TABLE II

POLARIZATIONS AND MOMENTS OF SUBSTITUTED PHENYLACETYLENES

Phenylacetylene	P_∞	MR_D	$10^{18}\mu$
p-Chloro-	58.85	39.71	0.96
p-Bromo-	61.26	42.61	.95
m-Chloro-	78.46	39.11	1.38
m-Bromo-	80.79	43.18	1.35
o-Chloro-	99.53	39.76	1.69
o-Bromo-	109.15	42.66	1.79
p-Ethyl-	67.47	44.62	1.05
p-Methyl-	60.09	39.14	1.01
p-Isopropyl-	75.24	49.23	1.12
p-Nitro-	286.7	45.00[a]	3.42

[a] Taken from Bergmann and Tschudnowsky, Ref. 1.

Discussion of Results

The paraffin hydrocarbons like methane and ethane have no moment. This is also true of benzene. If however a phenyl group is substituted for a hydrogen atom of methane the compound formed, toluene, has a moment of 0.4 *D*. From the moments of the various derivatives of toluene it has been shown that the plus end of the toluene moment is toward the methyl group. An inspection of the values of Table II will show that the moment of the phenylacetylene is in a direction opposite to that in toluene. By taking the values of the moments of chlorobenzene, bromobenzene, toluene and nitrobenzene as 1.52, 1.50, 0.40 and 3.98, respectively, the moments of the para-substituted phenylacetylenes give values of 0.56, 0.55, 0.61 and 0.56 for the moment of phenylacetylene. The error in neglecting P_A is smallest with *p*-nitrophenylacetylene and 0.56 will be accepted as the best value for the phenylacetylene moment. Using a value of 0.56 for the phenylacetylene moment, the moments of the meta-substituted phenylacetylenes can be calculated. For *m*-chlorophenylacetylene the calculated moment is 1.34 as compared to an observed value of 1.38. For *m*-bromophenylacetylene the calculated moment is 1.31 and the observed 1.35. No numerical calculations were attempted with the ortho substituted compounds as usually the results are erroneous because owing to the close proximity of the groups inductive effects are very prominent. In spite of the "ortho effect" the moments of the ortho substituted phenylacetylenes are considerably greater than those of the meta compounds. This is of course as expected.

Summary

1. The replacement of a hydrogen of acetylene with a phenyl group causes a redistribution of electricity such that the compound has a moment of approximately 0.56 *D*.

2. This moment is opposite in direction to that present in toluene.

3. Electric moments have been determined for *p*-chloro-, *p*-bromo-, *m*-chloro-, *m*-bromo-, *o*-chloro-, *o*-bromo-, *p*-methyl-, *p*-ethyl-, *p*-isopropyl-, and *p*-nitrophenylacetylenes.

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

The Catalytic Decomposition of Hydrogen Peroxide in an Acid Chlorine–Chloride Solution. II. The Steady State Function at 0 to 25°

BY BENJAMIN MAKOWER

Introduction

The catalytic decomposition of hydrogen peroxide in the presence of chlorine and hydrogen chloride has been shown by Livingston and Bray[1] to be closely related to the two chemical reactions

$$H_2O_2 + 2H^+ + 2Cl^- = Cl_2 + 2H_2O \quad (1)$$

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

and is believed to be due to the occurrence of these two compensating reactions at equal rates. In any given experiment, a steady state is established in which the concentrations of Cl_2, H^+ and Cl^- remain constant and the net result is

$$2H_2O_2 = O_2 + 2H_2O \quad (3)$$

At the steady state, the concentration relations and the rate of disappearance of H_2O_2 were found by Livingston and Bray[1] to be governed by the equations

$$R = (Cl_2)/(H^+)^2(Cl^-)^2 \quad (4)$$

and

$$d(H_2O_2)/dt = k(H_2O_2)(H^+)(Cl^-) \quad (5)$$

These results, and the analogy to the corresponding bromine system studied previously by Bray and Livingston[2] led to the following interpretation.

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

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

Reactions 1 and 2 involve, respectively, the formation and removal of HOCl which exists at a concentration determined by the hydrolysis equilibrium of chlorine, $Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$. The rate law for Reaction 1 is assumed to be

$$-d(H_2O_2)/dt = k_1(H_2O_2)(H^+)(Cl^-) \qquad (6)$$

where $k_1 = k/2$; that for Reaction 2 is

$$-d(H_2O_2)/dt = \kappa_2(H_2O_2)(HOCl) = k_2(H_2O_2)(Cl_2)/(H^+)(Cl^-) \qquad (7)$$

where $k_2 = K'\kappa_2$ (K' is the equilibrium constant for the hydrolysis of chlorine). The steady state function, Equation 4, is derived by equating the above two rate expressions, thus giving rise to the relation

$$R = k_1/k_2 \qquad (8)$$

That at a distance from the steady state the rate law for Reaction 2 has the form predicted by Equation 7 has already been shown by Makower and Bray;[3] a similar test for Reaction 1 is not possible because of the rapidity with which the steady state is realized. A further verification, presented in the present paper, consists of showing that the value of R obtained from the measurements at the steady state is numerically equal to the quotient $k/2k_2$ or k_1/k_2, and that the temperature coefficient of R can be calculated from the independently measured temperature coefficients of k_1 and k_2.

Concentration Relations at the Steady State

Livingston and Bray[1] have measured the concentration of chlorine at the steady state over a small range of hydrochloric acid concentrations (4.55 to 5.86 M) by extracting the chlorine from the steady state mixture with carbon tetrachloride and determining its amount iodimetrically. For the purpose of comparison with kinetic data, it was desirable to extend these measurements to lower acid concentrations. Since under this condition the above method proved unsatisfactory because of analytical difficulties in determining minute amounts of chlorine, a new procedure, capable of giving more accurate results, was designed.

Approximately 150 cc. of a steady state mixture composed of known hydrogen chloride solution and 1 to 2 cc. of "Superoxol" (30% H_2O_2) was placed together with about 75 cc. of carbon tetrachloride in a 250-cc. glass-stoppered bottle and kept in a thermostat at 25° for about eight hours. During that interval, the flask was very frequently shaken by hand to establish equilibrium distribution of chlorine between the two phases. An electrically driven stirrer was used for that purpose in the experiments at lower temperatures, Table III, where the approach to the steady state was rather slow. Ten- to 25-cc. samples of the carbon tetrachloride layer were then pipetted and analyzed iodimetrically for chlorine until further shaking produced no increase in its concentration. In some experiments an excess of chlorine was introduced initially and the approach to the steady state was then marked by a diminution of its concentration to a value which agreed well with the one obtained by the former procedure.

The concentration of total available chlorine, (ΣCl_2), (where $(\Sigma Cl_2) = (Cl_2) + (Cl_3^-)$),[4] in the aqueous phase, was calculated from the known distribution ratio of chlorine between the carbon tetrachloride and the given hydrogen chloride solution. The steady state constant, R (Equation 4), was evaluated by means of the equations

$$R' = (\Sigma Cl_2)/(H^+)^2(Cl^-)^2 \qquad (9)$$

and

$$R = R'(Cl_2)/(\Sigma Cl_2) \qquad (10)$$

where the term $(Cl_2)/(\Sigma Cl_2)$ is the correction factor for the presence of trichloride ion.

The value of the distribution ratio of Cl_2 between CCl_4 and the aqueous phase, $(Cl_2)_{CCl_4}/[a_{Cl_2}]_{H_2O} = 29.4$ at 25°, was obtained from the data given by Lewis and Randall.[5] a_{Cl_2} is the activity of the chlorine equal to $m_{Cl_2}\gamma_{Cl_2}$, where m is "molality" in moles per 1000 g. of water, and γ is the activity coefficient.[5] Another, more serviceable form of the above equation was used in practice, namely

$$(Cl_2)_{CCl_4}/[m_{\Sigma Cl_2}]_{H_2O} = 29.4\ \gamma_{Cl_2}\ [(Cl_2)/(\Sigma Cl_2)]_{H_2O}$$

The values of γ_{Cl_2} were taken from the data of Sherrill and Izard,[6] and the values of the factor $(Cl_2)/(\Sigma Cl_2)$ from the calculations of Makower and Bray (Ref. 3, Table II). In a number of experiments (Nos. 1, 5 and 7 in Table I) the distribution ratio was determined experimentally and found to check with the calculated values to within 3 per cent.

The results of the measurements are summarized in Table I.

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(3) Makower and Bray, THIS JOURNAL, 55, 4765 (1933).

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

(5) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 502.

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

TABLE I

MEASUREMENTS OF THE STEADY STATE CONCENTRATIONS AT 25°

Expt.	(HCl) × 10^4	$(Cl_2)_{CCl_4}$	$\frac{(Cl_2)_{CCl_4}}{(\Sigma Cl_2)_{H_2O}}$	$10^5\,(\Sigma Cl_2)_{H_2O}$	$R'(10^8)$	$\frac{(Cl_2)}{(\Sigma Cl_2)}$	$R(10^8)$
1	2.84	0.23	22.3	0.103	1.59	0.635	1.01
2	3.27	.66	21.4	.308	2.72	.590	1.61
3	3.78	3.00	20.4	1.47	7.24	.545	3.94
4	3.90	4.25	20.1	2.12	9.17	.535	4.90
5	3.98	4.70	19.9	2.36	9.48	.530	5.03
6	4.60	25.0	19.0	13.2	29.7	.485	14.4
7	5.25	120	18.3	64.5	85.5	.440	37.6

Calculation of *R* from the Kinetic Data at a Distance from the Steady State.—The validity of Equation 8 will now be tested by comparing the measured values of the steady state constant, *R*, with those calculated from the kinetic measurements, namely, with the values of k_1/k_2. The values of k_1 obtained by Livingston and Bray,[1] the values of k_2 measured by Makower and Bray,[3] and the calculated values of k_1/k_2 were all plotted against (HCl) and are represented by smooth curves in Fig. 1. The measured values of *R* taken from Table I were plotted on the same figure (solid circles) and are seen to fall almost exactly on the theoretical curve of k_1/k_2 against (HCl).

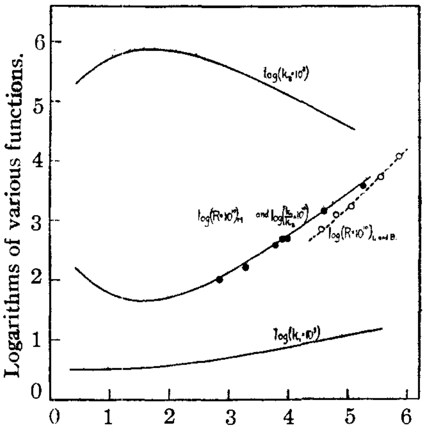

Fig. 1.—Measured values of *R* at 25°: ○, Livingston and Bray; ●, Makower. The ordinates are: for upper curve, log $k_2(10^2)$; for middle curves, log $R(10^{10})$ and log $[k_1/k_2]10^{10}$; for lower curve, log $k_1(10^5)$.

A plot of the results of the measurements of *R*, which were made earlier by Livingston and Bray[1] and which were recalculated in order to allow for the (Cl_3^-), is also shown in Fig. 1. The two sets of results are in good agreement except for a small discrepancy at lower acid concentrations, which is undoubtedly due to an experimental error inherent to the method used in the earlier work.

It remains now to explain the great variation in the value of *R*, which, according to the results in Table I, undergoes a 37-fold decrease between 5.25 and 2.84 *M* HCl. Since *R* represents a ratio of two specific rates, k_1/k_2, any correction factors which account for the variation of k_1 and of k_2 with (HCl) (see Fig. 1) will also account for the corresponding variation in the value of *R*. The corrected steady state function, ρ, will now be defined by the equation

$$\rho = k_1/\chi_2 \qquad (11)$$

where χ_2 is the specific rate for Reaction 2 corrected for the equilibrium salt effect (*cf.* Ref. 3).

TABLE II

CALCULATION OF ρ AT 25°

(HCl)	$k_1(10^5)$	$\chi_2(10^{-2})$	$\rho(10^9)$
0.5	3.16	13.2	24
1.0	3.24	37.0	8.8
1.5	3.31	59.5	5.6
2.0	3.72	73.5	5.1
3.0	5.14	73.5	6.9
4.0	7.40	59.5	12.4
5.0	11.7	39.5	29.6

The values of k_1 from Fig. 1, the values of χ_2 from data of Makower and Bray,[3] and the calculated values of ρ are given in Table II and are represented graphically in Fig. 2.

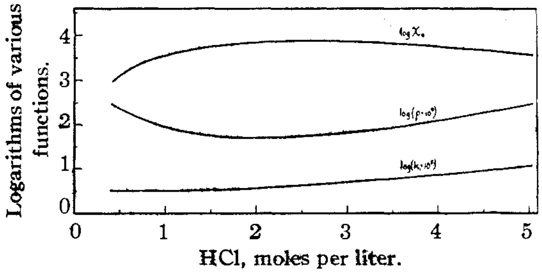

Fig. 2.—The ordinates are: for upper curve, log χ_2; for middle curve, log ρ × 10^{10}; for lower curve, log $k_1(10^5)$.

It is evident from the results in Figs. 1 and 2, that for (HCl) higher than 2 M, while R undergoes a 75-fold increase with increasing (HCl), the corresponding values of ρ vary only six-fold. An inspection of Fig. 2 reveals that this remaining variation is primarily due to that in the value of k_1 and is a manifestation of the kinetic salt effect on Reaction 1.

Livingston and Bray[1] attempted to account for this effect by the application of Brönsted's[7] activity rate theory. Their results at higher concentrations of hydrochloric acid were recalculated using more accurate values of the activity coefficients, but these new results show as much variation with (HCl) as the original experimental values of k_1. This fact casts some doubt on the applicability of the Brönsted theory to this reaction.

When (HCl) is lower than 2 M, the rapid increase in the value of ρ with decreasing (HCl) results from the corresponding decrease in the value of χ_2 (*cf.* Ref. 3). It is worthy of note that an experimental confirmation of the increase in the value of R (or ρ) in this region of (HCl) is almost impossible because the concentration of chlorine at the steady state is too small to be determined by ordinary quantitative methods.

Effect of Temperature

The variation with the temperature of the steady state function can be predicted by the use of Equation 8, from the temperature coefficients of the two compensating reactions, Equations 1 and 2. The use of a modified form of Equation 8, namely

$$R' = k_1/k_2' \qquad (12)$$

was necessitated by the fact that no data are available for the variation of the chlorine–trichloride ion equilibrium with the temperature; k_2' is the specific rate of Reaction 2 expressed in terms of (ΣCl_2) (*cf.* Ref. 3, Equation 7).

By applying the Arrhenius equation to each term of Equation 12, it follows that

$$\Delta H_{R'} = \Delta H_{k_1} - \Delta H_{k_2'} \qquad (13)$$

To verify this relation measurements of R' and k_2' were made at one concentration of hydrogen chloride (3.84 M) over a range of temperature. The results are summarized in Tables III and IV A, respectively. Linear graphs are obtained when log k_2' and log R' are plotted against $1/T$.

TABLE III

STEADY STATE CONCENTRATIONS AT VARIOUS TEMPERATURES IN 3.84 M HCl SOLUTIONS

Run	T°C.	$10^4(Cl_2)_{CCl_4}$	$(Cl_2)_{CCl_4}/(\Sigma Cl_2)_{H_2O}$	$10^6(\Sigma Cl_2)_{H_2O}$	$R'(10^3)$
8	2.8	1.00	15.1[a]	6.63	3.05
9	15.9	2.27	18.3[a]	12.4	5.70
10	21.5	3.24	19.2[a]	16.9	7.77
From Table I	25.0	3.59	19.5	18.4	8.46

[a] The distribution ratio in these experiments was determined experimentally.

TABLE IV

RATE OF OXIDATION OF HYDROGEN PEROXIDE BY CHLORINE IN 3.84 M AND 0.496 M HYDROCHLORIC ACID AT VARIOUS TEMPERATURES[a]

A. Experiments in 3.84 M HCl

Run	I	II	III	IV	V
T, °C.	1.8	6.9	16.0	21.5	25.5
k_2' (10^{-2})	1.14	1.90	3.91	6.25	8.61

B. Experiments in 0.496 M HCl

Run	VI	VII	VIII	IX
T, °C.	0.4	7.5	16.6	21.5
k_2' (10^{-2})	3.76	6.10	10.2	13.5

[a] The experimental procedure used in making these measurements is the "sampling method" described in Ref. 3, p. 4767.

The heat of activation of Reaction 2, based on the measurements in Table IV A, was calculated to be, $\Delta H_{k_2'}$ = 13,700 ± 300 calories; that for Reaction 1, from the data of Livingston and Bray[1] and Budge[8] is equal to ΔH_{k_1} = 21,000 calories. The calculated value of $\Delta H_{R'}$ is therefore equal to

$$\Delta H_{R'} \text{ (calcd.)} = 21{,}000 - 13{,}700 = 7300 \text{ cal.}$$

From the results in Table III, the experimentally observed value, $\Delta H_{R'}$ (obs.) = 7800 ± 400 calories is in good agreement with that calculated above from the kinetic data.

This agreement and the fact that Equation 8 was shown to hold over a large range of hydrochloric acid concentrations prove conclusively that the catalytic decomposition of hydrogen peroxide can be completely accounted for by the two compensating reactions, Equations 1 and 2, irrespective of the "intimate" or "detailed" mechanism that may be assigned to each of these reactions.

In this connection it should be mentioned that it is difficult to understand the linear character of the plot of log k_2' against $1/T$, which signifies a constant heat of activation, $\Delta H_{k'}$, for Reaction 2 between 0 and 25°. According to the

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(7) Brönsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, New York, 1927.

(8) Budge, THIS JOURNAL, **54**, 1777 (1932).

assumed mechanism for this reaction, ΔH_{k_2} or $\Delta H_{k'_2}$ should exhibit a considerable variation with the temperature inasmuch as $k_2 = K'\kappa_2$ (*cf.* Eq. 7 and Ref. 3, Eq. 5) and the value of the heat of hydrolysis of chlorine, $\Delta H_{K'}$, according to Jakowkin[9] undergoes a marked decrease with increasing temperature—from 10,000 cal. at 0° to 6,000 cal. at 25°. No evidence of a corresponding variation is shown by the experimental results at 3.84 M hydrochloric acid (Table IV A); nor is it shown in another set of rate measurements at 0.496 M HCl in a range of temperature between 0 and 25° (Table IV B), where $\Delta H_{k'_2}$ (or ΔH_{k_2}) was found to be equal to 9600 ± 300 cal. (At this low concentration of chloride ion $(\Sigma Cl_2) = (Cl_2)$ and $k'_2 = k_2$.)

Three alternatives may be offered to account for this discrepancy: (1) Jakowkin's measurements may be wrong; (2) the heat of activation of the bimolecular reaction between HOCl and H_2O_2, ΔH_{κ_2}, may undergo a marked change with the temperature, and (3) the detailed mechanism for Reaction 2 may be more complex than has been assumed heretofore. There is some evidence in support of the last alternative, namely, the rapid decrease in the value of k_2 and κ_2 with decreasing (HCl) when (HCl) is less than 2 M,[10] and the decrease in the value of $\Delta H_{k'_2}$ with decreasing concentration of hydrochloric acid, from 13,700 cal. at 3.84 M HCl to 9,600 cal. at 0.496 M HCl. It is hoped that more evidence on this subject will be obtained from the direct measurements of the rate of the reaction between HOCl and H_2O_2 which are now in progress in this Laboratory.

Summary

1. The concentrations of chlorine at the steady state, in the catalytic decomposition of hydrogen peroxide, were measured at various concentrations of hydrochloric acid. These results together with the older measurements of Livingston and Bray[1] cover a concentration range from 2.84 to 5.86 M hydrochloric acid. A new experimental method was employed which involved the distribution of chlorine between the steady state mixture and carbon tetrachloride. The concentration in the former solution was obtained from the known distribution ratio and the analysis of the relatively richer in chlorine non-aqueous layer.

2. The experimental values, thus determined, of the steady state function

$$R = (Cl_2)/(H^+)^2(Cl^-)^2 \qquad (4)$$

were found to agree closely, at the corresponding acid concentrations, with the values calculated from the expression

$$R = k_1/k_2 \qquad (8)$$

where k_1 and k_2 are, respectively, the specific rates for the reactions

$$H_2O_2 + 2H^+ + 2Cl^- = Cl_2 + 2H_2O \qquad (1)$$

and

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

3. From the results of additional measurements of k_2 and R at various temperatures between 0 and 25° in 3.84 M hydrochloric acid, it has been demonstrated that the measured temperature coefficient of R is equal, within the experimental error, to that calculated by means of Equation 8 from the independently measured temperature coefficients of k_1 and k_2.

4. The validity of Equation 8 offers additional proof that the catalysis can be completely accounted for by means of the two compensating reactions, Equations 1 and 2.

5. A discrepancy concerning the detailed mechanism of Reaction 2 has been discussed.

BERKELEY, CALIFORNIA RECEIVED APRIL 9, 1934

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[9] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899). See also Ref. 5, p. 508.

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