The Journal of the
American Chemical Society
with which has been incorporated
The American Chemical Journal
(Founded by Ira Remsen)

VOL. 47 AUGUST, 1925 No. 8

[Contribution from the Chemical Laboratory of the University of California]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN AN ACID CHLORINE-CHLORIDE SOLUTION

By Robert S. Livingston and William C. Bray

Received February 16, 1925 Published August 5, 1925

That an acid chlorine-chloride solution might be expected to accelerate the decomposition of hydrogen peroxide follows from a consideration of the free energies of the substances involved. A general discussion of the choice of catalysts by means of free-energy data has been presented by Bray and Livingston,[1] and the subject is mentioned by Lewis and Randall.[2] This expected acceleration would be the result of the simultaneous occurrence of the two following reactions:

$$2H^+ + 2Cl^- + H_2O_2 = Cl_2 + 2H_2O;\ \Delta F^\circ = -48{,}470 \qquad (1)$$
$$Cl_2 + H_2O_2 = O_2 + 2Cl^- + 2H^+;\ \Delta F^\circ = -32{,}920 \qquad (2)$$

While the fact that the ΔF° terms[3] for both reactions have large negative values indicates that it is possible for the chlorine-chloride pair to accelerate the reaction, it is not sufficient to prove that they will constitute an effective catalyst. The reports of several early experiments[4] suggest that both reactions (1 and 2) are comparatively rapid, and that a dissolved chloride measurably catalyzes the decomposition of hydrogen peroxide.

We undertook an investigation of the kinetics of this catalyzed reaction, with the expectation that the results would be similar to those of the bromine-bromide catalysis.[1] It must be noted, however, that the "law of

---

[1] Bray and Livingston, This Journal, **45**, 1253 (1923).

[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 601.

[3] Computed from values tabulated in Lewis and Randall's "Thermodynamics," p. 607.

[4] Ref. 1, footnote 1.

catalysis" for the bromine-bromide catalysis differs from that of the otherwise closely analogous iodine-iodide case.[5] Shortly after this work was started, Maass and Hiebert[6] published a paper discussing this reaction in some detail. Partly because the results they obtained in dilute solutions were not in accord with our own, and partly because some of their conclusions seemed to be in conflict with evidence already presented for the bromine-bromide case,[7] we felt that it was important to continue our investigation and to repeat part of their work.

Methods of Analysis

The methods of analysis were similar to those used in the study of the bromine-bromide catalysis.[1] Chloride was determined gravimetrically as silver chloride. The acid concentration was determined by titrating, methyl red being used as the indicator, with a standard solution of sodium hydroxide, for which fused sodium carbonate was the reference substance. Chlorine was determined by extracting with carbon tetrachloride, treating with an excess of potassium iodide and titrating with thiosulfate solution.

It was found that hydrogen peroxide could be titrated directly with permanganate solution, even in the presence of quite concentrated hydrochloric acid. The results of such direct titrations were in satisfactory agreement with those obtained by the indirect method,[8] used in the presence of bromide. In only one rate experiment (No. 17, Table I) was there a measurable concentration of chlorine present, and even in that case it was small enough to have negligible effect on the peroxide determinations.

Materials.—During the course of the investigation, hydrogen peroxide from three different sources was used. Two of them were 30% commercial solutions, known as "Superoxol" and "Perhydrol, für die Tropen;" both contained barbituric acid as a preservative. The third solution[9] was prepared by distillation under reduced pressure of a 3% commercial solution, which contained no preservative.

The stock hydrochloric acid was prepared by distilling an appropriate mixture of commercial C. P. hydrochloric acid and conductivity water. The constant-boiling fraction was redistilled and its first and last fractions were discarded.

The sodium chloride used was recrystallized from commercial C. P. material.

The perchloric acid used was obtained as a 60% C. P. solution from two different commercial sources. No attempt was made to repurify these solutions.

---

[5] Abel, *Z. Elektrochem.*, **14**, 598 (1908); *Monatsh.*, 41, 405 (1920); *Z. physik. Chem.*, **96**, 1 (1920).

[6] Maass and Hiebert, THIS JOURNAL, **46**, 290 (1924).

[7] Livingston and Bray, *ibid.*, **45**, 2048 (1923).

[8] Ref. 1, p. 1257. Procedure for the Determination of Hydrogen Peroxide in the Presence of Bromide.

[9] This solution was prepared by Harrison and Dempster of this Laboratory by fractional distillation under reduced pressure. [Compare Maass, THIS JOURNAL, **42**, 2548 (1920).] They used silver sulfate rather than sodium hydroxide, to prevent the volatilization of traces of hydrochloric acid.

Rate Measurements at the Steady State

The rate of the catalyzed reaction was followed by withdrawing samples of the reaction mixture at intervals and determining the peroxide concentration by titration with permanganate solution. Table I summarizes three series of experiments which were performed at 25° in a dark room. Mixtures of sodium chloride and hydrochloric acid and of perchloric acid and hydrochloric acid were used as well as solutions of hydrochloric acid alone. The concentrations of hydrochloric acid, given in the second column, were measured by direct titration after each run. The concentrations of sodium chloride, Col. 3, Expts. 18–23, were determined by adding a

Table I

Rate Measurements at 25°

No.	Concn. of HCl	Concn. of H_2O_2	$k \times 10^7$	$K \times 10^5$	γ	$x \times 10^5$
1	0.0592	0.212–0.210	2.26	6.45	0.848	9.00
2	.0600	.221– .219	2.38	6.61	.846	9.25
3	.1190	.20 – .19	9.43	6.58	.809	10.7
4	.1775	.21 – .20	20.3	6.45	.782	10.5
5	.1785	.22 – .20	19.1	6.00	.786	9.70
6	.234	.180– .175	33.6	6.13	.777	10.15
7	.418	.20 – .16	106	6.07	.762	10.5
8	.468	.18 – .16	136	6.20	.761	10.7
9	.468	.12 – .10*	135	6.15	.761	10.6
10	.470	.11 – .09*	139	6.29	.761	10.8
11	.630	.20 – .15	243	6.11	.772	10.2
12	.880	.18 – .13	510	6.54	.804	10.0
13	.880	.11 – .06*	500	6.45	.804	9.9
14	1.26	.20 – .10	1060	6.53	.869	8.83
15	1.89	.20 – .02	2720	7.61	1.005	7.56
16	2.91	.15 – .01	8700	10.20	1.35	5.60
17	4.80	.18 – .02	49700	21.6	2.32	4.01

No.	Concn. of HCl	Concn. of NaCl	Concn. of H_2O_2	$k \times 10^7$	$K \times 10^5$	μ	γ	$x \times 10^5$
18	0.444	0.50	0.17–0.15	269	6.06	0.94	(0.80)	(9.47)
19	.444	1.00	.17– .14	438	6.85	1.44	(.86)	(9.25)
20	.0984	2.00	.16– .14	139	6.74	2.10	.96	7.30
21	.222	1.89	.18– .15	351	7.49	2.11	(.97)	(7.95)
22	.0984	3.00	.17– .13	289	9.47	3.10	1.20	6.58
23	.0984	4.00	.16– .11	446	11.06	4.10	1.50	4.91

No.	Concn. of HCl	Concn. of $HClO_4$	Concn. of H_2O_2	$k \times 10^7$	$K \times 10^5$	μ	γ	$x \times 10^5$
24	0.303	0.276	0.07–0.06	106	8.08	0.579	0.77	10.3
25	.667	.360	.16– .10	455	6.87	1.03	.83	10.0
26	.445	.720	.16– .11	362	6.95	1.17	.85	9.6
27	.121	.921	.12– .11	90.7	7.18	1.04	.83	10.4
28	.121	1.38	.15– .12	143	7.85	1.50	.92	9.33
29	.222	1.45	.17– .12	300	8.08	1.67	.95	8.95
30	.222	2.17	.15– .09	554	10.44	2.39	1.15	7.91
31	.121	2.77	.13– .08	469	13.40	2.89	1.28	8.18

weighed amount of dried pure sodium chloride and making up the solution to a given volume. In Expts. 24–31 solutions containing both hydrochloric and perchloric acids were made up with standardized solutions of these acids and dilution to a definite volume; the concentrations were checked by measuring volumetrically the total acid. All concentrations are given as moles per liter. Both the initial and final concentrations of peroxide are given in the table. In those experiments marked with an asterisk, pure distilled peroxide was used. The values of the first-order constant were obtained by plotting the common logarithm of the concentration against time in minutes, and multiplying the slope of the curve by 2.30. In no case did any of the plots show curvature; that is, the reaction is accurately first order in respect to peroxide. The material given in the last columns under the headings K, μ, γ and χ will be discussed later.

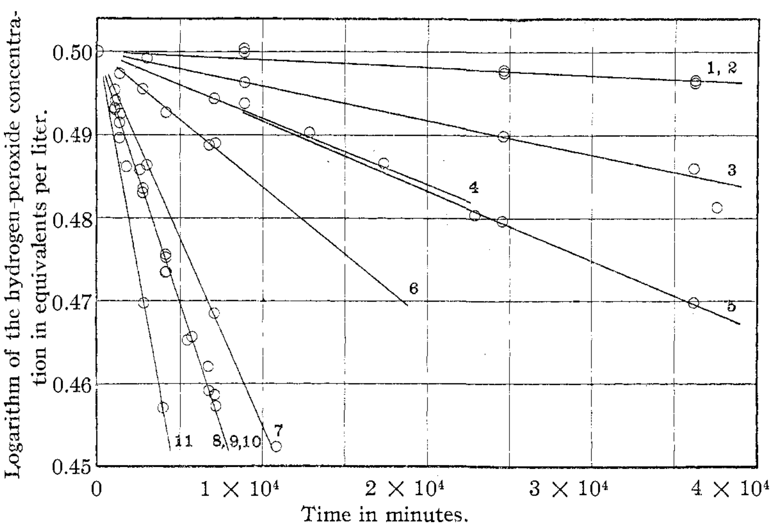

Fig. 1.

Since our results in dilute solution differ very widely from those published by Maass and Hiebert,[6] and since the results in this region are considered to be of the greatest importance in determining the rate equation, we have presented a series of log $C-t$ plots for the dilute-solution reactions, in Fig. 1. To simplify the plot, constant factors have been added to the values of log C in the several experiments, rendering these values identical at zero time. The numbers attached to the curves are the experiment numbers of Table I.

These comparatively accurate results for the rate of decomposition were not obtained until elaborate precautions had been taken to reduce to a minimum the "stray" catalysis, due to the walls of the vessel or traces of certain impurities. To realize the importance of this factor it is only necessary to remember the absolute magnitude of the measured rate in dilute solution; for example, at a hydrochloric acid concentration of 0.06 *M* the measured peroxide concentration decreased less than 1% in three weeks. Our success in eliminating the "stray" catalysis was probably due chiefly to the use of carefully cleaned wax bottles in place of glass, and the substitution of conductivity water for ordinary distilled water. The wax bottles, after being thoroughly rinsed with distilled water, were allowed to stand for several days, first with hydrogen peroxide solution and then with conductivity water. The fact that in all the experiments performed in the most dilute hydrochloric acid solutions, "Perhydrol" (which contained barbituric acid) was used, may help to account for the suppression of the "stray" catalysis.[10]

In the hope that the catalyzed rate would increase more rapidly than the "stray" rate, several experiments were performed at 40°. Here the difficulties proved to be even greater, and some of our preliminary experiments showed almost as high rates in dilute solution as those obtained by Maass and Hiebert.[6] It was not convenient to use wax bottles at this temperature, but we were able to obtain comparatively good results by using Pyrex glass flasks[11] that had been cleaned with chromic-sulfuric acid solution, rinsed with distilled water and then thoroughly steamed. The results of a few such experiments, all at concentrations greater than 0.25 *M*, are given in Table II. The notations are the same as in Table I. In this concentration range, the rate constant undergoes a 3.60-fold increase for a 10° rise in temperature. This value of the ratio is probably not in error by more than 10%, and thus appears to be somewhat larger than the value, 3.08, given by Rice[12] as typical of reactions catalyzed by strong acids.

Table II

Rate Measurements at 40°

No.	Concn. of HCl	Concn. of H_2O_2	$k \times 10^5$	$K \times 10^4$
1	0.244	0.14–0.11	2.09	3.52
2	.302	.12– .07	3.17	3.48
3	.314	.13– .08	3.07	3.12
4	.478	.15– .09	7.71	3.38
5	.498	.13– .05	8.25	3.33

---

[10] The presence of any of a number of organic preservatives is capable of greatly reducing the "stray" catalysis without appreciably affecting the halogen-halide catalysis. In support of the latter statement compare Expts. 8 and 9, as well as 12 and 13, in Table I. For additional evidence see Ref. 1, Table III. For a possible explanation of this effect, and a demonstration that various organic preservatives, even at moderately high concentration, do not affect the iodine-iodide catalysis, see Bohnson, *J. Phys. Chem.*, **25**, 19 (1921).

[11] "Well seasoned" soda glass bottles gave rates which, for 0.25 *M* hydrochloric acid at 40°, were consistently 8% or 10% greater than those obtained in Pyrex flasks.

[12] Rice, This Journal, **45**, 2815 (1923).

The Law of Catalysis

The detailed results of the rate experiments (compare Fig. 1) demonstrate that the reaction is accurately first order in respect to hydrogen peroxide, for concentrations from 0.22 *M* to 0.02 *M*. That this is also true for more concentrated solutions was demonstrated by Maass and Hiebert (compare Ref. 6, Fig. 3).

By analogy with the bromine-bromide case it is to be expected that the rate is first order in respect to both hydrogen ion and chloride ion. If we neglect the activity correction, the rate equation has the form

$$-d[H_2O_2]/dt = K[H_2O_2]\,[H^+]\,[Cl^-] = K[H_2O_2]C^2_{HCl} \qquad (3)$$

The first 14 experiments in Table I may be cited in support of this equation. In these experiments the concentration of hydrochloric acid undergoes a 20-fold change, while the maximum variation in the values of *K* (Col. 5, Table I) is only 10%. As additional evidence, Expts. 18 to 23, where the concentrations of chloride ion were much greater than those of hydrogen ion, and Expts. 24 to 31, where the concentrations of hydrogen ion were much greater than those of chloride ion, should be considered.

Although the experiments at high concentration show definitely that this expression does not fit the facts accurately, it does give the order of the reaction, and affords a convenient method of estimating the experimental accuracy of the determinations and of judging between the various possible "corrected" equations. Such comparisons have been made graphically in Fig. 2, where *K* has been plotted against the total ionic strength.[13] This type of curve has two important advantages over a plot of the first-order constant, *k*, against some function of the hydrochloric acid concentration; first, it allows a direct comparison of the several rate hypotheses to be made on one plot, and second and more important, it places equal emphasis on the experiments in dilute and concentrated solutions. Any systematic variation of or erratic errors in the experiments in dilute solution may be entirely obscured by the latter method of plotting, since the absolute magnitudes of the first-order constants are very small for dilute-solution experiments.[14]

In Fig. 2 the circles and "branched" circles represent the data summarized in Table I. A series of values of *K* (indicated as ×) have been

---

[13] Compare Ref. 7, Fig. 2 and Footnote 14. In the present paper concentrations in moles per liter have been used instead of molalities.

[14] As an illustration of this effect, compare Figs. 6 and 7 of Ref. 6 with Fig. 2 of this paper and Fig. 2 of Ref. 7, respectively. It should be pointed out that Figs. 4, 6 and 7 of Maass and Hiebert[6] are rendered even more misleading by the fact that the straight lines were so drawn that they do not pass through the origin. If these curves were to be considered as correct, it would follow that hydrobromic acid in concentrations less than 0.035 *M* would have no catalytic effect, and that hydrochloric acid would be capable of producing a by no means negligible decomposition even when present at zero concentration.

computed from data given by Maass and Hiebert (Ref. 6, Table III), by means of the equation, $K = 2.30\ k'/C^2_{\mathrm{HCl}}$.

By assuming some one value of K as a standard, we may compute the variation of K with concentration which would occur if any one of the several reaction hypotheses were true. It seems very probable that any valid equation will hold most accurately in the dilute solution range. Since the values at greatest dilution are rendered somewhat uncertain by experimental difficulties, we will take $K = 6.0 \times 10^{-5}$ at $C_{\mathrm{HCl}} = 0.20\ M$ as our standard value.

If the rate were proportional to the stoichiometrical concentrations of the reacting substances (that is, if Equation 3 were exact), the plot of K against the ionic strength (μ) would be a straight horizontal line (represented as a dotted line in Fig. 2). If, in exact analogy to the bromine-bromide case, the rate were proportional to the activity product of hydrochloric acid and to the concentration of hydrogen peroxide, the following equation would hold accurately.

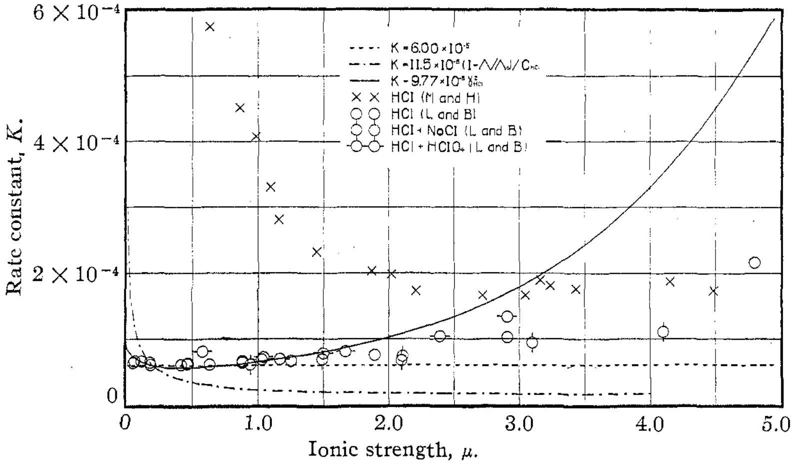

Fig. 2.

$$-d[\mathrm{H_2O_2}]/dt = \chi[\mathrm{H_2O_2}]\ [\mathrm{H^+}]\ [\mathrm{Cl^-}]\gamma^2_{\mathrm{HCl}} \quad (4)$$

Combining Equations 3 and 4, we obtain

$$K = \chi\gamma^2_{\mathrm{HCl}} \quad (5)$$

Assuming χ constant and equal to $6.0 \times 10^{-5}/\gamma^2_{\mathrm{HCl}\,=\,0.2\,M}$ or 9.77×10^{-5}, we can use Equation 5 to compute a value for K corresponding to any concentration. A plot of such values[15] is represented by a solid line in Fig.

---

[15] The values of γ_{HCl}, for pure hydrochloric acid, were taken from Lewis and Randall's "Thermodynamics," p. 336. For solutions containing sodium chloride three values were interpolated from the measurements of Harned (Ref. 2, p. 367); three others enclosed in parentheses were obtained by an arbitrary method of extrapolation. For solutions containing perchloric acid the values were computed by assuming the ionic strength principle [compare Ref. 2, Chap. 28, and Schuhmann, This Journal, **46**, 58 (1924)].

2. The "conductivity hypothesis" of Maass and Hiebert leads directly to a rate equation of the following form

$$-d[H_2O_2]/dt = K'[H_2O_2]C_{HCl}(1 - \Lambda/\Lambda_0) \qquad (6)$$

Combining Equations 5 and 6, we obtain

$$K = K'(1 - \Lambda/\Lambda_0)C_{HCl} \qquad (7)$$

Using Equation 7, the value of K at 0.20 M, and the published values of Λ_{HCl} and Λ_{0HCl},[16] we have computed and plotted as a dot-dash line, the values which K would have if K' were constant and equal to 11.5×10^{-5}.

A consideration of this plot shows that either Equation 3 or 4 will fit the experimental points for concentrations below 1.0 M, while Equation 6 cannot be brought into even approximate agreement with the data in this range.[17] If it were not for the analogy with the bromine-bromide case, there would be little evidence to enable us to decide between the concentration and the activity laws (Equations 3 and 4). However, a comparison with the bromine-bromide case (Ref. 7, Table II) leaves little doubt that if it were possible to obtain accurate measurements in very dilute solutions, these measurements would be in agreement with the activity law.

For more concentrated solutions the experimental observations do not agree with predictions based upon any of the three hypotheses. Either or both of two possible factors may be responsible for this deviation from the predictions of the activity law at high concentration. If we assume that the rate is directly proportional to the activity of each of the components,[18] then the observed departure indicates that the activity coefficient of hydrogen peroxide is less than unity in the presence of moderately concentrated hydrochloric acid. If we assume that Brönsted's hypothesis[19] is true, the departure indicates that, in solutions of ionic strength greater than 1, the activity coefficient of the neutral "reaction complex" is greater than that of hydrogen peroxide. A more complete discussion of this departure from the activity law will be presented in a later paper.

The Steady-State Function

That there must be a functional relation between the concentrations of the several components of the catalyst (that is H^+, Cl^- and Cl_2) follows from the general nature of chemical catalysis. It is to be expected that

---

[16] For hydrochloric acid concentrations above 0.31 M we have calculated values of $(1 - \Lambda/\Lambda_0)$ from data given by Maass and Hiebert in Table III, p. 299, which are based on conductivity measurements by Kohlrausch. In more dilute solutions we have made use of the conductivity data of Bray and Hunt [THIS JOURNAL, **33**, 787 (1911)]. (In the first line of Table III of Bray and Hunt's paper, 86.7 is a misprint for 89.7.)

[17] It is only fair to add that, while Equation 6 cannot be brought into agreement with our data over any range, it can, by a suitable choice of the "standard" value for K, be made to fit the data of Maass and Hiebert over the range 1.5 M to 5.5 M.

[18] Compare Harned and Seltz, THIS JOURNAL, **44**, 1480 (1922), and Ref. 7, p. 2054.

[19] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

this function will have the same form as that already determined for the bromine-bromide catalysis.

The results of several measurements of the chlorine concentration under steady-state conditions, which were made to test this prediction, are listed in Table III. The hydrochloric acid concentrations, Col. 2, were determined by taking known volumes of a standard hydrochloric acid solution and making up to 100 cc. with 2 cc. of Perhydrol and the necessary amount of distilled water. The chlorine concentrations were measured, by the method already described, after the solutions had stood for 24 hours at 25° in the dark. It should be noted that Expt. 2 differs from the others in being the result of chlorine determinations made during and after the rate measurements on Solution 17, Table I.

TABLE III

CONCENTRATION MEASUREMENTS AT THE STEADY STATE

No.	Steady-state concn. HCl	$Cl_2 \times 10^5$	$R \times 10^7$	γ_{HCl}	$[\rho = R/\gamma^4_{HCl}] \times 10^8$
1	4.55	6.1	1.47	2.10	0.76
2	4.80	14	2.70	2.32	.93
3	5.06	24	3.66	2.60	.80
4	5.56	124	13.0	3.00	1.60
5	5.86	349	29.6	3.25	2.64

The values of R, the steady-state function, were computed by means of the following equation, analogous to that used in the bromine-bromide case.

$$R = [Cl_2]/[H^+]^2\,[Cl^-]^2 \qquad (8)$$

The values of R undergo a 20-fold increase for a variation of the hydrochloric acid concentration from 4.55 M to 5.86 M. Since R is, by definition (compare Ref. 1, p. 1262), the ratio of two rate constants, activities rather than concentrations should be used in its evaluation. If we assume, as a first approximation, that the activity coefficient of neutral chlorine is in all cases unity, we may write

$$\rho = [Cl_2]/a^2_{H^+} \times a^2_{Cl^-} = R/\gamma^4_{HCl} \qquad (9)$$

The values of ρ,[20] Col. 5, show only a 3-fold variation in this concentration range. This departure from constancy can be explained as due to a change of the activity coefficient of the chlorine molecule; or, in the light of the Brönsted theory, as due to a change in the ratio of the activity coefficients of the two "reaction complexes."[21]

[20] The corresponding calculations were not made for the bromine-bromide case, since the necessary activity data were not available. A determination of these data is now in progress in this Laboratory, and preliminary calculations have shown that R/γ^4_{HBr} is more nearly constant than R. Detailed results will be published shortly.

[21] It should be noted that, although an equilibrium constant must be exactly equal to the ratio of the activity products of the resultants and components, a steady-state constant will involve another term. This is due to the fact that the reaction complexes involved in an equilibrium are identical [compare Brönsted, Ref. 19, p. 205; also Christiansen, *Z. physik. Chem.*, **113**, 37 (1924)], while those involved in a steady state are not identical.

This conception of the steady state leads directly to an explanation of Maass and Hiebert's measurements of what they have called "critical concentrations." They measured the amount of chlorine carried off by the evolved oxygen into a potassium-iodide trap. Whether the amount produced during a definite time interval or during the complete decomposition was taken, is not stated definitely. In either case the volume of oxygen evolved will be proportional to the initial concentration of hydrogen peroxide; and, assuming that the steady-state condition has been approximately reached early in the reaction, the amount of chlorine carried over will be proportional to the amount of oxygen evolved. This explains the *apparent increase* of the chlorine concentration with an increase in the initial concentration of hydrogen peroxide. These "critical concentrations" obviously have no simple or direct relation to the kinetics of the reactions studied.

Mechanism of Catalysis

The simplest theory of the chlorine-chloride catalysis is that there are two compensating reactions, related to Reactions 1 and 2, the rates of which are equal at the steady state. Since both the "law of catalysis" (Equations 3 and 4) and the "steady-state function" (Equations 8 and 9) are analogous to those of the bromine-bromide case, we may assume that the *mechanisms* of the two reactions will be similar.[22] The two compensating irreversible reactions (Equations 10 and 11) determine the rate of the catalytic decomposition.

$$H^+ + Cl^- + H_2O_2 = HClO + H_2O \qquad (10)$$
$$HClO + H_2O_2 = H^+ + Cl^- + H_2O + {}^1/_2O_2 \qquad (11)$$

The rapid reversible hydrolysis[23] of chlorine (Equation 12) occurs simultaneously with the two "compensating reactions," and fixes the concentration of hypochlorous acid.

$$Cl_2 + H_2O = H^+ + Cl^- + HClO \qquad (12)$$

If the activity corrections be neglected, the rate equations corresponding to Reactions 10 and 11 will be

$$d[HClO]/dt = K_1[H_2O_2]\,[H^+]\,[Cl^-] \qquad (13)$$
$$-d[HClO]/dt = K_3[H_2O_2]\,[HClO] \qquad (14)$$

---

[22] For the reasoning involved in the development of the mechanism see Ref. 1, pp. 1261–2.

[23] Maass and Hiebert state that the attainment of this equilibrium may be a slow process, but we can find no evidence in support of this view. Moreover, it is inconsistent with the data on the steady state presented in the present paper. Substances known to hydrolyze slowly are those in which the coördination number of the central atom is satisfied and in which the bond is very strong, as in carbon tetrachloride, the chloropentammine cobaltic ion $[Co(NH_3)_5Cl]^{++}$, and violet chromic salts. Of the two articles cited by Maass and Hiebert, p. 305, the first refers to violet chromic salts, and the second does not mention slow hydrolysis.

Since Reaction 12 represents an equilibrium condition, we may give Equation 14 the following form

$$-\mathrm{d}[HClO]/\mathrm{d}t = K_2[H_2O_2]\,[Cl_2]/[H^+]\,[Cl^-] \tag{15}$$

Since $K_1 = {}^1/_2K$, and by definition (Ref. 1, p. 1262) $R = K_1/K_2$, we may write

$$K_2 = K/2R \tag{16}$$
$$K_3 = K/2R\,K_{eq.} \tag{17}$$

where $K_{eq.}$ is the chlorine-hydrolysis equilibrium constant. Taking the measured values of K and R for 4.80 M (No. 16, Table I and No. 2, Table III) and the known value of the hydrolysis equilibrium constant,[24] we obtain an approximate value of K_3, 8.5×10^5. This is surprisingly close to the value (Ref. 1, p. 1270) of the rate constant of the corresponding hypobromous acid reaction 6.7×10^6.

The mechanism outlined here does not differ fundamentally from that outlined (compare Equations 1, 2, 3 and 4, Ref. 6) by Maass and Hiebert. It is indeed very probable that the real components of Reaction 10 are hydrogen peroxide and undissociated hydrochloric acid, and we have no objection to offer to their assumption that the formation of hypochlorous acid and water is preceded by the "formation of an oxonium compound." We have omitted these speculations from our summary of the mechanism, since there is no way of testing their validity by means of existing data. Maass and Hiebert's analysis of their assumed mechanism leads them to certain conclusions at variance with our steady-state measurements and general rate equation, but we believe that this is due entirely to their faulty analysis of these assumptions.

The Approach to the Steady State

The question of the time required for the steady state to be practically reached has been brought up by Maass and Hiebert.[25] Partly for this reason and partly for the sake of completeness, we feel that it is worth while to indicate a method by which an estimate of this time may be made. A very thorough discussion of this question has already been presented by Abel[26] for the iodine-iodide case. Indeed, the first part of the following treatment (as far as Equation 29) is little more than a direct application of his method to our case.

We may write the rate equations, corresponding to Reactions 10 and 11, in the following form

$$\mathrm{d}x_1/\mathrm{d}t = K_1[H_2O_2]\,[Cl^-]\,[H^+] \tag{18}$$
$$\mathrm{d}x_2/\mathrm{d}t = K_2[H_2O_2]\,[Cl_2]/[H^+]\,[Cl^-] \tag{19}$$

where x_1 and x_2 are quantities defined by Equations 20 and 21.

$$x_1 + x_2 = \Delta[H_2O_2] \tag{20}$$
$$x_1 - x_2 = \Delta[Cl_2] = y \tag{21}$$

---

[24] Ref. 2, p. 508. $K_{eq.} = 4.84 \times 10^{-4}$.

[25] Ref. 6, pp. 298, 305.

[26] Abel, *Monatsh.*, **41**, 405 (1920).

Although the method is adaptable to a perfectly general application, we shall, for convenience, consider only those cases where the initial concentration of chlorine is zero; that is

$$y = [Cl_2] \tag{22}$$

Since, in all cases investigated, the amount of chlorine formed was negligibly small in comparison with the amount of hydrochloric acid present, it will not introduce any appreciable error to assume that the concentrations of chloride and hydrogen ions are constant during any one experiment. Therefore, we may write Equation 8 in the following form

$$R = y_s/[Cl^-]^2\ [H^+]^2 \tag{23}$$

where y_s is the steady-state concentration of chlorine. Dividing Equation 19 by 18, we obtain

$$dx_2/dx_1 = [K_2/K_1]\ [Cl_2]/[Cl^-]^2\ [H^+]^2 = [Cl_2]/[Cl^-]^2\ [H^+]^2R \tag{24}$$

Substituting from Equation 23, we find that

$$dx_2/dx_1 = y/y_s \tag{25}$$

Differentiating Equation 21, we obtain

$$dx_1 - dx_2 = dy \tag{26}$$

Upon eliminating successively dx_2 and dx_1 from Equation 25 and making the necessary rearrangements, it follows that

$$dx_1 = y_s dy/(y_s - y) \tag{27}$$

and

$$dx_2 = y dy/(y_s - y) \tag{28}$$

By integrating Equations 27 and 28 between the limits 0 and ay_s, where a is any positive real number less than unity, we obtain Equations 29 and 30.

$$x_1 = y_s \int_0^{ay_s} dy/(y_s - y) = -y_s \Big| ln(y_s - y) \Big|_0^{ay_s} = y_s ln\ 1/(1 - a) \tag{29}$$

$$x_2 = \int_0^{ay_s} y dy/(y_s - y) = \Big| y_s - y - y_s ln(y_s - y) \Big|_0^{ay_s} = y_s[ln\ 1/(1 - a) - a] \tag{30}$$

Combining Equations 20, 28 and 29, we may write

$$\Delta[H_2O_2] = y_s(2\ ln\ 1/(1 - a) - a) \tag{31}$$

Since the concentrations of chloride and hydrogen ion are assumed to be constant, we may derive the following expression by integrating Equation 3,

$$ln(1 - \Delta[H_2O_2]/[H_2O_2]_0) = -K[H^+]\ [Cl^-]t \tag{32}$$

where $[H_2O_2]_0$ represents the initial concentration of hydrogen peroxide. Combining Equations 31 and 32, we obtain the following relation between the concentrations of chloride and hydrogen ions and the time t required for the chlorine concentration y to reach any arbitrary fraction a of its steady-state value y_s.

$$t = -\frac{2.30}{K[Cl^-]\ [H^+]} \log \left[1 + \frac{ay_s - 4.61y_s \log 1/[1 - a]}{[H_2O_2]_0}\right], \tag{33}$$

or in so far as R is a true constant[27]

$$t = -\frac{2.30}{\mathrm{K}[\mathrm{Cl}^-]\,[\mathrm{H}^+]} \log \left[1 + \frac{R[\mathrm{Cl}^-]^2\,[\mathrm{H}^+]^2\,[a - 4.61 \log 1/(1 - a)]}{[\mathrm{H_2O_2}]_0}\right] \qquad (34)$$

It follows from Equation 34 that the time required for the chlorine concentration to reach some definite fraction of its steady-state value increases with an increase of the hydrochloric-acid concentration or a decrease of the hydrogen-peroxide concentration. As Abel[26] has pointed out, the steady state is a limiting condition which can never be exactly realized, unless the initial hydrogen peroxide concentration is infinite, and then only in infinite time. However, the steady state may be *practically* reached in a comparatively short time. For example, consider Expt. 17, Table I. By means of Equation 33 we find that the time intervals corresponding to values of a of 0.75, 0.99 and $(1 - 10^{-10})$ are 0.28, 0.86 and 89 minutes respectively. For Expt. 5, Table III, the time required, when a is 0.99, is 11 minutes. These results may be taken as ample justification of the statement of Maass and Hiebert.[28] "If Bray and Livingston's explanation of the mechanism is a correct one, then the steady state is approached more rapidly in the case of hydrochloric than in the case of hydrobromic acid."[29]

Since Maass and Hiebert were apparently somewhat uncertain in regard to the effect of the distance from the steady state upon the measured rate,[30] it may be worth while to point out that when the ratio of the chlorine concentration to its steady-state value is a, the ratio of the observed value of the first-order rate constant k to its steady-state value is $(1 + a)/2$.

---

[27] Inasmuch as the steady-state function (9) and the rate equation (4) both involve the activities of chloride and hydrogen ions rather than their concentrations, it would probably have been more logical to have used these activity terms in the foregoing derivation. This would not have introduced any new difficulties, since the concentrations of chloride and hydrogen ion, and therefore their respective activity coefficients, were assumed to be constant for any given reaction. The use of activities would not change the form of Equation 33, except to substitute $a_{\mathrm{Cl}^-}\,a_{\mathrm{H}^+}$ for $[\mathrm{Cl}^-]\,[\mathrm{H}^+]$.

[28] Ref. 6, p. 298, line 37.

[29] Equations of the form of (33) and (34) can be applied to the bromine-bromide case only when the concentrations of bromide and hydrogen ion are practically constant. Expt. 3, Table II, Ref. 7, meets these conditions, and here we find that the bromine concentration reaches 95% of its final value in 12 minutes and 99% in 215 minutes.

Maass and Hiebert determined the relative concentrations (in weight per cent.) of hydrobromic acid and hydrogen peroxide which would produce, in an hour's time, a sufficiently high concentration of bromine to give a visible color. Excepting those experiments where the peroxide concentration was so high that the activity of the water, and therefore the bromine hydrolysis equilibrium, was appreciably altered, these measurements should be explicable in terms of an equation having the form of Equation 34 or 33.

[30] Compare Ref. 6, p. 305, line 11. The statement, "that k (that is, the first-order rate constant) was constant long before the steady state as measured by Bray and Livingston by the rise in the bromine concentration had been reached," is misleading. Our measurements of the "rise in the bromine concentration" were all made at higher concentrations of bromide and hydrogen ion than Maass and Hiebert's oxygen evolution rates, and therefore should not be used for direct comparison.

Summary

1. The steady-state rate of the chlorine-chloride decomposition catalysis of hydrogen peroxide has been measured, at 25°, in solutions of hydrochloric acid of concentrations varying from 0.06 *M* to 4.80 *M*. Rates in solutions containing sodium chloride or perchloric acid in addition to hydrochloric acid have also been measured. A few rates at 40° have been measured.

2. At the steady state in solutions of ionic strength less than 1.0μ, the rate of decomposition of hydrogen peroxide is represented by the following equation within the limits of experimental error: $-d[H_2O_2]/dt = (0.000101 \pm 0.000005)[H_2O_2][H^+][Cl^-]\gamma^2_{HCl}$. In more concentrated solutions a negative departure occurs, for which possible explanations have been advanced in terms of the "activity rate" and Brönsted's theories. Other rate equations have been examined and have been shown to be less satisfactory.

3. The steady-state chlorine concentration has been determined for solutions whose hydrochloric acid concentrations varied from 4.55 *M* to 5.86 *M*, and it has been shown that the following relation between the steady-state concentration holds with reasonable accuracy: $1.5 \times 10^{-8} = [Cl_2]/[H^+]^2[Cl^-]^2\gamma^4_{HCl}$.

4. A mechanism consistent with the steady-state measurements and analogous to that determined for the bromine-bromide catalysis has been suggested.

5. The rate of reaction of hydrogen peroxide with hypochlorous acid has been shown to be very great and of the same order of magnitude as that with hypobromous acid.

6. The time required for the chlorine concentration to reach any fractional part of its steady-state value, and the relation between this fraction and the measured rate has been discussed. An equation relating this time interval and the initial concentrations of hydrogen peroxide and hydrochloric acid has been derived.

7. Some discussion of a recent paper, by Maass and Hiebert, in this field, has been included.

BERKELEY, CALIFORNIA