oscillating contact on the thermoregulator, gives a temperature regulation never varying over 0.01°, and with an average deviation of ±0.003° for an hour in spite of the large radiating surface of the water jacketed gas burets.

Promotion by Manganese Chloride at Low Concentrations.—The manganous chloride used in this study was carefully purified from the best available material. A solution of the salt was first treated with a quantity of freshly precipitated, well-washed manganous carbonate to remove iron present in large amounts. The solution was then filtered, saturated with hydrogen chloride and allowed to crystallize. This recrystallization was repeated. The salt was then crystallized from water, sucked dry upon a Büchner funnel and dried in a desiccator for several hours. This process yielded a moisture-free product which gave a clear solution neutral to litmus. The catalyst solutions were made by appropriate dilutions of a standard solution made from this material.

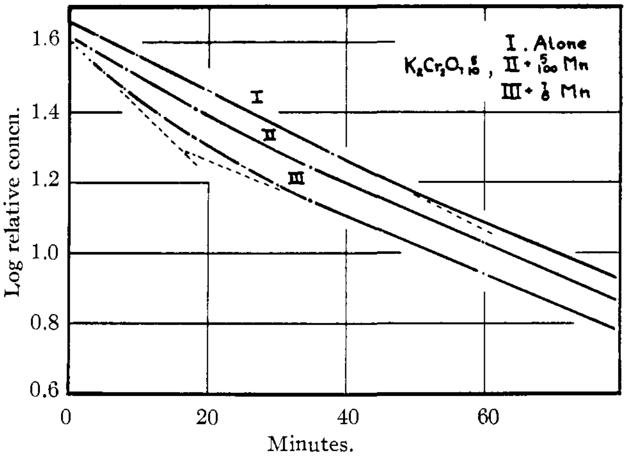

Fig. 1.—Concn.-time curves of typical examples.

The manganous chloride is rather a poor catalyst when used alone, giving a reaction constant of the order of 5 for a concentration of 0.04 *M*. Its effect when used alone is autocatalytic, but when the salt is used as a promoter the reaction as a whole is not. Instead of being strictly of the first order, as with cobalt for a promoter, the reaction constants decrease with time in the manner shown in Fig. 1, where the logarithms of the concentration ratios are plotted as ordinates against the time in minutes as abscissas. The velocity constant for the reaction remains unchanged at first, as shown by the slope of the curve, but later decreases. The curve appears to merge into another approximately straight line.

More concordant results were obtained upon repetition of the experiments when the catalyst was added to the solution rather than the reverse. It was necessary to adopt this method although it involved a more exacting technique and made the preparation of the catalyst solutions somewhat less accurate.

This curve was studied critically by plotting the results on a large scale. It appeared that the curve was made up of two superimposed exponential functions, which will be discussed later. This fact indicates the simultaneous presence of two first-order reactions in the catalytic process.

Catalytic Nature of the Reaction

The fact that the relationships were complicated and that several effects were present at the same time led to the suspicion that the reaction might not be truly catalytic in its outcome. This is disproved by the fact that when a mixture 0.0, 0.0005, 0.089 and 0.445 *M* in manganous chloride as promoter ran to completion (nine hours) the volumes of gas evolved were 45.10, 45.55, 45.55 and 45.65 cc., respectively. These differences are less than the usual, except for the first case where the reaction possibly had not enough time to complete its course. Since the calculated amount of oxygen necessary to oxidize one millimole per liter of bivalent metal to the quadrivalent state for a sample of 25 cc. is 0.0311 cc. of gas, it is seen that the reaction oxidizes very little manganese if any, although manganese salts are notoriously easily oxidized if the solutions are not neutral, even air effecting this change. Neither is an appreciable amount of the dichromate reduced, as shown by the color of the solution. From these facts it may be concluded that when the manganese and dichromate act together the reaction is still purely catalytic in character, these substances being left unchanged in amount and kind at the end of the reaction.

Preliminary experiments have shown that the reaction with manganese alone was somewhat autocatalytic in character. It was suspected that this effect might be due to the alkali ground off the flasks by the beads,

TABLE I

EFFECT OF CONDITIONS UPON THE CATALYSIS BY MANGANESE CHLORIDE

Concn. of $MnCl_2$, *M*	Time	x	K_R	x	K_R	x	K_R	x	K_R
0.025	0	0.00	..	0.00	..	0.00	..	0.00	..
Bakelite	7	.06	0.35	.06	0.57	1.0	0.46	.02	0.86
beads	32	.27	.31	.20	.50	.15	.75	.12	1.15
	184	1.76	.37	1.13	.48	.91	.77	.62	1.05
	∞	111.6	..	55.8	..	27.9	..	14.0	..

	Time	x	K_R	Time	x	K_R
0.040	0	0.00	..	0	0.00	..
	7	.55	4.2	6	.37	3.3
Glass beads	13	1.15	4.5	13	1.25	5.1
	23	2.50	5.7	18	1.97	5.8
	195	28.10	8.9	106	17.25	9.6
	∞	85.5	..	∞	83.7	..

and measures were taken to surmount this difficulty. This was accomplished by using new, unscarred Pyrex flasks and by substituting bakelite beads and capsules for glass. These substitutes served their purpose well since this material is one of the most resistant toward chemicals. Although it was somewhat brittle, the bakelite secured for this purpose could be worked in the lathe after a few trials. The capsules were apparently unaffected by the reagents used and gave determinations which checked well with those determined in the usual way.

The data are recorded in Table I for runs made with the new equipment. It can be seen by reference to this table that the reaction between hydrogen peroxide and manganous chloride gives good first-order constants. They show but a slight trend with time and are quite small, all this in contrast to the case where the reaction is complicated by the presence of traces of alkali derived from the glass.[6]

Spitalsky also has shown that the reaction between hydrogen peroxide and potassium dichromate[7] is purely catalytic for low concentrations of this salt.

The catalytic nature of the two component reactions has now been established and it has been shown that when the reactions occur together the reaction is still catalytic. The promotion reaction may, therefore, be considered in the same manner as in previous studies and the conception of the steady state may be utilized as has been done before.

Interpretation of the Data

As stated previously, the shape of the curve shows the presence of two superimposed first-order reactions. This condition in cases of promotion was postulated previously,[8] but due to the nature of the reactions it has not been possible to resolve the effect into its component parts. The previous inability to divorce the effects which cause promotion is no doubt due to the fact that either the amount of the hydrogen peroxide involved in the reaction which causes the promotion was small, or the rate of this promoting reaction was only slightly faster than the reaction which it supplanted; or it may have been that both the amount of substrate involved and its rate of reaction were small. In any event the effect, as a whole, was so small that when it was superimposed upon the regular reaction it did not change the *nature* of the concentration-time curve to such an extent that it could be detected by analysis of the experimental data.

---

[6] This alkali does not cause any disturbance when manganese is used in the presence of dichromate, since a small amount of the catalyst is converted into the chromate and the reaction of the solution remains unchanged. The usual concentration of alkali produced was shown by experiments performed for another purpose to be in the order of 10^{-6} *M*. This is 0.2% of the concentration of the catalyst.

[7] Spitalsky, *Z. anorg. Chem.*, **53**, 187 (1907).

[8] Ref. 4, p. 2076.

The difficulties of resolving the promotion effect into its parts are much less formidable in the case where manganese is used as the promoter. Since the curve consists of two superimposed exponential functions, it is necessary to resolve the promotion effect into two parts. This may best be done by considering the chemical reactions involved. Therefore, the exponential expression is written in the logarithmic form commonly used by chemists, $Kt = \log f/f - x_1 + \log d/d - x_2$ and the rate expressed in the following manner

$$K = 0.4343\ K \times 10^4 = \frac{F}{t} \log \frac{f}{f - x_1} + \frac{D}{t} \log \frac{d}{d - x_2} \qquad (1)$$

where f is the amount of hydrogen peroxide taking part in the non-promoted reaction, d the amount of hydrogen peroxide involved in the promotion reaction and F and D are the rates of these respective reactions. Thus stated, F and D are not the same constants as those used in the previous paper. These values are related to the specific velocity constants, while those used before[8] represent the gross effect. Here the effects causing promotion have been resolved into their components. The values x_1 and x_2 are variables comparable to x. Their significance will be apparent by looking at the sample calculation in Table II.

A number of runs was made with the concentration of the potassium dichromate fixed at 0.0005 M and with the manganese varying in concentration between 0.000001 and 0.145 M. Upon inspection it appeared that the relationships were different for the concentrations of manganese above 0.001 or 0.002 M than for those below. The treatment for the present is confined to the region between 0 and 0.0025 M in manganese. The higher concentrations will be considered later.

Upon inspecting log concentration-time graphs, similar to those shown in Fig. 1, in which various amounts of manganese were used, it appeared that the last portion of the curve had the same slope in all cases, while only the first portion showed a variation due to the promotion effect. Since the last portions of the curves for systems exhibiting promotion have the same slope as the unpromoted curve, it indicates that the primary reaction upon which the promotion effect is superimposed is not changed in rate by the presence of the promoting reaction. In preliminary studies it had been thought that this rate might be changed, but if a variation does occur it lies within the limits of experimental error. Therefore, it was assumed that the effect due to the second reaction could be obtained by subtracting the effect due to an unpromoted reaction from the observed values. Upon proceeding to calculate the results to determine the nature of this superimposed reaction a difficulty becomes apparent, since the unpromoted reaction, when followed over a long period of its life, begins to decrease in velocity although the reaction is pseudo-unimolecular and should, therefore, give good velocity constants. An examination of Spitalsky's data shows the presence of a similar effect.[7] This cannot be accounted for by assuming that there is a diminution of the concentration of the catalyst due to the reduction of chromium, since this effect has been shown to be absent by means of chemical analysis. Again, a direct test shows that the effect cannot be due to the solubility of the glass ground off by the beads.

In order to make the calculations of the superimposed reaction more easily interpreted, the velocity constant for the early part of the reaction was arbitrarily set at 100 (later it dropped to 90). It happens that the "break" for all the log concentration-time curves comes in the region where the reaction rate for the non-promoted reaction is still 100, so this assignment of values is quite justified. Therefore, when a line representing a reaction rate of 100 is drawn tangent to the curve passing through the points representing the experimental values and is extrapolated back to zero time or the beginning of the reaction, the intersection of this line with the zero ordinate represents the concentration of the hydrogen peroxide, f, involved in the non-promoted reaction at the beginning. The valid assumption must be made that the velocity constant F is the same for this slightly lower concentration of hydrogen peroxide. The difference between this calculated concentration and the original concentration of hydrogen peroxide represents the amount of hydrogen peroxide going through the reactions which cause the promotion. Fig. 2 represents the operation schematically. This difference is obtained by reading off the logarithms of the extrapolated line; these values are called log $(f - x_1)$ and are recorded in the sample calculation in Col. 3. The numbers $(f - x_1)$ are now entered in Col. 5 and subtracted from the values $(a - x)$, which are the actual concentrations. This difference is called $(d - x_2)$, where d is the concentration of hydrogen peroxide which at the beginning of the reaction enters into the promotion reaction. In order to see how the promotion reaction proceeds, the logarithms of $(d - x_2)$ are plotted against time in the same manner as for any other first order

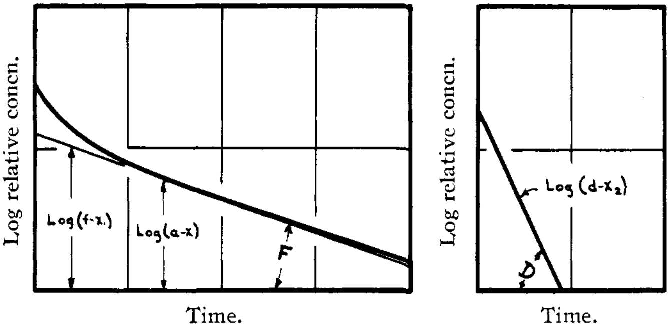

Fig. 2.

reaction. The points fall on a straight line, the slope of which gives the reaction rate of this reaction. This slope is the D of Equation 1.

A synthetic curve formed from the constants obtained approaches the original curve for this region to less than 0.1 cc., and seldom departs farther than 0.2 cc. Considering the uncertainties attending the exact determination of the end-point and the time of mixing, the values are very satisfactory indeed. In the sample calculations shown in Table II, the calculated and observed values of $(d - x_2)$ are recorded in the last columns.

At the beginning of the reaction several minutes must be allowed for the time of mixing and the attainment of the new steady state which, however, is more rapid in this case than when cobalt is used for the promoter. It is necessary to apply a small correction in order to determine the most probable value of d. This is done by a back extrapolation on the graph of the buret readings, which gives the actual time when the reaction began. The zero time is marked on the graph of log $(d - x_2)$ and the corrected value is then read off from the intersection of these lines.

TABLE II

SAMPLE CALCULATIONS

F, 100 by definition; f, 31.1 cc.; D, 570; d, 8.9 cc. or 21.9%

	x	$\log(f-x_1)$	$(a-x)$	$(f-x_1)$	$(d-x_2)$, obs.[a]	$(d-x_2)$, calcd.[a]
0	2.05	1.496	40.65	31.33	9.32	8.50
1	4.75	1.486	37.95	30.62	7.33	7.30
2	6.20	1.476	36.50	29.92	6.58	6.50
3	7.80	1.466	34.90	29.24	5.66	5.65
5	10.35	1.446	32.35	27.93	4.42	4.30
8	13.70	1.416	29.00	26.06	2.94	2.95
13	17.95	1.366	24.75	23.23	1.52	1.50
18	21.42	1.316	21.28	20.70	0.58	0.77
25	25.00	1.246	17.70	17.62	0.08	0.03
30	27.00	1.196	15.70	15.70	0.00	..
35	28.70	1.146	14.00	14.00	0.00	..
92	37.80	...	4.90	...	..	..
∞	42.70	...	...	...	..	..

[a] d corrected to zero time, 8.9.

In Fig. 3 the values of d are plotted against the concentration of promoter in millimoles per liter. The unit of measurement is the percentage fraction of the hydrogen peroxide present at the beginning of the reaction. The maximum in the curve may have some relation to the stoichiometric ratios involved in the promotion reaction, as seems probable from previous studies with copper as a promoter for iron. At very low concentrations this system showed a maximum in the curve where the "promotion factor" was plotted against the mole fraction of total heavy metal present. This maximum corresponded to a molar ratio which agreed well with the reaction[3]

$$2FeO_3 + 3CuO \longrightarrow Fe_2O_3 + 3CuO_2 \qquad (2)$$

which was followed by a very rapid reaction which produced the accelerating effect. This concept is based on the reasonable supposition that the maximum effect should be obtained in the promotion reaction when the reactants are present in ratios corresponding to their reacting masses.[9]

Further studies were not carried out to test this point since the entrance of disturbing effects due to the presence of a reaction which predominates at higher concentrations of manganese renders such experiments of dubious value. If the maximum be at 0.001 *M*, it indicates that the intermediate is manganese with a valence of three, since the system is one using potassium dichromate at a concentration of 0.0005 *M*. Equation 3 represents the reaction; the formula of the intermediate due to the promoter is written $HMnO_2$ here only to depict the trivalence of manganese.

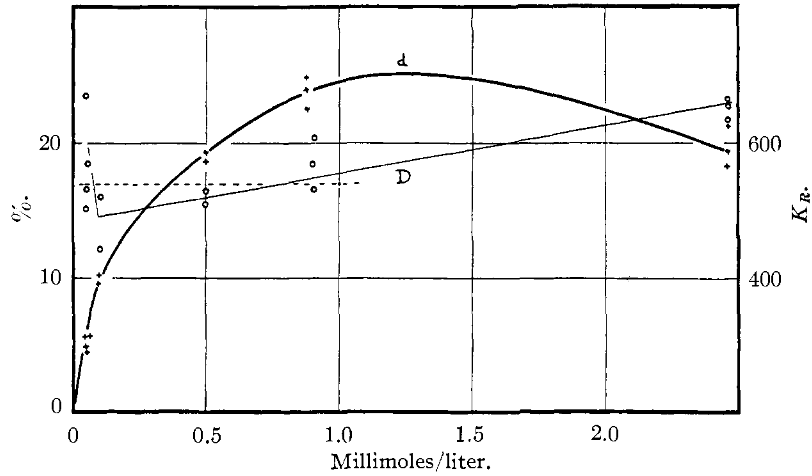

Fig. 3.—Relation between *d*, *D* and the concn. of promoter.

Spectrographic studies have been made with solutions of manganese salts of varying valence.[10] While these measurements are only of qualitative value they show that this method cannot be used to determine whether the valence is three or four.

The values of *D*, the reaction rate for the promotion reaction, are also plotted in Fig. 2. The scale of ordinates for this series is placed on the right of the graph. The points, excepting the first few corresponding to very low concentration of promoter, fall upon a straight line.

---

[9] A maximum was not found in the promotion curve when cobalt was used as the promoter. It seems probable that this effect can only be expected when the concentration of the second intermediate due to the promoter is substantially equal to the concentration of the first intermediate due to the catalyst. Otherwise the "cyclic" nature of the reactions obscure the relationship.

[10] Jaeschke and Meyer, *Z. physik. Chem.*, **83**, 281 (1913).

In those experiments, the duration of the superimposed reaction is so very short compared to the time for the others that the time of mixing becomes a large factor, and errors are to be expected. It was impossible for this reason to assign any values at all when 0.000001 *M* manganese was employed as the promoter. The variable time of mixing no doubt accounts for the variable values in this part of the curve. The slope of the line is so slight that it seems logical that it might be zero. In this case it would represent a rate which is related to the specific velocity constant of some rapid reaction such as

$$2HMnO_2 + 4HCl + H_2O_2 \longrightarrow 2MnCl_2 + 4H_2O + O_2 \qquad (3)$$

This is the reaction which gradually supplants the reaction

$$2KCrO_4 + H_2O_2 \longrightarrow K_2Cr_2O_7 + H_2O + O_2 \qquad (4)$$

normally taking place in the non-promoted reaction; the difference between these rates of reaction is apparent in the acceleration of the reaction as a whole. The reaction represented by Equation 3 can take place because of the "transition" reaction shown in Equation 5.

$$2KCrO_4 + 2MnCl_2 + 3H_2O \longrightarrow K_2Cr_2O_7 + 2HMnO_2 + 4HCl \qquad (5)$$

This transition reaction is more rapid than the others; for the sake of simplification its rate will be considered as instantaneous until a method is found by which it may be evaluated. This assumption is necessary in order that the equation of promotion (and negative catalysis, also) may be developed quantitatively, using the concept of the steady state as the basis for calculations.

The slight slope of the line passing through the values for *D* is due to traces of the reaction which predominates at the higher concentrations of manganese; the probable interference of the reaction has been noted before.

It was not deemed necessary to study the effect of the hydrogen-ion concentration further, since an investigation of the effect of cerous salts as promoters promises to cast much more light upon this relationship.

Effect of Higher Concentrations of Manganese

It was noticed early in the investigation that the larger amounts of manganese caused the reaction to follow a much more complicated course. Therefore, a number of experiments were devised to determine more about the nature of this complicating reaction. The results are not completely reproducible and do not lend themselves to exact treatment, but they are definite enough so that valid conclusions may be drawn from them.

The first step was to determine how the promotion reaction was influenced by changes in the concentration of the hydrogen peroxide. When a reaction mixture 0.0005 *M* in potassium dichromate was promoted with either 0.0025 or 0.02 *M* manganese, the value of *d* decreased one half or one fourth for a similar decrease in the concentration of hydrogen peroxide. However, doubling the concentration of hydrogen peroxide more than doubles the value of *d*. In both cases the value of the reaction constant *D* is substantially the same, although slightly larger with 0.02 *M* manganese.

Thus it is seen that the amount of the intermediate due to the promoter is proportional to the amount of hydrogen peroxide used. Although the reaction satisfies the equation for a first-order process, it is only pseudo-unimolecular, being actually a real second-order reaction. This fact was suspected earlier in the investigation, so care was taken that the experiments summarized in Fig. 3 were performed with hydrogen peroxide of exactly the same concentration. To accomplish this end the runs were made consecutively within a few days, during which time the sample of peroxide changed but little in concentration.

These experiments represent a steady-state condition, as shown by the fact that the results are the same with a concentration of 0.00001 *M* manganese whether the concentrated peroxide is dropped into the catalyst or whether a concentrated catalyst solution is dropped into the dilute peroxide. This condition does not exist when 0.0005 *M* manganese is used, indicating that the interfering reaction noted at higher concentrations of manganese is not a steady-state condition. Therefore all the experiments in Fig. 3 were performed with dil. hydrogen peroxide, so the effect of the interfering reaction would be minimized.

When the concentration of manganese is 0.09 *M* or more, the experimental results cannot be consistently presented as in the previous case. The reaction does not follow either a first- or second-order equation. Although the effects are very complicated and practically impossible to resolve, it seems probable that the high concentrations of intermediate due to the catalyst present before the steady state is attained, oxidize some of the manganese to a form which is reduced at a different rate from the intermediate normally formed by the manganese.

By determining the time required to decompose various fractions of the hydrogen peroxide present and taking the reciprocals of these values, it is possible to gain an insight into the course of the reactions. These values should be constant for a first-order reaction and should vary directly with a second-order reaction.

When the concentration of manganese is 0.0025 *M*, the reciprocals increase somewhat, as shown in Fig. 4. The solid lines represent 0.0025 *M* and the dotted lines 0.09 *M* manganese added to the dichromate. By this slope in the line, the presence of the complicating reaction detected before may again be noted when the concentration of manganese is 0.0025 *M*, but when 0.09 *M* is used this complicating effect, instead of being larger, disappears. The dotted lines have practically no slope and show that by the half-life criterion the reaction is unimolecular. The reaction doubtless is not so simple. Considerations based upon spectrographic studies indicate that this reaction involves the formation and decomposition of a permanganate, and it is not to be expected that this process is unimolecular.

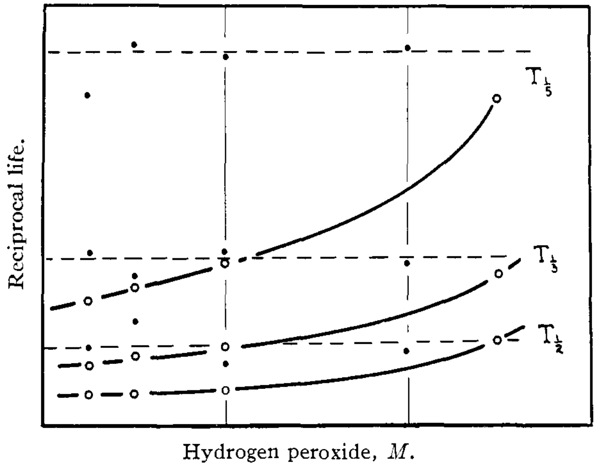

Fig. 4.

Spectrographic Studies

The study of the absorption spectra of solutions undergoing catalytic change has proved a powerful tool in this series of studies upon catalysis and promoter action. The first application was to show the presence of an intermediate compound formed from the catalyst and to show its chemical nature by comparison with a solution containing a substance of known composition. In another case the presence of the "promoter" in a new form was shown by this method. In a third study the "first intermediate" was shown to decrease in concentration when the catalytic change was promoted.

Optical methods are almost essential in studying intermediate compounds, which are by definition unstable, and in very few cases can be handled by the time-honored methods of the analytical chemist. Bray and Livingston[11] were able to isolate and measure quantitatively the intermediate in the reaction which they were studying, because of the low rate of the reactions involved.

The effect of manganous chloride upon the concentration of the intermediate due to the catalyst is very large indeed, as shown by Fig. 5. One millimole per liter reduces its concentration about 75% and 2.5 millimoles per liter practically removes all trace of the substance. The

[11] Bray and Livingston, THIS JOURNAL, **45**, 1256 (1923).

absorption now shows only the presence of potassium dichromate; there are no new absorption regions in the visible, hence the nature of the new compound of manganese cannot be determined by this method.[10]

When more manganese is used, for example, 0.02 *M*, the results vary with time; a steady-state condition does not prevail. In Fig. 6 the results are shown graphically. A maximum has appeared in the curve in a region which gave complete transmission when 0.0025 *M* manganese was present. This maximum corresponds almost exactly to the peak of the absorption curve for a solution of potassium permanganate. If this be true, the concentration of permanganate is about 0.000005 *M*. These results are calculated from the molar extinction coefficient for potassium permanganate obtained by other workers.[12] Their value agrees well with one obtained by the use of diluted volumetric solutions of known oxidimetric value. This concentration of manganese as permanganate is 2.5×10^{-4} of that added as the promoter. It appears that the formation of permanganate is the cause of the complicated behavior found in some of the reactions.

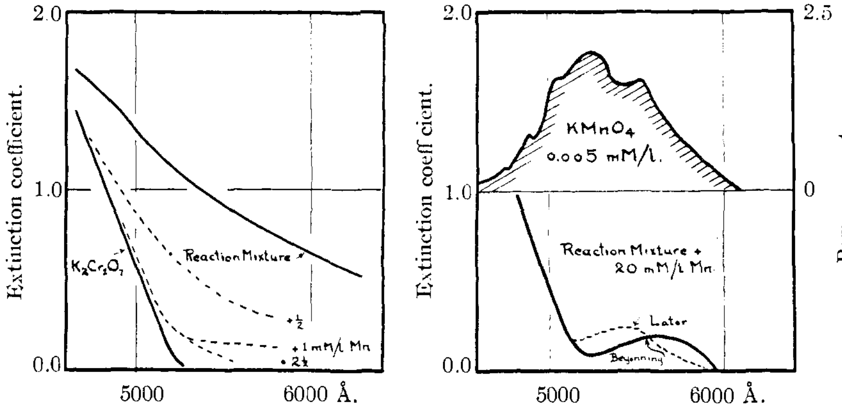

Fig. 5. Fig. 6.

Effect of promoter upon absorption spectra.

This vanishingly small concentration of intermediate, a concentration which probably could only be detected by spectrographic means, indicates the necessity of investigating very closely the course of reactions before postulating the mechanism.

This research is based upon preliminary observations noted in studies carried on at the University of Wisconsin with Professor J. H. Walton. The final work was conducted at the California Institute of Technology and was aided by a grant made to Professor A. A. Noyes by the Carnegie Institution.

---

[12] Hagenbach and Percy, *Helv. Chim. Acta*, **5**, 461 (1922).

Summary

1. The catalytic decomposition of hydrogen peroxide by potassium dichromate is promoted by manganese salts. The reaction does not follow a simple unimolecular course.

2. The nature of the separate reactions has been investigated and discussed. Anomalous effects due to the solubility of the glass capsules and beads were avoided by the use of bakelite.

3. The promotion effect has been shown to consist of two superimposed reactions. The results agree with the explanation previously advanced for the relations between promoter and catalyst, and by resolving the promotion effect into two parts, one related to the concentration of intermediate due to the promoter, and the other, a rate related to the specific velocity constant of the promotion reaction, the interpretation offers a striking confirmation of the earlier work.

4. The addition of promoter causes the diminution of the concentration of the first intermediate. In the simpler reaction the nature of the intermediate due to the catalyst is not known definitely. When the concentration of manganese is higher, the relation is much more complex. The intermediate in this case is probably a permanganate, as shown by spectroscopic studies.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE ATOMIC WEIGHT OF SCANDIUM[1]

BY NICOL HAMILTON SMITH

RECEIVED MARCH 15, 1927 PUBLISHED JULY 5, 1927

Introduction

Until 1919 there had been considerable doubt as to the true value for the atomic weight of scandium. The atomic weight adopted by the International Committee on Atomic Weights was 44.1, which was considered to be a representative value based upon determinations made by previous investigators. These investigators had employed the usual sulfate method and had obtained values ranging from 43.90 to 45.23 as follows. Cleve, 44.96;[2] Nilson, 44.13;[3] Meyer and Winter, 44.94;[4] Meyer and Goldenberg, 44.09;[5] Meyer and Schweig, 45.23.[6]

---

[1] From a thesis done in coöperation with Hiram S. Lukens, and submitted by Nicol H. Smith, in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania.

[2] Cleve, *Compt. rend.*, **89**, 419 (1879).

[3] Nilson, *ibid.*, **91**, 56, 118 (1880).

[4] Meyer and Winter, *Z. anorg. Chem.*, **67**, 398 (1910).

[5] Meyer and Goldenberg, *ibid.*, **102**, 12 (1912).

[6] Meyer and Schweig, *ibid.*, **108**, 303 (1919).