[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The Interaction of Hydrogen Peroxide and Hypochlorous Acid in Acidic Solutions Containing Chloride Ion

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Introduction

The reaction between hydrogen peroxide and chlorine in hydrochloric acid solutions proceeds according to the equation

$$H_2O_2 + Cl_2 = O_2 + 2H^+ + 2Cl^- \qquad (1)$$

The rate of this reaction has been studied by Makower and Bray.[1] In hydrochloric acid solutions of greater than one molal concentration they found the rate law to be

$$-\frac{d(H_2O_2)}{dt} = -\frac{d(Cl_2)}{dt} = k\,\frac{(H_2O_2)(Cl_2)}{(H^+)(Cl^-)} \qquad (2)^{1a}$$

They accounted for this equation by assuming that the chlorine was in rapid equilibrium with its hydrolysis products and that the rate determining step was the reaction between hydrogen peroxide and hypochlorous acid, *i.e.*

$$H_2O + Cl_2 = H^+ + Cl^- + HOCl \qquad (3)$$

$$HOCl + H_2O_2 \longrightarrow H_2O + O_2 + H^+ + Cl^- \qquad (4)$$

At hydrochloric acid concentrations below one molal, Makower and Bray found that the rate was less than that to be expected on the basis of the above equation. Later, in experiments at quite low hydrochloric acid concentration, Makower[2,3] showed that the specific rate of the reaction was much less than for strong acid solutions, indicating that the above mechanism cannot be correct.

It was suggested to me by Professor Bray in 1939 that the experimental results might be explained by the following mechanism

$$H_2O_2 + Cl_2 \underset{k_b}{\overset{k_a}{\rightleftarrows}} H^+ + Cl^- + HOOCl \qquad (5)$$

$$HOOCl \xrightarrow{k_c} O_2 + H^+ + Cl^- \qquad (6)$$

The resulting rate law is

$$-\frac{d(H_2O_2)}{dt} = \frac{k_ck_a(H_2O_2)(Cl_2)}{k_b(H^+)(Cl^-) + k_c} \qquad (7)$$

For high values of the product of the hydrogen ion and chloride ion concentrations, this rate law reduces to that found experimentally by Makower and Bray, equation (2). At lower concentrations of H^+ and Cl^-, the rate should decrease below that indicated by equation (2) as k_c becomes significant, and at sufficiently low concentrations of H^+ and Cl^- should approach the expression

$$-\frac{d(H_2O_2)}{dt} = k_a\,(H_2O_2)(Cl_2) = \frac{k_a}{K}\,(H_2O_2)(HOCl)(H^+)(Cl^-) \qquad (8)$$

where K is the hydrolysis constant for chlorine.

The present study was undertaken to investigate the validity of this rate law expression at low concentrations of H^+ and Cl^-, and hence, to test the proposed mechanism. Makower's[2] preliminary experiments had indicated that the rate law under these conditions was complex.

Experimental

Reagents.—Considerable care was taken to exclude impurities because of their possible catalytic effect on the reaction. Conductivity water, prepared by redistillation of distilled water from alkaline permanganate solution in a tin still, was used throughout.

Hydrogen peroxide solutions were made by dilution of Merck Superoxol, free from preservative. Solutions prepared from different bottles of this reagent showed no experimental differences in reaction rates.

Chlorine solutions were prepared by heating manganese dioxide with 4 *M* hydrochloric acid and passing the evolved gas through two bubblers filled with water and then into conductivity water. No differences in behavior were ever detected among the many solutions prepared in this way.

Hypochlorous acid solutions, which were used in a few experiments, were prepared by adding excess mercuric oxide to a chlorine solution and distilling off the hypochlorous acid. These solutions showed no detectable decomposition during a storage period of two months.

Solutions of sodium perchlorate were prepared by neutralizing pure 60% perchloric acid with sodium bicarbonate. Solutions of sodium chloride were prepared from the C. P. salt.

Analyses.—The reaction was followed by measuring the sum of the hydrogen peroxide and hypochlorous acid (or chlorine) concentrations. This was determined by adding samples from the reaction mixture to solutions made from 1 ml. of 1 *M* potassium iodide, 1 ml. of 1 *M* sulfuric acid, 1 drop of 0.05 *M* ammonium molybdate and 20 ml. of water, and titrating the liberated iodine with standardized sodium thiosulfate. The very rapid reduction of the hypochlorous acid (or chlorine) by iodide stopped the reaction. The ammonium molybdate was used as a catalyst[4] for the relatively slow reduction of hydrogen peroxide by iodide ion. Samples were allowed to stand ten minutes in the dark before titration with the thiosulfate to insure completion of the reaction.

In a few experiments the hypochlorous acid concentration alone was obtained by adding the sample to a potassium iodide solution at 0°, containing low acid and no molybdate, and titrating quickly with thiosulfate. By this procedure the reaction of hydrogen peroxide with iodide ion is made negligible. The results were concordant with those based on the other method of analysis.

Experimental Procedure.—Measured volumes of solutions of hypochlorous acid and hydrogen peroxide of known concentration were placed in separate glass-stoppered flasks and were brought to the reaction temperature by immersion in a thermostat for over an hour. Added hydrogen ion and chloride ion were contained in either or both of the flasks. The reaction was started by pouring

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[1] B. Makower and W. C. Bray, THIS JOURNAL, **55**, 4765 (1933). For results on the catalytic decomposition of hydrogen peroxide by the simultaneous occurrence of this reaction and the oxidation of Cl^- to Cl_2, by hydrogen peroxide, see Livingston and Bray, *ibid.*, **47**, 2069 (1925), and Maass and Hiebert, *ibid.*, **46**, 290 (1924).

[1a] Parentheses indicate the concentration of the enclosed substance in moles per liter of solution.

[2] B. Makower, Thesis, University of California, 1932.

[3] W. C. Bray, *Chem. Rev.*, **10**, 175 (1932).

[4] I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, New York, N. Y., 1929, p. 393.

TABLE I

DATA FOR $k_4°$ AT 25°

Initial concentrations in moles per liter.

Expt.	H_2O_2 × 10^4	HOCl + Cl_2 × 10^4	HOCl × 10^4	Cl^- × 10^4	H^+ × 10^4	$(H^+)(Cl^-)$ × 10^5	k_4 × 10^{-7}	μ	$k_4°$ × 10^{-7}
75 VII	17.83	30.25	29.87	29.87	29.87	0.885	2.00	0.0958	3.14
90 VI	11.66	5.27	4.48	105.0	118.0	12.39	1.90	.103	3.01
96 IV	9.61	7.15	6.03	69.4	186	12.9	1.71	.289	2.95
9 V	9.33	6.39	5.40	189.6	71.2	13.50	1.75	.158	2.89
6 V	9.34	6.37	5.34	69.7	205	14.29	1.70	.160	2.81
92 VI	11.52	5.02	4.04	527	33.7	17.76	2.04	.149	3.36
102 IV	9.60	6.80	2.92	70.2	1393	97.8	1.74	.146	2.86
107 VI	2.688	1.485	0.1133	919	919	845	1.50	.0920	2.3
110 VI	2.681	2.294	0.1698	936	936	876	1.55	.0937	2.4

the contents of one flask into the other, zero time being taken at the start of the mixing. For rapid reactions this "zero" time was not used. Immediately after mixing, the reaction flask was withdrawn from the bath, shaken vigorously, and immediately replaced. The mixing and shaking required from ten to fifteen seconds. No effects attributable to variations in the order or manner of mixing were ever observed.

Samples were removed at convenient time intervals with a 20-ml. pipet, the time being recorded when the pipet had half emptied into the potassium iodide solution. The pipet used for the more rapidly changing reaction mixtures had a delivery time of less than five seconds.

In all experiments sodium perchlorate was used to adjust the ionic strength to the desired value.

Calculation of Reaction Rates.—Titers of the different samples were plotted against time and a smooth curve drawn through the points. Slopes were measured at various points on the curve and these values, when multiplied by a suitable factor, gave the rate of disappearance of hydrogen peroxide, $-d(H_2O_2)/dt$. Rate constants were calculated using these figures together with the concentrations of the reacting species at the time at which the slope was measured. All concentrations have been expressed in moles per liter of solution at the temperature of the experiment and time in minutes.

In runs at high concentrations of hydrochloric acid there was appreciable loss of chlorine because of its volatility. This was assumed to have occurred principally during the equilibration and mixing period. Consequently, for such experiments the initial concentrations of chlorine were calculated from the final titer of the reagent present in excess and the initial concentration of hydrogen peroxide. For cases in which the chlorine concentration was small relative to the hypochlorous acid concentration, this correction was small, but amounted to as much as 15% for cases in which chlorine was the principal species. Hence, the results of these latter experiments are less accurate than the others.

A comparison of the final titer of the reaction mixture with the difference in the initial concentrations of hydrogen peroxide and hypochlorous acid (or chlorine) showed that the assumed stoichiometry was closely followed for experiments in which loss of chlorine was not to be expected. Makower[2] had previously shown that the volume of oxygen liberated under these conditions is in accord with this stoichiometry.

Results and Discussion

The k_4 Law.—When the product of the hydrogen ion and chloride ion concentrations lies within the limits 10^{-1} to 10^{-5}, the experimentally determined rate law is

$$-d(H_2O_2)/dt = k_4(HOCl)(H_2O_2)(H^+)(Cl^-) \quad (9)$$

Table I is a summary of the runs used in establishing this law. The headings are self-explanatory except for the last two columns which are respectively the ionic strength, μ, and the values of k_4 extrapolated to zero ionic strength (to be discussed later). Each value of k_4 represents the average of several values for that experiment calculated at different times.

In calculating the true concentration of hypochlorous acid, it was necessary to use the chlorine hydrolysis constant. The extensive measurements of Jakowkin[5] on this equilibrium were recalculated by Lewis and Randall[6] and have been reviewed once again in the present work.[7] The selected values, given in Table II, agree fairly well with those of Lewis and Randall. The uncertainty in the values is much larger than is indicated by the significant figures recorded, but the relative accuracy is probably greater than the absolute accuracy.

TABLE II

HYDROLYSIS CONSTANT OF CHLORINE

$K = (HOCl)(H^+)(Cl^-)\gamma^2_{\pm HCl}/(Cl_2)$

Temp., °C.	$K \times 10^4$
0.0	1.45
12.8	2.88
25.0	4.47
35.0	5.68

In each experiment there were large changes in the hypochlorous acid (or chlorine) and hydrogen peroxide concentrations, as well as smaller changes in the hydrogen ion and chloride ion concentrations. Thus it is difficult to study the concentration dependence for a single substance, but rather all must be considered simultaneously. In the following analysis the effects have been separated as completely as possible, but it is realized that the best proof of the k_4 law is the agreement of the data taken as a whole.

Hydrogen Peroxide and Hypochlorous Acid Dependence.—It was not possible to vary the initial hydrogen peroxide and hypochlorous acid concentrations greatly, since they had to be small to give a measurable rate and much further decrease greatly reduced the accuracy of titration. Also, they had to be of the same order of

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(5) A. A. Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

(6) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, p. 508.

(7) R. E. Connick, Thesis, University of California, 1942.

magnitude since the sum of the two was measured and the concentration of the less abundant species determined by difference. The hydrogen peroxide dependence is best tested by an experiment in which its initial concentration is less than that of the hypochlorous acid, so that it falls to zero at completion of the reaction. The data for such a run are given in Table III. For approximately an eight-fold variation of peroxide concentration the value of k_4 is essentially constant. Similarly all other experiments of Table I showed a first order hydrogen peroxide dependence.

TABLE III

DEPENDENCE OF RATE ON HYDROGEN PEROXIDE CONCENTRATION

Expt. 75 VII, temp. 25°, μ = 0.0958

Time, min.	(H_2O_2) $\times 10^4$ moles/liter	(HOCl) $\times 10^4$ moles/liter	(HCl) $\times 10^4$ moles/liter	$-\frac{d(H_2O_2)}{dt}$ $\times 10^4$	k_4 $\times 10^{-7}$
0.483	13.72	25.70	33.92	7.97	1.97
0.842	11.06	23.02	36.56	6.74	1.98
1.277	8.40	20.35	39.21	5.36	2.04
1.87	5.75	17.71	41.81	3.59	2.02
2.88	3.09	15.06	44.54	1.89	2.05
3.81	1.76	13.75	45.89	1.02	2.00

TABLE IV

DEPENDENCE OF RATE ON HYPOCHLOROUS ACID CONCENTRATION

Expt. 96 IV, temp. 25°, μ = 0.289

Time, min.	(H_2O_2) $\times 10^4$ moles/liter	(HOCl) $\times 10^4$ moles/liter	(Cl^-) $\times 10^3$ moles/liter	(H^+) $\times 10^3$ moles/liter	$\frac{-d(H_2O_2)}{dt}$ $\times 10^4$	k_4 $\times 10^{-7}$
0.59	5.62	2.66	7.40	19.1	3.59	1.70
1.04	4.46	1.69	7.54	19.2	1.78	1.63
1.57	3.72	1.06	7.62	19.3	1.02	1.76
1.86	3.46	0.84	7.65	19.3	0.76	1.77

The data of Table IV illustrate the first order dependence of the rate on the hypochlorous acid concentration over a three-fold variation. If the dependence on H^+ and Cl^- is assumed to be known, a nearly three-hundred-fold variation of HOCl concentration may be obtained by comparing experiments 75 VII and 107 VI of Table I. The relatively small discrepancy in the $k_4°$ values is probably due to an error in the chlorine hydrolysis constant, which as pointed out earlier is subject to considerable uncertainty.

Hydrogen Ion and Chloride Ion Dependence.—The product of the hydrogen ion and chloride ion concentrations was varied over a very wide range in the experiments of Table I. The data have been plotted in Fig. 1 using a rate constant, $k_2°$, defined by the equation

$$-\,d(H_2O_2)/dt = k_2^0(H_2O_2)(HOCl) \qquad (10)$$

(k_2^0 is the value of the rate constant at zero ionic strength obtained by the method described in the following section). In agreement with the k_4 law the plot of log $k_2°$ against log $(H^+)(Cl^-)$ yields a straight line of unit slope at low hydrochloric acid concentrations. Above $(H^+)(Cl^-)$ = 0.1 the points fall off to a horizontal line which is Makower and Bray's[1] limiting law for high hydrochloric acid.

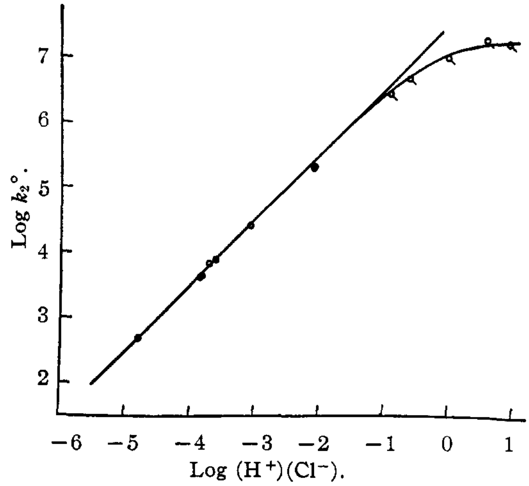

Fig. 1.—k_2^0 as a function of hydrogen and chloride ion concentrations: ○ data from this paper; ⚲ data from Makower and Bray.[1]

Ionic Strength Dependence.—The variation of k_4 with ionic strength at low hydrochloric acid concentration is shown in Table V. The experimental conditions were similar for all runs except for the variation of ionic strength which was altered by the addition of sodium perchlorate (see Table I for typical conditions for run 75 VII).

TABLE V

EFFECT OF IONIC STRENGTH ON k_4 AT 25°

Expt.	μ	$k_4 \times 10^{-7}$
Extrapolated	0	3.13
89 VII	0.0036	2.76
86 VII	.0242	2.41
75 VII	.0958	2.00
80 VII	.3725	1.98
84 VII	1.015	2.16

One might expect the ionic strength effect to be related to the change in the activity coefficient of hydrochloric acid. In Fig. 2, it is seen that this expectation is well fulfilled. The solid line is a plot of the mean activity coefficient of hydrochloric acid against the square root of the ionic strength, which in this case is the square root of the hydrochloric acid concentration. The solid circles are the data tabulated in Table V, the quantity plotted being $^1/_2$(log k_4 − 7.496). One point is placed arbitrarily on the hydrochloric acid curve, the position of the remaining points then being fixed. The factor of one-half is necessary since the logarithm of the mean activity coefficient of hydrochloric acid is plotted. All values including activity coefficients are based on concentration units of moles per liter.

From Fig. 2 it is clear that the main effect of ionic strength on k_4 is equal to the change in the activity coefficients of hydrogen ion and chloride

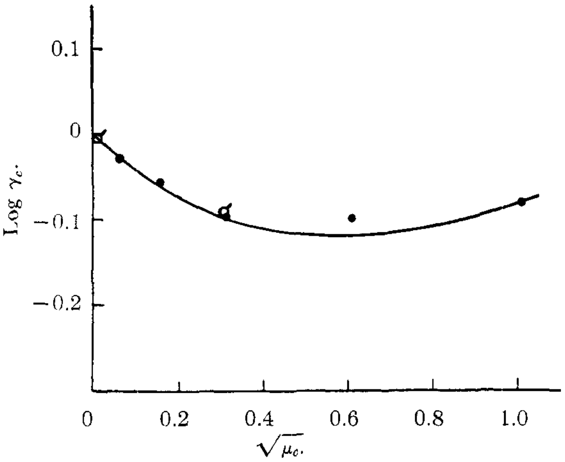

Fig. 2.—Effect of ionic strength on k_4: ●, $^1/_2$ (log k_4 − 7.496), ♂, $-^1/_2$ (2.238 + log k_B) (see section on hypochlorite reaction), solid curve, log $\gamma_{\pm \text{HCl}}$.

ion. The point at $\sqrt{\mu} = 0.610$ may be in error, but actually deviations of the points from the curve at high ionic strength would not be surprising since in one case the ionic strength is due to hydrochloric acid and in the other case mainly to sodium perchlorate. Values read from the hydrochloric acid activity coefficient curve were used to correct values of k_4 to zero ionic strength, *i. e.*, to obtain k_4^0.

Temperature Dependence of k_4.—Values of k_4 at various temperatures are given in Table VI. The conditions were similar for each experiment (see Table I and III for details for run 75 VII). Within experimental error the values of k_4 lie on a straight line when plotted against the reciprocal of the absolute temperature.

TABLE VI

EFFECT OF TEMPERATURE ON k_4

Expt.	Temp., °C.	$k_4 \times 10^{-7}$
101 VII	0.00 ± 0.05	1.05
106 VII	12.80 ± .05	1.48
75 VII	25.00 ± .05	2.00
109 VII	35.00 ± .05	2.62

A single experiment at 0° in the presence of a high concentration of hydrochloric acid, which repressed the hydrolysis of chlorine, gave $k_4^0 = 1.41 \times 10^7$. This value corresponds to $k_4 = 0.90 \times 10^7$ at $\mu = 0.0958$, the ionic strength used in the experiments of Table VI. The most likely cause of the 15% discrepancy with experiment 101 VII is an error in the hydrolysis constant of chlorine which had to be used to calculate k_4 for the experiment at high hydrochloric acid concentration.

Discussion of the k_4 Law.—The experimental results amply confirm the mechanism proposed by Bray, which was discussed in the Introduction. The extent of the agreement is shown in Fig. 1, where the solid curve was calculated from equation (7) by fitting the curve to the k_4 law at low values of $(H^+)(Cl^-)$ and using Makower and Bray's limiting rate at high values of $(H^+)(Cl^-)$. The curve quite accurately follows the experimental points, even through the transition region.

Since no other reasonable mechanism has been found which fits the experimental data, it is believed that the above mechanism is correct and that chlorine and hydrogen peroxide react to form the peroxy compound, HOOCl, which then decomposes to give oxygen, hydrogen ion and chloride ion. The rate determining step depends on the hydrochloric acid concentration, and is the decomposition of HOOCl at high values of $(H^+)(Cl^-)$ and the reaction of chlorine with hydrogen peroxide at low values. The experimental results are consistent with the idea that the concentration of HOOCl is always small relative to the hydrogen peroxide and hypochlorous acid (or chlorine) concentrations.

According to the above mechanism, variation of the ionic strength can affect k_4 through changes in K and k_a. The principal effect on K is caused by changes in the activity coefficients of hydrogen ion and chloride ion, while there should be little effect on k_a, the rate constant for the reaction between two uncharged molecules. Then the change in k_4 should correspond to that of the product of the activity coefficients of hydrogen and chloride ions—a result which has already been verified (see Fig. 2).

At high concentrations of hydrochloric acid where the rate law is that given by equation (2), the main effect of changing ionic strength should be to alter the value of the equilibrium constant of reaction (5). This assumes a negligible effect of ionic strength on the rate of decomposition of the neutral molecule HOOCl. The equilibrium constant of reaction (5) will be affected principally by the change in the activity coefficients of hydrogen ion and chloride ion, which is just the ionic strength effect found by Makower and Bray.[1]

The value of the specific rate, k_a^0, for the bimolecular reaction between hydrogen peroxide and chlorine is found to be 1.1×10^4 liters moles^{-1} min.$^{-1}$ at 25°, and 2.1×10^3 at 0°. These data were taken from the experiments at $(H^+)(Cl^-) = 0.008$ in order to avoid the use of the hydrolysis constant for which the temperature dependence is uncertain. The activation energy, E, defined by the equation

$$k = Ze^{-E/RT} \qquad (11)$$

(where E and Z are assumed to be temperature independent) is calculated to be 10,700 calories. There are indirect indications that this activation energy is not actually temperature independent. The data of Table VI show that the k_4 reaction has a constant activation energy of 4,500 calories from 0 to 35°. This value combined with the ΔH of the hydrolysis reaction should give the activation energy for the bimolecular reaction between chlorine and hydrogen peroxide, calculated above. According to Jakowkin,[5] there is a large variation of ΔH hydrolysis with temperature and hence, the activation energy for the bimolecular reaction should show a similar large variation with temperature. This would mean that the value of 10,700 calories would be too small at 0° and too large at 25° and the variation would be of the order of 2000 calories from the mean. But before any significance can be attached to this conclusion, the anomalous variation of the hydrolysis constant with temperature should be checked.

Using 10,700 calories for the activation energy one calculates an Arrhenius constant, Z, for equation (11), of 0.8×10^{12} liters $\text{moles}^{-1}\text{min.}^{-1}$ at 25°, which is roughly a factor of twenty smaller than that to be expected from collision theory. On the basis of absolute reaction rate equations, the entropy of activation is -14.6 entropy units when concentrations are expressed in moles per liter.

The Hypochlorite Reaction

At very low hydrogen ion concentrations the reaction of hydrogen peroxide with hypochlorous acid becomes much faster than would be predicted from the k_4 law, thus indicating the existence of a new reaction path. To study this reaction, it was necessary to drown out other reaction paths by using very low concentrations of hydrogen ion and chloride ion.

The experimental results are given in Table VII. Listed are the initial concentrations of the reactants, the ionic strength μ, and two rate constants defined by the equations

$$-\,\mathrm{d}(\mathrm{H_2O_2})/\mathrm{d}t = k_2(\mathrm{H_2O_2})(\mathrm{HOCl}) \qquad (12)$$

$$-\,\mathrm{d}(\mathrm{H_2O_2})/\mathrm{d}t = k_\mathrm{B}(\mathrm{H_2O_2})(\mathrm{HOCl})/(\mathrm{H^+}) \qquad (13)$$

TABLE VII

EXPERIMENTAL DATA FOR THE HYPOCHLORITE REACTION

Expt.	$(\mathrm{H_2O_2}) \times 10^4$	$(\mathrm{HOCl}) \times 10^4$	$(\mathrm{Cl^-}) \times 10^4$	$(\mathrm{H^+}) \times 10^4$	μ	k_2	$k_\mathrm{B} \times 10^2$
			TEMP. 25°				
13 VII	2.52	1.97	1.97	6.21	0.092	25	1.50
15 VII	2.54	3.70	3.70	3.70	.092	31	1.23
9 VII	2.54	2.03	2.03	2.03	.092	43	0.94
18 VII	2.54	1.92	5.09	1.92	.092	49	1.06
5 VIII	2.05	2.64	~0	~0	.092		0.88
65 VII	2.31	2.67	~0	~0	.0001		.58
			TEMP. 0°				
119 VII	2.08	2.67	~0	~0	.0001		0.051

The values for k_2 and k_B were calculated for a time shortly after the start of the reaction. Therefore, one cannot use the initial hydrogen ion concentration of column 5 to calculate one from the other, since the hydrogen ion concentration changes considerably during the reaction.

The values of k_B in Table VII decrease with decreasing acidity but appear to be approaching a value of *ca.* 0.90×10^{-2}. (Experiment 65 VII is at a different ionic strength and should not be compared with the others.) This trend in the value of k_B is due to another reaction path which will be discussed later. Experiments 9 VII and 18 VII, where the contribution from this extraneous reaction is small, show the reaction to be independent of the chloride ion concentration. Comparison of 15 VII and 18 VII gives some evidence of first order dependence on hypochlorous acid concentration.

In the first four experiments of Table VII the value of k_B increased throughout each experiment, since the formation of hydrogen ion caused an increase in the contribution from the extraneous reaction. In the last three experiments hypochlorous acid was used, rather than chlorine, in order to minimize the initial hydrogen ion concentration. Values of k_B in the early part of the reaction, where the hydrogen ion concentration was very low, gave quite constant results as shown by the data of Table VIII. The high value at the start is probably attributable to the uncertainty in measuring the large initial value of $-\mathrm{d}(\mathrm{H_2O_2})/\mathrm{d}t$. These data illustrate very clearly the inverse first power dependence on hydrogen ion concentration. There is also good evidence for a first power hydrogen peroxide dependence.

TABLE VIII

Experiment 65 VII; Temp. 25°; $\mu = 0.0001$; initial concentrations: $(\mathrm{H_2O_2}) = 2.31 \times 10^{-4}\ M$, $(\mathrm{HOCl}) = 2.67 \times 10^{-4}\ M$, $(\mathrm{Cl^-}) = \sim 0$, $(\mathrm{H^+}) = \sim 0$

Time, min.	$(\mathrm{H_2O_2}) \times 10^4$	$(\mathrm{HOCl}) \times 10^4$	$(\mathrm{H^+}) \times 10^4 = (\mathrm{Cl^-}) \times 10^4$	$-\dfrac{\mathrm{d}(\mathrm{H_2O_2})}{\mathrm{d}t} \times 10^4$	$k_\mathrm{B} \times 10^2$
0.63	2.123	2.485	0.189	0.187	0.68
2.18	1.946	2.308	.361	.074	.59
5.45	1.769	2.131	.538	.0404	.58
11.03	1.591	1.953	.716	.0253	.58
19.67	1.414	1.776	.893	.0169	.60

Discussion of the Mechanism of the Hypochlorite Reaction.—The experimental data indicate that the rate law for the hypochlorite reaction is

$$-\frac{\mathrm{d}(\mathrm{H_2O_2})}{\mathrm{d}t} = k_\mathrm{B}\,\frac{(\mathrm{H_2O_2})(\mathrm{HOCl})}{(\mathrm{H^+})}$$

This is most simply interpreted by the following mechanism

$$\mathrm{HOCl} \overset{K_\mathrm{B}}{=} \mathrm{H^+} + \mathrm{ClO^-} \qquad (14)$$

$$\mathrm{ClO^-} + \mathrm{H_2O_2} \xrightarrow{k_\mathrm{d}} \mathrm{H_2O} + \mathrm{O_2} + \mathrm{Cl^-} \qquad (15)$$

The rapid equilibrium (14) followed by the rate determining step (15) leads to the rate law given above, with

$$k_\mathrm{B} = k_\mathrm{d}K_\mathrm{B} \qquad (16)$$

From a comparison of this rate law with the k_4 law, it is clear that this reaction path is only important relative to the k_4 path at very low hydrogen ion and/or chloride ion concentrations.

According to the Brönsted theory of neutral salt effects, k_d should vary little with ionic strength; however, K_B will vary greatly because of the change in the activity coefficients of $\mathrm{H^+}$ and $\mathrm{ClO^-}$. Substituting $\mathrm{H^+}$ and $\mathrm{Cl^-}$ for $\mathrm{H^+}$ and $\mathrm{ClO^-}$, for which there are no data available, one predicts that k_B should increase with increasing ionic strength in accordance with the change of the activity coefficient of hydrochloric acid. The data for experiments 65 VII and 5 VIII, of ionic strength 0.0001 and 0.092, respectively, have been plotted in Fig. 2 and are indicated by the symbol σ'. The quantity plotted is $-\frac{1}{2}$ (2.238 + log k_B) where 2.238 is used to fix one point on the hydrochloric acid curve while the factor $\frac{1}{2}$ is necessary because $\gamma_{\pm}$ of hydrochloric acid is plotted. It is seen that the points agree well with the predictions of the Brönsted theory. The values chosen at zero ionic strength for k_B are 5.7×10^{-3} min.$^{-1}$ at 25° and 5.0×10^{-4} min.$^{-1}$ at 0°.

Using the ionization constant of hypochlorous acid, it is possible to calculate the specific rate of reaction, k_d, of ClO^- and hydrogen peroxide. The ionization constant was taken to be 3.44×10^{-8} at 25° and 1.82×10^{-8} at 0°. These values were calculated from Ingham and Morrison's[8] value at 18°, using the heat of ionization of hypochlorous acid[9] and Pitzer's[10] equation for the change of the ionization constant of acids with temperature. The value of $k_d{}^0$ is then equal to 1.7×10^5 at 25° and 2.8×10^4 at 0°. Calculation by equation (11) yields an activation energy of 11,600 calories and an Arrhenius constant of 5.4×10^{13}. In terms of statistical rate theory the entropy of activation is −6.1 entropy units, when concentrations are expressed in moles per liter.

The observed rate law can also be interpreted by the following mechanism

$$H_2O_2 \overset{K_0}{=} H^+ + HO_2^- \qquad (17)$$

$$HO_2^- + HOCl \xrightarrow{k_0} H_2O + O_2 + Cl^- \qquad (18)$$

Making use of the ionization constant of hydrogen peroxide,[11] the activation energy and Arrhenius constant for reaction (18) are calculated to be 7,700 calories and 1.1×10^{15} liters moles^{-1} min.$^{-1}$, respectively. The value of the Arrhenius constant seems too great and, therefore, the hypochlorite mechanism is preferred.

Rate of Reaction in Region $(H^+)(Cl^-) = 10^{-5}$ to 10^{-8}.—In the region of $(H^+)(Cl^-)$ from 10^{-5} to 10^{-8} the reaction is faster than can be accounted for by the k_4 and hypochlorite paths. This additional reaction was difficult to study because of the large correction for the contributions from the k_4 and hypochlorite paths, which seldom was less than 50%. Several characteristics of the new reaction path may be mentioned. The rate is nearly or completely independent of the hypochlorous acid concentration but first order with respect to the peroxide concentration. There is a less than first power dependence on both hydrogen ion and chloride ion concentrations. The rate is not completely reproducible and somewhat more than one mole of hypochlorous acid seems to disappear per mole of hydrogen peroxide reacted. A careful attempt to exclude all impurities failed to eliminate this reaction. It was not possible to formulate a rate law.

Some experiments were performed in an acetic acid–sodium acetate buffer mixture. Below 10^{-5} *M* hydrogen ion concentration the reaction was mainly due to the hypochlorite path under the conditions used. Above this concentration the rate was greater by a factor of 20 to 30 than under the same conditions in the absence of the buffer. Similar results have been reported by Makower.[2] The specific nature of this catalytic action of the acetic acid–sodium acetate buffer is not known.

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Summary

The kinetics of the reaction between hydrogen peroxide and chlorine to give oxygen and chloride ion was investigated in dilute hydrochloric acid solutions. The present results, when combined with those of Makower and Bray for higher hydrochloric acid concentrations, lead to the following mechanism for the reaction

$$H_2O_2 + Cl_2 \underset{k_b}{\overset{k_a}{\rightleftarrows}} H^+ + Cl^- + HOOCl$$

$$HOOCl \xrightarrow{k_c} O_2 + H^+ + Cl^-$$

In the region above 1 *M* hydrochloric acid the decomposition of HOOCl is the rate determining step while at lower acidity the slow step is the reaction of hydrogen peroxide with chlorine.

The second order rate constant, k_a, was found to have a value of 1.1×10^4 liters moles^{-1} min.$^{-1}$ at 25° and zero ionic strength. The activation energy for the reaction is 10,700 calories.

In the region of hydrochloric acid concentrations of $10^{-4}M$ and less, where the chlorine is essentially all hydrolyzed to hypochlorous acid, the mechanism of reaction becomes

$$HOCl = H^+ + ClO^-$$

$$ClO^- + H_2O_2 \xrightarrow{k_d} H_2O + O_2 + Cl^-$$

The rate determining step is the reaction of hydrogen peroxide with hypochlorite ion. The second order rate constant was found to be 1.7×10^5 liters moles^{-1} min.$^{-1}$ at 25° and zero ionic strength and the reaction between ClO^- and hydrogen peroxide has an activation energy of 11,600 calories.

In the region of $(H^+)(Cl^-)$ equal to 10^{-5} to 10^{-8} the reaction proceeds partly by the above two mechanisms and partly by a third mechanism. Several characteristics of this last reaction path are mentioned.

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