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

The Rate of Oxidation of Hydrogen Peroxide by Chlorine in the Presence of Hydrochloric Acid

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The rapid reaction between hydrogen peroxide and chlorine

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

has been shown by Livingston and Bray[1] to be involved in the catalytic decomposition of hydrogen peroxide in the presence of hydrochloric acid and chlorine. By analogy with the bromine–bromide system,[2] the mechanism of Reaction 1 was interpreted in terms of a single rate-determining reaction

$$H_2O_2 + HOCl \longrightarrow O_2 + H^+ + Cl^- + H_2O \qquad (2)$$

and a rapid reversible equilibrium, the hydrolysis of chlorine

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

The kinetic investigation presented in this paper was undertaken to test the predicted rate law

$$-d(H_2O_2)/dt = \kappa_2(H_2O_2)(HOCl) = k_2(H_2O_2)(Cl_2)/(H^+)(Cl^-) \qquad (4)$$

where

$$k_2 = \kappa_2 K' \text{ and } K' = (HOCl)(H^+)(Cl^-)/(Cl_2) \qquad (5)$$

The corresponding rate law has already been verified in the case of the closely related peroxide–bromine reaction[3] and the methods described below are similar to those used in the earlier investigation.

Methods

The rate of Reaction 1 was measured by following iodimetrically the decrease in total oxidizing power. The reaction was "quenched" by rapidly mixing a known volume of the reaction mixture with a solution which contained sufficient amounts of potassium iodide and $Na_2HPO_4 \cdot 12H_2O$ to have 2% potassium iodide and not over 0.2 M H^+ in the final solution. The resulting mixture was set aside in the dark for about one hour to allow time for the relatively slow reduction of hydrogen peroxide, and the liberated iodine was then titrated with thiosulfate. The low concentration of acid and the protection from light were necessary in order to minimize the oxygen error due to the reaction between O_2, I^- and H^+ (ref. 3, p. 1658).

At concentrations of hydrochloric acid between 0.35 and 2 N, the reaction was so rapid that it was necessary to resort to a special method of starting and quenching the reaction, namely, the *flow method;* at higher concentrations of the acid, when the rate was sufficiently low, the reaction mixtures

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(1) Livingston and Bray, THIS JOURNAL, **47**, 2069 (1925).

(2) Bray and Livingston, *ibid.*, **45**, 1251 (1923).

(3) Bray and Livingston, *ibid.*, **50**, 1654 (1928).

were analyzed by extracting samples at various time intervals. This was called the *sampling method.*

The application of the *flow method* to the study of high reaction velocities in solutions was first made by Hartridge and Roughton[4] and later by Roughton,[5] Bray and Livingston,[3] Saal,[6] Schmid[7] and La Mer and Read.[8] The principle of the method and the type of apparatus used in the present work are given in detail by Bray and Livingston.[3] Only certain modifications and improvements of the apparatus, Fig. 1, some of which are due to personal suggestions of Dr. Roughton, will be discussed here.

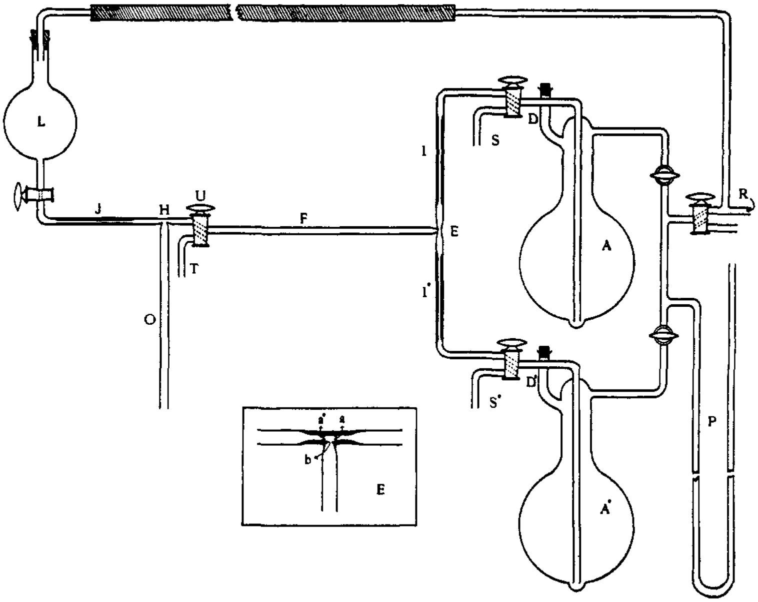

Fig. 1.—The flow apparatus.

On the application of pressure the component solutions of known concentrations (one containing hydrogen peroxide and the other chlorine) were forced to flow from A and A′ through I, I′, and to mix in a T-shaped mixing chamber E in less than one-fiftieth of a second. The reaction mixture then moved along the tube F, mixed with the "quenching solution" from L in another slightly larger mixing chamber H, and was finally collected in a two-liter volumetric flask placed beneath the tube O. An aliquot portion of this solution was later analyzed for the iodine content to determine the extent to which the reaction had proceeded. The time of the reaction, τ, was that necessary for the reaction mixture to travel from the first to the second mixing chamber. It was calculated from the expression $\tau = ut/V$, where u is the known volume of the reaction tube between E and H, and V is the volume of the solution delivered through tube O

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(4) Hartridge and Roughton, (a) *Proc. Roy. Soc.* (London), **A104,** 376 (1932); (b) *Proc. Camb. Phil. Soc.*, **22,** 426 (1924), and **23,** 450 (1926).

(5) F. J. W. Roughton, *Proc. Roy. Soc.* (London), **A126,** 439 (1930).

(6) R. N. J. Saal, *Rec. trav. chim.*, **47,** 73 (1926).

(7) H. Schmid, *Z. physik. Chem.*, **A141,** 41 (1929).

(8) La Mer and Read, THIS JOURNAL, **52,** 3098 (1930).

in the time t. The mixing chamber E (also shown in the inset E) was of a simple type originated by Hartridge and Roughton (Ref. 4a, p. 378). It consisted of a T-tube of low resistance to flow, and was made of 7-mm. tubing which was reduced at "a" to 2 mm. and at "b" to 3 mm. The cross sectional area at "b" was approximately twice that at "a." The Y-shaped mixing chamber, previously used by Bray and Livingston,[3] had determined the rate of flow because of its very high resistance. The rate of flow in the present apparatus was controlled more conveniently by means of capillary tubing in the system. I and I′ were 1-mm. capillaries 7 cm. long; J was a 2-mm. capillary 23 cm. long, so chosen that a volume of the reacting solution mixed with an approximately equal volume of the quenching solution from the liter flask L.

Details of operation and principles underlying the construction of a flow apparatus are given by Makower.[9]

The sampling method procedure was as follows. A measured volume of the reaction mixture containing all reagents with the exception of hydrogen peroxide was placed in a 500-cc. glass-stoppered flask and allowed to attain temperature equilibrium in a thermostat. Two 20-cc. samples of this mixture were withdrawn and analyzed iodimetrically for chlorine. The run was then started by adding 3 cc. of stock hydrogen peroxide solution with a pipet. After replacing the stopper, the flask was shaken vigorously by hand outside the thermostat; the time of the shaking was taken as the initial time for the reaction. At intervals, 20-cc. samples of the reaction mixture were pipetted into 125-cc. glass-stoppered flasks containing the quenching solution and were analyzed by the method described above. The time at which the pipet was half empty was taken as the quenching time. At the end of the run a portion of the remaining reaction mixture was analyzed for the concentration of acid by titration with a standardized solution of sodium hydroxide. If any chlorine was still present it interfered with the titration by destroying the indicator. Excess of hydrogen peroxide was therefore added to remove the chlorine and the sample was then titrated using methyl red as the indicator. The error due to formation of more hydrogen ion by this process is negligible. Incidentally, methyl red may be used to detect very small traces of chlorine in solution.

The concentrations of any other reagents used in the preparation of the reaction mixture were calculated from known weights or concentrations of these substances initially added and from the final volume of the reaction mixture. The specific gravities of concentrated reaction mixtures were also determined.

In the calculation of specific rates, since the concentrations of H^+ and Cl^- ions were relatively high and remained virtually constant during any one experiment, Equation 4 could be used in the form

$$-\mathrm{d}(H_2O_2)/\mathrm{d}t = k(H_2O_2)(\Sigma Cl_2) = k(A - x)(B - x) \tag{6}$$ [10]

where $(\Sigma Cl_2) = (Cl_2) + (Cl_3^-)$ and $k_2 = k(H^+)(Cl^-)[(\Sigma Cl_2)/(Cl_2)]$. A and B, are, respectively, the initial (H_2O_2) and (ΣCl_2). x is the decrease in (ΣCl_2) or (H_2O_2) in the time t minutes, and is calculated from the relation, $x = [(A + B) - (A + B - 2x)]/2$.

In the flow method experiments, k was calculated from the integrated expression for a second order reaction

$$k = \frac{2.303}{(A - B)_T} \log \frac{(A - x)\,(B)}{(B - x)\,(A)}$$

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(9) Makower, Ph.D. Thesis, May, 1932, University of California Library. This thesis may also be consulted for details omitted in the present paper.

(10) The symbol "( )" will be used to indicate "concentration of" in moles per liter.

while in the experiments done by the sampling method the calculations were carried out by the usual graphical method of plotting log $[(A - x)/(B - x)]$ against t, and multiplying the slope of the line by $2.303/(A - B)$.

The experimental results were expressed in terms of the specific rate k_2' which is related to k and k_2 by the equations

$$k_2' = k(\mathrm{H}^+)(\mathrm{Cl}^-) \quad \text{and} \quad k_2 = k_2'(\Sigma\mathrm{Cl}_2)/(\mathrm{Cl}_2) \tag{7}$$

Experimental Results at 25°

The Effect of Varying (HCl).—The results of the experiments at 25° in the presence of hydrochloric acid are summarized in Table I according to increasing concentration of the acid.

TABLE I

EXPERIMENTAL RESULTS IN SOLUTIONS OF HCl AT 25°

Run	$(H_2O_2)\ 10^3$	$(\Sigma Cl_2)\ 10^3$	(HCl)	$x(10^3)$	$\tau\ (10^2)$, min.	$k_2'(10^{-3})$
36	7.27	1.64	0.357	1.13	1.84	1.23
37	7.27	1.64	.357	1.26	2.32	1.28
47	7.11	10.10	.368	4.72	1.63	1.29
59	16.59	5.78	.369	5.16	1.74	1.35
60	16.59	5.78	.369	5.14	1.73	1.33
65	18.29	6.11	.378	5.55	1.68	1.42
66	18.29	6.11	.378	5.52	1.70	1.36
45	6.43	0.443	.381	0.786	2.08	1.15
46	6.43	.443	.381	.317	2.16	1.35
40	6.80	6.03	.385	3.42	2.00	1.37
38	7.06	2.52	.386	1.69	2.14	1.30
39	7.06	2.52	.386	1.43	1.69	1.21
41	6.59	10.07	.387	4.55	1.65	1.54
42	6.59	10.07	.387	4.80	2.08	1.40
43	6.85	7.82	.390	4.22	2.06	1.42
44	6.85	7.82	.390	3.91	1.68	1.46
69	7.45	5.39	.593	2.82	1.55	2.92
70	7.45	5.39	.593	2.94	1.77	2.76
27	8.87	10.75	1.13	4.36	2.27	4.69
28	8.87	10.75	1.13	4.65	2.70	4.43
25	15.66	10.36	1.51	5.23	2.28	5.44
26	15.66	10.36	1.51	5.62	2.70	5.39
S-1	1.14	1.63	1.88			6.00
81	10.54	9.33	2.08	2.87	2.65	6.59
82	10.49	9.33	2.08	3.05	2.98	6.56
S-2	1.28	1.80	3.03			2.24
S-3	1.11	2.45	3.94			0.792
S-5	7.16	7.16	5.30			.116

The original experimental numbers have been retained and they show the order in which the experiments were performed. The experiments by the sampling method (prefixed in the table by the letter "S") were carried out after those by the flow method had been completed. The preliminary experiments (1 to 24) not shown in the table were done in conjunction with H. A. Bois and experiments 25 to 37 were performed in collaboration with H. A. Young. Reasonably good agreement between the sampling and the flow methods is found by comparing experimental results of S-1 with the results of experiments 25, 26, 81 and 82. The relatively large number of experiments in the neighborhood of 0.4 *M* HCl shows the reproducibility of the flow method results and also serves to illustrate the bimolecular character of the reaction at one (HCl) when (Cl_2) and (H_2O_2) are varied. The hydrolysis of chlorine was less than one per cent. at the lowest acid concentration (0.36 *M* in Expt. 36) and was very much smaller in all other experiments.

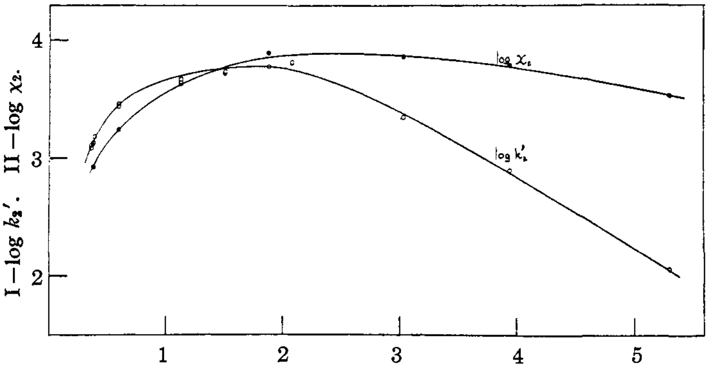

Fig. 2.

That the value of k_2' is not constant but has a maximum in the neighborhood of 2 *M* HCl is indicated by Curve I in Fig. 2, where log k_2' from Table I is plotted against (HCl). This variation, at least for (HCl) higher than 2 *M*, will be shown to be primarily a manifestation of the "secondary or equilibrium salt effect,"[11] namely, the salt effect on the chlorine hydrolysis equilibrium, Equations 3 and 5.

A relatively small part of the variation of k_2' with (HCl) is accounted for by the trichloride correction (Equation 7) expressed by means of the factor (ΣCl_2)/(Cl_2). This factor can be calculated from the relation,

$$(\Sigma Cl_2)/(Cl_2) = 1 + K_{Cl_3^-}\gamma_{Cl_2}m_{Cl^-} \quad (8)$$

where $K_{Cl_3^-} = (Cl_3^-)/m_{Cl^-}(Cl_2)\gamma_{Cl_2}$ is an equilibrium constant specially defined[13] for the reaction, $Cl_2 + Cl^- \rightleftharpoons Cl_3^-$. m_{Cl^-} is the "molality" of chloride ion in moles per 1000 g. of water, and γ_{Cl_2} is the activity coefficient of chlorine as defined by Lewis and Randall.[12] The values of

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[11] (a) Brönsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, New York, 1927; (b) Livingston, "Introduction to Chemical Catalysis in Homogeneous Systems," *J. Chem. Ed.*, **7**, 2887 (1930); (c) La Mer, *Chem. Rev.*, **10**, 179 (1932); (d) Liebhafsky, THIS JOURNAL, **54**, 1803 (1932), Footnote 15.

[12] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Co., New York, 1923.

$(\Sigma Cl_2)/(Cl_2)$ and of k_2 at various concentrations of hydrochloric acid have been calculated by means of Equations 7 and 8 and are listed in Table II. The value of $K_{Cl_3^-} = 0.17$ for hydrochloric acid solutions at 25° was obtained from the data of Sherrill and Izard[13] and the activity coefficient of chlorine, γ_{Cl_2}, was calculated by means of the Debye–McAuley law[14] for non-electrolytes, $\log \gamma = c\mu$, where μ is the ionic strength[12] expressed in terms of moles/1000 g. of water. The value of the constant $c = 0.02$ for hydrochloric acid solutions at 25° was obtained from unpublished work of M. H. Gorin of this Laboratory, and it agrees well with similar data published later by Sherrill and Izard.[13]

TABLE II

VALUES OF $[(Cl_2) + (Cl_3^-)]/(Cl_2)$ AND OF k_2 IN HYDROCHLORIC ACID SOLUTIONS AT 25°

HCl, mole/liter	0	0.5	1.0	2.0	3.0	4.0	5.0
$(\Sigma Cl_2)/(Cl_2)$	1	1.09	1.18	1.39	1.63	1.90	2.20
k_2 (10^{-3})		2.39	5.40	7.30	3.82	1.31	0.39

In order to allow for the "equilibrium salt effect," the concentration of HOCl (*cf.* Equation 4) must be calculated from the chlorine hydrolysis equilibrium expression $K = a_{HOCl}a_{H^+}a_{Cl^-}/a_{Cl_2}a_{H_2O}$, defined in terms of the "activities"[12] of the substances involved. Since the activity coefficients for HOCl are not known it will be convenient to assume that $(HOCl) = a_{HOCl}$. This assumption is not unreasonable inasmuch as concentrations do not usually differ greatly from activities in the cases of neutral substances.

The rate law for Equation 1 will now be given by the equation

$$-d(H_2O_2)dt = \kappa_2(H_2O_2)(HOCl) = \chi_2(H_2O_2)\; a_{Cl_2}a_{H_2O}/a_{H^+}a_{Cl^-}] \qquad (14a)$$

where

$$\chi_2 = \kappa_2 K \qquad (14b)$$

Comparison of Equation 14 with Equations 6 and 7, yields

$$\chi_2 = k_2' \frac{(Cl_2)\; a_{H^+}a_{Cl^-}}{a_{Cl_2}\,(H^+)(Cl^-)\; a_{H_2O}} \frac{(\Sigma Cl_2)}{(Cl_2)} \qquad (15)$$

Since in any given reaction mixture $(Cl_2)/m_{Cl_2} = (H^+)/m_{H^+}$

$$\chi_2 = k_2' \frac{m_{Cl^-}\gamma^2_{\pm HCl}}{(Cl^-)a_{H_2O}\gamma_{Cl_2}} \frac{(\Sigma Cl_2)}{(Cl_2)} \qquad (16)$$

Values of χ_2 were calculated from Equation 16 for a number of representative experiments using the results of Table II for $(\Sigma Cl_2)/(Cl_2)$ and data of Randall and Young[15] for the activities of hydrochloric acid and water. The values of χ_2 are given in Table III and are plotted in Fig. 2 (Curve II).

A comparison with Curve I indicates that while below 2 *M* hydrochloric acid there still exists a rapid decrease of χ_2 with decreasing (HCl), above

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(13) Sherrill and Izard, THIS JOURNAL, **53**, 1667 (1931).

(14) Debye and McAuley, *Physik. Z.*, **26**, 22 (1922).

(15) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

TABLE III

CALCULATION OF χ_2

Run	$k_2'(10^{-3})$	(HCl)	m_{HCl}	$\gamma_{\pm HCl}$	a_{H_2O}	γ_{Cl_2}	$\chi_2(10^{-3})$
65	1.38	0.38	0.38	0.76	0.99	1.02	0.85
69	2.82	.59	.59	.76	.98	1.03	1.77
27	5.10	1.13	1.15	.84	.96	1.06	4.31
S-1	6.10	1.88	1.95	1.00	.92	1.09	7.90
S-2	2.38	3.03	3.22	1.39	.85	1.16	7.20
S-3	0.79	3.94	4.28	1.90	.79	1.22	6.20
S-5	.116	5.30	5.92	3.15	.68	1.30	3.39

that concentration of the acid the value of χ_2 remains practically constant; in other words, in this region of high (HCl) the difference between Curves I and II is satisfactorily explained by the equilibrium salt effect on Reaction 1.

This "salt effect" is further demonstrated by an additional set of experiments in which (H^+) and (Cl^-) were varied independently at a constant value of the ionic strength, approximately 5 mole/liter. Exact results can scarcely be expected since the calculations of χ_2, Table IV, involve the application of the laws listed below which are strictly valid only at low ionic strengths.

γ_{HCl} and a_{H_2O} at any ionic strength are equal, respectively, to γ and a of these substances in a solution of pure hydrochloric acid of the same ionic strength. γ_{Cl_2} was calculated from the Debye–McAuley law[14] with the aid of a further assumption that for a mixture of electrolytes, $\log \gamma_{Cl_2} = c_1\mu_1 + c_2\mu_2 + \ldots c_i\mu_i$, where μ_i is the contribution to the total ionic strength of the particular electrolyte i. The values of c_i as compiled by M. H. Gorin are: $c_{HCl} = 0.02$; $c_{HClO_4} = -0.02$; $c_{NaCl} = 0.11$; $c_{NaClO_4} = 0.06$; $c_{NaNO_3} = 0.03$.

TABLE IV

RESULTS AT CONSTANT IONIC STRENGTH AT 25°

Run	(H^+)	(Cl^-)	(H^+)(Cl^-)	μ in[c] m/liter	f[a]	$\gamma_{\pm HCl}$	$10 \times a_{H_2O}$	$10^2 \times K_{Cl_3^-}$[b]	γ_{Cl_2}	$\frac{(\Sigma Cl_2)}{(Cl_2)}$	k_2' (10^{-2})	χ_2 (10^{-2})
S-17	2.08	2.08	4.33	5.01	1.22	3.30	6.84	7.1	1.84	1.33	3.70	52.3
S-10	2.07	3.05	6.31	5.00	1.17	3.12	6.78	7.2	2.05	1.53	4.75	59.2
S-11	2.07	4.00	8.27	4.97	1.14	2.88	6.96	7.4	2.26	1.76	5.00	52.4
S-13	2.04	4.95	10.10	4.95	1.11	2.76	7.06	7.4	2.52	2.02	5.25	50.0
S-14	2.94	1.96	5.75	4.90	1.22	3.14	6.74	8.7	1.42	1.30	3.35	52.5
S-15	3.98	2.04	8.11	4.95	1.21	3.16	6.74	11.8	1.18	1.34	1.68	34.2
S-16	4.95	2.02	10.00	4.95	1.20	3.14	6.74	17.0	0.95	1.39	1.16	29.8
S-22	0.414	0.414	0.171	4.91	1.19	3.05	6.84	5.5	1.85	1.05	6.80	59.5
S-20	.210	.803	.169	4.95	1.18	3.12	6.79	5.3	2.13	1.11	6.15	54.3
S-21	.748	.198	.148	4.91	1.21	3.13	6.75	5.7	1.77	1.02	5.30	53.8

[a] The factor "f" when multiplied by concentration in moles per liter gives "molality," or moles per 1000 g. of water; it was calculated from the specific gravities of the reaction mixtures.

[b] The results of Sherrill and Izard[13] indicate great variations in the value of $K_{Cl_3^-}$ with (Na^+). For reaction mixtures containing this ion empirical values of the constant given by these authors have been used.

[c] Added electrolytes in the various experiments are as follows: in S-17 $NaClO_4$; in S-10 and S-11 $NaClO_4$ and NaCl; in S-14 and S-15 $NaClO_4$ and $HClO_4$; in S-16 $HClO_4$; in S-22 $NaNO_3$; in S-20 $NaNO_3$ and NaCl; in S-21 $NaNO_3$ and $HClO_4$.

The results of this set of experiments (Table IV) are shown to be in agreement with those of the previous set (Table III) when the values of log χ_2 taken from both tables are plotted against the square root of the activity of HCl, $\sqrt{a_{HCl}} = \sqrt{a_{H^+}a_{Cl^-}} = a_{\pm HCl}$, in Fig. 3. All the results fall on a well-defined curve with the exception of two, Runs S-15 and S-16, which are characterized by high ($HClO_4$). This deviation can, perhaps, be accounted for by the approximate nature of the assumptions (*cf.* preceding paragraph) used in calculating χ_2.

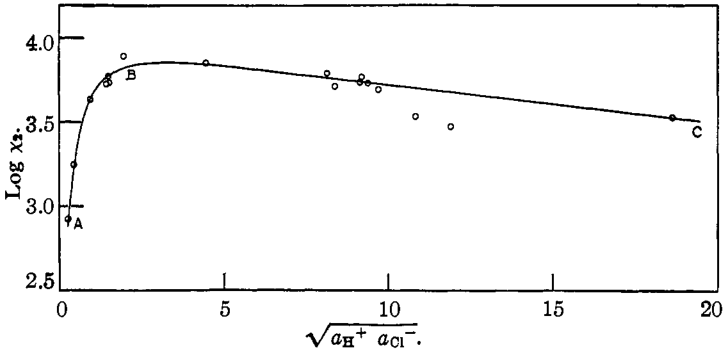

Fig. 3.

In the region BC of Fig. 3, in which the value of the product, $a_{H^+}a_{Cl^-}$, changes 90-fold (from 4 to 360), the value of k_2' changes 55-fold (from 6000 to 110) while the value of χ_2 undergoes only a two-fold variation (from 7000 to 3500). This variation can be ascribed to the assumption involved in formulating Equation 14(a). If the average value of χ_2 is taken as $5(10^3)$ and $K = 4.84(10^{-4})$ is adopted for the hydrolysis equilibrium constant at 25° (Lewis and Randall, Ref. 12, p. 508), then the specific rate, κ_2, of the bimolecular reaction, Equation 2, can be calculated by means of Equation 14(b)

$$\kappa_2 = \frac{\chi_2}{K} = \frac{5(10^3)}{4.84(10^{-4})} = 1(10)^7 \text{ at } 25° \qquad (17)$$

Discussion of Results at Low Values of the Activity of Hydrochloric Acid.—It is evident from Fig. 3 (region AB), that, when $a_{\pm HCl}$ is less than 2, the value of χ_2 suffers a rapid decrease which cannot be explained by the equilibrium salt effect. That this decrease is a function of the activity of hydrochloric acid and not of its concentration can be shown by comparing the result of experiment S-22 (Table IV), carried out at high ionic strength, with the results previously obtained under different conditions.

The possibility that either (H^+) or (Cl^-) has a specific effect on the rate is eliminated by the results of Experiments S-20, S-21 and S-22 (Table IV). Although individual concentrations of H^+ and Cl^- ions are different, the

TABLE V

RELATION OF χ_2 TO ACTIVITY OF HYDROCHLORIC ACID

	Ionic strength	$\sqrt{(H^+)(Cl^-)}$	$\sqrt{a_{H^+}a_{Cl^-}}$	$\chi_2(10^{-2})$
Run S-22	4.91	0.414	1.50	59.5
From Fig. 2	0.414	.414	0.097	9.55
From Fig. 2	1.65	1.65	1.53	64.0

activities of hydrochloric acid and therefore the values of χ_2 in the three experiments are nearly the same. Similar evidence is obtained from the results of additional experiments given in Table VI.

TABLE VI

THE EFFECT OF VARYING THE PRODUCT (H^+) (Cl^-) ON THE VALUE OF k_2' AT 25°

Run	$(H_2O_2)10^3$	$(\Sigma Cl_2)10^3$	(H^+)	(Cl^-)	$(H^+)(Cl^-)$	μ in m/l.	$k_2'(10^{-3})$	Added electrolyte
71	7.78	6.42	0.256	0.607	0.155	0.607	1.36	NaCl
72	7.78	6.42	.256	.607	.155	.607	1.34	NaCl
73	8.01	6.51	.611	.257	.157	.611	1.39	$HClO_4$
74	8.01	6.51	.611	.257	.157	.611	1.39	$HClO_4$
From Fig. 2 for comparison			.396	.396	.156	.396	1.50	
			.609	.609	.370	.609	2.95	
61	6.88	6.70	.589	.198	.117	.589	1.05	$HClO_4$
62	6.88	6.70	.589	.198	.117	.589	1.08	$HClO_4$
From Fig. 2 for comparison			.342	.342	.117	.342	1.10	
			.589	.589	.347	.589	2.80	
75	7.78	6.76	.512	2.02	1.03	2.02	4.33	NaCl
76	7.78	6.76	.512	2.02	1.03	2.02	4.17	NaCl
From Fig. 2 for comparison			1.015	1.015	1.03	1.015	4.70	
			2.02	2.02	4.08	2.02	5.80	

This series of experiments consists of three groups. Since in each group the ionic strength is relatively small and nearly constant, it is possible to use the product $(H^+)(Cl^-)$ instead of $a_{H^+}a_{Cl^-}$, and k_2' instead of χ_2, for the purpose of comparison. In each group it is shown that the value of k_2' depends primarily on the value of the product $(H^+)(Cl^-)$, and that a change in ionic strength at constant value of the product has only a small effect, proving that the variation of χ_2 with the activity of hydrochloric acid is not the ordinary kinetic salt effect[11d] but has another significance. In terms of the postulated mechanism this result represents a decrease in the specific rate, κ_2, of the rate determining step, Equation 2. In the region AB, Fig. 3, the value of κ_2 (*cf.* Eq. 14b) changes from $7500/4.8(10^{-4}) = 1.5(10^7)$ to $850/4.8(10^{-4}) = 1.7(10^6)$, a nearly ten-fold decrease for a corresponding change in the value of $a_{H^+}a_{Cl^-}$ from 4.0 to 0.16. In another investigation begun in this Laboratory the above decrease was found to extend to very low activities or concentrations of hydrochloric acid, or to the coincidentally high concentrations of HOCl. A direct measurement of the rate of the reaction between HOCl and hydrogen peroxide yielded an amazingly small value for the specific rate of this bimolecular reaction, varying between 14 and 2000, depending on the (HCl) and other conditions of the experiment. No kinetic explanation of this phenomenon can as yet be offered.

Effect of Temperature.—Additional measurements of the rate of Reaction 1 were performed by means of the sampling method at 10 and 0.6°. The results, together with values at 25° taken from Fig. 2, are summarized in Table VII.

TABLE VII

THE VARIATION OF k_2' WITH THE TEMPERATURE

	k_2'				k_2'		
(HCl)	25°	10°	0.6°	(HCl)	25°	10°	0.6°
0.414	1580	530		1.99	5300	2000	
.408	1580		320	2.06	5150		900
.998	4580	1720		4.11	590	165	
.986	4500		1030	3.89	795		105

The over-all heat of activation, Q_1, of Reaction 1, in the region in which χ_2 remains nearly constant (2 *M* HCl and above) was calculated to have an average value of 12,000 ± 2000 calories; in the region of the rapid decrease of χ_2 it was somewhat smaller, 11,000 ± 2000 cal.

The value of Q_2, or the heat of activation of Reaction 2, is obtained by subtracting from Q_1 the value of ΔH, the heat of reaction for the hydrolysis of chlorine. The value of ΔH as given by Lewis and Randall (Ref. 12, p. 508) undergoes a considerable variation with the temperature, from 10,000 cal. at 0° to 6000 cal. at 25°, and the value of Q_1 should exhibit a corresponding decrease if the assumed mechanism is correct. However the present data at 0.6 and 10° are not accurate enough to test this prediction.

If 8000 cal. be taken as the average value of ΔH, the value of $Q_2 = 12{,}000 - 8000 = 4000 \pm 2000$ cal. and the change of the specific rate, κ_2, of the bimolecular reaction with the temperature (*cf.* Equation 17) can be given approximately by the expression $\kappa_2 = 10^{10}e^{-4000/RT}$ where $10^{10 \pm 1.5}$ is the order of magnitude of the Arrhenius constant.

A Possible Detailed Mechanism.—We consider the conclusion that the reaction between H_2O_2 and HOCl is bimolecular to be a definite result; and realize that an attempt to select a detailed mechanism for a reaction that takes place in the presence of water molecules must be regarded as highly speculative. Nevertheless, it is of interest to apply to this reaction the new method of attack recently proposed by Olson.[16] Each of the reacting molecules has seven pairs of valence electrons which presumably form a tetrahedron around the oxygen or chlorine kernel. The new idea is that the separation of Cl^- (with eight electrons) takes place gradually as the hydrogen peroxide molecule approaches the HOCl molecule, and supplies a pair of electrons (on one of the oxygen atoms of hydrogen peroxide) to form a new bond at the face of the tetrahedron opposite to the chlorine;

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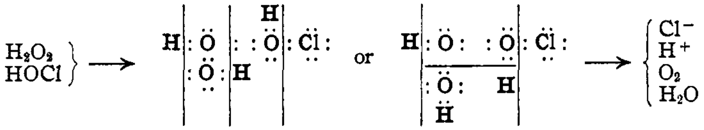
[16] Olson, *J. Chem. Phys.*, **1**, 418–423 (1933).

the separation of Cl^- and the formation of the new bond are simultaneous processes. While this "inversion" is taking place the $H_3O_3^+$ is splitting into H^+, O_2 and H_2O. The whole process may be represented diagrammatically as follows



On account of the symmetry of the $H_3O_3^+$ radical, the two diagrams represent the same process. It is thus impossible to decide whether the resulting oxygen molecule consists of two atoms from one peroxide molecule or one atom from each of the reaction molecules.

The assumption that HOCl in some of its reactions dissociates into HO^+ and Cl^- has been made by W. A. Noyes[17] and has been applied by him to the reaction with hydrogen peroxide.[18] The detailed mechanism here suggested is similar in so far as the dissociation of chlorine is concerned but denies the actual existence of HO^+ at any stage of the process.

Summary

1. The rate of the rapid reaction

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

has been measured over a large (0.4 to 5.2 M) range of hydrochloric acid concentrations. A "flow method" was used at 25° when the activity of the acid was low, because of the high speed of the reaction. A "sampling method" was used in all other experiments.

2. The rate of the reaction was found to agree in general with the rate law predicted by Livingston and Bray[1]

$$-\frac{d(H_2O_2)}{dt} = \chi_2 \frac{(H_2O_2)\, a_{Cl_2} a_{H_2O}}{a_{H^+} a_{Cl^-}} \qquad (14a)$$

When the activity of hydrochloric acid is higher than 2 M, χ_2 is nearly constant, and has a value of $5(10^3)$ at 25°. These results furnish further evidence that the rate-determining step for Reaction 1 involves the bimolecular reaction

$$H_2O_2 + HOCl \xrightarrow{\kappa_2} O_2 + H_2O + H^+ + Cl^-, \quad \text{where} \qquad (2)$$
$$-d(H_2O_2)/dt = \kappa_2(H_2O_2)(HOCl)$$

3. The bimolecular reaction has the maximum specific rate, $\kappa_2 = 1(10^7)$ at 25°, when (HOCl) is 10^{-7} or less. At other temperatures the rate constant is at least approximately represented by the equation, $\kappa_2 = 10^{10 \pm 1.5} e^{(-4000 \pm 2000)/RT}$. At low concentrations of hydrochloric acid and the corresponding high concentrations of HOCl this law is not obeyed and κ_2 is much smaller.

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(17) W. A. Noyes, THIS JOURNAL, **51**, 2391 (1929).

(18) Letter to W. C. Bray of May 29, 1933.

4. A possible detailed mechanism for the bimolecular reaction has been discussed.

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Phase Rule Equilibria of Acid Soaps. IV. The Three-Component System Potassium Laurate–Lauric Acid–Water[1]

BY JAMES W. MCBAIN AND MALCOLM C. FIELD

In the past no attempt has been made to study the equilibria in aqueous solutions or suspensions of acid soaps by application of the phase rule. It is not surprising that this field has been neglected, because the phases which exist are in all cases very difficult to examine by the usual means. Generally, the separation even of two isotropic liquid phases is hindered by high viscosity. The authors have kept such systems for months in a thermostat at 90°, and in most cases at the end of this period very little separation had taken place.[2] We had to develop, therefore, a completely new technique.

Previous observations on the much disputed subject of acid soaps[3] mostly consist of analyses of sediments obtained from more or less dilute soap solutions. As found by Chevreul in 1823, and confirmed by Krafft and many others, these sediments exhibit a composition intermediate between that of neutral soap and fatty acid. However, in most cases this by no means indicates the composition or even establishes the existence of acid soaps because the sodium soaps and the higher potassium soaps are themselves fairly insoluble at room temperature and the sediments may consist of chance heterogeneous mixtures of variable composition usually containing both acid soap and soap itself.[4] On the other hand, the crystalline sediments from dilute solutions of a soluble soap such as potassium laurate are unquestionably acid soaps. However, in no case had sufficient care been taken to identify and characterize these different constituents.

In the corresponding anhydrous systems the acid soaps have now been definitely characterized as well-crystallized chemical substances of definite composition, not entering into isomorphous mixtures or solid solutions. Complete phase rule diagrams have been obtained for several of these anhydrous two-component systems.[1] Likewise, the other two-component system, potassium laurate–water, was mapped out in a previous study.[5]

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(1) This is the fourth of a series of studies of acid soaps carried out at Bristol University, England, in 1925–1927. For previous references see J. W. McBain and M. C. Field, *J. Phys. Chem.*, **37**, 675 (1933); J. W. McBain and M. C. Field, and J. W. McBain and A. Stewart, *J. Chem. Soc.*, 920, 924, 928 (1933); see also J. W. McBain and A. Stewart, *ibid.*, 1392 (1927).

(2) Compare R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, **24**, 1329 (1932).

(3) See references given in the first communication of this series.

(4) Examples of such experiments leading to erroneous conclusions are R. Zsigmondy and W. Bachmann, *Kolloid-Z.*, **11**, 156 (1912); W. Prosch, *Z. deut. Öl- Fett-Ind.*, **42**, 450 (1922).

(5) J. W. McBain and M. C. Field, *J. Phys. Chem.*, **30**, 1545 (1926).