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

The Catalytic Decomposition of Hydrogen Peroxide by the Iodine–Iodide Couple. IV. The Approach to the Steady State[1]

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Hydrogen peroxide added to an acid iodide solution is at first reduced according to the stoichiometric equation

$$H_2O_2 + 2H^+ + 2I^- = I_2 + 2H_2O \qquad (1)$$

Conversely, hydrogen peroxide added to an aqueous iodine solution may be oxidized

$$H_2O_2 + I_2 = 2H^+ + 2I^- + O_2 \qquad (2)$$

Once these facts have been established by experiment, it follows that neither reaction can be absolutely isolated so long as its products are not completely removed. If the products of Reaction 1 (Reaction 2) are permitted to accumulate, then the *relative* rate of Reaction 2 (Reaction 1) will increase; and, if enough peroxide is present, this increase will continue until a steady state has been reached where the two rates are equal, and where the only measurable reaction is the sum of Reactions 1 and 2, namely

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

the decomposition of hydrogen peroxide. The reaction system involving the peroxide and the iodine–iodide couple, together with associated substances like hydrogen and tri-iodide ions, may pass through three contiguous phases which will be described as follows. The reaction system is *at a distance from the steady state* if either Reaction 1 or 2 is proceeding at a negligible relative rate; in this phase either the quantitative reduction or the quantitative oxidation of hydrogen peroxide occurs. The reaction system is *in the approach to the steady state* if neither reaction can be neglected and their relative rate is changing. And finally, it is *at the steady state* when the rates of the two reactions are equal, and hydrogen peroxide is the only substance undergoing a concentration change. The last phase is unique, but the other two may be found either on the iodide or on the iodine side of the steady state (that is to say, either in the region where Reaction 1, or in the region where Reaction 2 predominates). It has been shown[2] that the same rate-determining steps, which have constant specific rates, are involved whether Reactions 1 and 2 proceed at the steady state or at a distance from it; but clear proof that this simplicity extends also to the intermediate (and most complex) phase—the approach to the steady state—is not yet available. Such proof would remove the last serious difficulty associated with the iodine–iodide catalysis at 25°.

This proof can be obtained provided the experimental conditions are simplified by adding to the reaction mixture amounts of peroxide so small that no great change has occurred in the concentration of any other substance when the peroxide has been consumed completely in Reactions 1 and 2. Under these conditions average values may be substituted in the rate laws for all concentrations except that of the peroxide. To aid in achieving such conditions, the reaction mixtures will contain a potassium phosphate buffer to regulate the activity of hydrogen ion; further, (I^-) will be appreciable (greater than 0.05 M) so that (I_2) may be kept nearly constant by the operation of the equilibrium

$$I_3^- \rightleftharpoons I_2 + I^- \qquad (4)$$

Whenever a mole of hydrogen peroxide is reduced in Reaction 1, a mole of iodine is formed; similarly, the oxidation of one mole of peroxide in Reaction 2 consumes one mole of iodine and forms one mole of gaseous oxygen. These generally valid stoichiometric considerations may naturally be applied when a limited amount of peroxide is

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[1] The earlier members of this series are Liebhafsky, I, THIS JOURNAL, **54**, 1792 (1932); and II and III, *ibid.*, **54**, 3499 (1932). References to earlier work are to be found in I and also in the comprehensive review of the whole subject by Bray, *Chem. Rev.*, **10**, 161 (1932).

The usual conventions will be employed. Numerical values of specific rates (k's) and equilibrium constants (K's) are for 25°. ( ) usually denotes "concentration of" in moles/liter. $\longrightarrow$ is restricted to steps that may be rate-determining. Unit time is the minute. Certain methods of calculation and experimental procedures are described in earlier members of this series and will not be given in detail.

The meaning of "iodine" will be clear from the context; in connection with stoichiometry, "iodine" means $\Sigma I_2 = I_2 + I_3^-$; when mechanism is being discussed, it means I_2. When iodine is consumed in Reaction 1 and the reaction mixture contains a phosphate buffer, $H_2PO_4^-$ (and not H^+) is consumed and HPO_4^{--} is formed; the application to Reaction 2 is obvious; any such change occurring in the buffer is thus related to the change in the iodine content of the reaction mixture and may be calculated from it.

For the sake of simplicity, the rate-determining step involving hypoiodous acid and hydrogen peroxide, which becomes important at 25° only when the activity of hydrogen ion exceeds 10^{-4} M, will be neglected in the present discussion. There is no obvious reason why the conclusions reached therein should not apply to this rate-determining step also.

[2] I and II; also Liebhafsky and Mohammad, THIS JOURNAL, **55**, 3977 (1933).

completely consumed by Reactions 1 and 2 proceeding concurrently; their application to this special case involves the equations

$$\Sigma I_2 = I_2 + I_3^- \qquad (4a)$$

$$H_2O_2 \text{ oxidized} = \text{Ox} = \Sigma I_2 \text{ consumed (total)} = O_2 \text{ evolved} \qquad (5)$$

$$H_2O_2 \text{ reduced} = \text{Red} = \Sigma I_2 \text{ formed (total)} \qquad (6)$$

$$\Sigma I_2 \text{ formed (total)} - \Sigma I_2 \text{ consumed (total)} = \Delta\Sigma I_2 \text{ (net)} \qquad (7)$$

whence

$$\text{Red} = \Sigma I_2 \text{ consumed} + \Delta\Sigma I_2 = \text{Ox} + \Delta\Sigma I_2 \qquad (8)$$

and

$$\text{Cons} = \text{Ox} + \text{Red} = 2\text{Ox} + \Delta\Sigma I_2 = 2O_2 + \Delta\Sigma I_2 \qquad (9)$$

(The arbitrarily chosen units for all these equations are millimoles for a liter of reaction mixture; $\Delta\Sigma I_2$ may be either positive or negative.)

Therefore

$$\text{Ox/Red} = O_2/[O_2 + \Delta\Sigma I_2];\quad \text{Ox/Cons} = O_2/[2O_2 + \Delta\Sigma I_2];\quad \text{Red/Cons} = [O_2 + \Delta\Sigma I_2]/[2O_2 + \Delta\Sigma I_2] \qquad (10)$$

If the rate of Reaction 2 remains in constant ratio to the rate of Reaction 1 for the entire course of an experiment, then the ratio of these rates must be identical with the stoichiometric ratio Ox/Red, which is obtained when the experiment is concluded. Further, if Ox/Red remains thus constant, Ox/Cons and Red/Cons also remain constant[3] during the experiment; and consequently the rates of Reactions 1 and 2 each remain proportional to their sum, the rate at which the peroxide is being consumed. Under our experimental conditions the rate of Reaction 1 is given by (see I and Ref. 2)

$$-d(H_2O_2)/dt = k_1^0(I^-)(H_2O_2) \qquad (11)$$

while that of Reaction 2 follows the law (see II)

$$-d(H_2O_2)/dt = k_2' \frac{(I_2)}{(\alpha_{H^+})^2(I^-)} (H_2O_2) \qquad (12)$$

So long as (I^-), α_{H^+} and (I_2) are constant, the proportionalities of the various rates are secured even though (H_2O_2), which is common to both rate laws, varies. In actual practice it is impossible to maintain the first three quantities rigorously constant, for enough peroxide must be consumed in an experiment to permit reasonably accurate measurements of the rate of oxygen evolution, of the change in the iodine content of the reaction mixture, and of the total volume of evolved oxygen. The success of the proposed experimental method depends on choosing the amounts of peroxide to be consumed large enough to ensure reasonable accuracy in these measurements and small enough so that averages of the initial and final values of (I^-), α_{H^+} and (I_2) may for all practical purposes be regarded as constant quantities applying throughout an experiment.

If the rate at which hydrogen peroxide is consumed (the sum of Equations 11 and 12) is proportional to the rate of Reaction 2 (Equation 12), in which oxygen is evolved, the rate of oxygen evolution may be used to measure the rate at which the peroxide is disappearing. Under these conditions.

$$-d(H_2O_2)/dt \text{ (total)} = \left[k_1^0(I^-) + k_2' \frac{(I_2)}{(\alpha_{H^+})^2(I^-)}\right](H_2O_2) = k(H_2O_2) \qquad (13a)$$

$$+dx/dt = k[a - x] \qquad (13b)$$

The rates in these two equations are proportional (not equal), but the k's are identical. Since the k thus defined does not involve concentration units, the concentration of peroxide may be measured in any convenient unit whatever, as, for example, in cc. of oxygen evolved from the reaction mixture. x then is the cc. of oxygen evolved up to time t, and a is the value of x when the reaction has gone to completion. The method of evaluating k from such data has been given in I and need not be repeated here.

The proportionalities, which have been discussed above, that apply to the various rates so long as (I^-), α_{H^+} and (I_2) are (virtually) constant may now be formulated as follows

$$\text{Rate of reduction: } k_1^0(I^-)(H_2O_2) = [\text{Red/Cons}]k(H_2O_2) \qquad (14)$$

$$\text{Rate of oxidation: } k_2' \frac{(I_2)}{(\alpha_{H^+})^2(I^-)} (H_2O_2) = [\text{Ox/Cons}]k(H_2O_2) \qquad (15)$$

(H_2O_2) appears on both sides of each equation and may therefore be omitted. The calculation of k_1^0 and k_2' from k then presents no difficulty if average values for the other concentrations and the values of Red/Cons are available. These equations also suggest an empirical method of ascertaining whether or not (I^-), α_{H^+} and (I_2) remain nearly enough unchanged so that k_1^0 and k_2' may be evaluated in the way proposed: If no trend can be detected in k as the experiment proceeds (*i. e.*, if a log $a - x$ *vs.* t plot gives a straight line, *cf.* I, Fig. 2) the use of our simple, but approximate, method of calculation is justified. The few experiments in which the rate measurements did not meet this test are pointed out in Table I.

The object of this investigation may now be restated. It is to prove that k_1^0 and k_2' are indepen-

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[3] If Ox/Red represents the constant ratio of the rate of oxidation of hydrogen peroxide in Reaction 2 to its reduction in Reaction 1, then [1 + Ox/Red] = [Red + Ox]/Red = Cons/Red is also constant; the extension to the ratios given above is obvious.

dent of the ratio Ox/Red, which serves to characterize the various phases in which the reaction system may be found. The experimental method consists of following (by means of the apparatus described in I) the rate at which oxygen is evolved from reaction mixtures buffered with respect to hydrogen ion and iodine, and determining the change in total iodine by titration with thiosulfate when the reaction is complete. From the initial values of (I^-), α_{H^+} and (I_2), and from the change in total iodine, final or average values for these quantities may be calculated. In these calculations, 0.00140[4] was used throughout for the dissociation constant of tri-iodide ion. Values of α_{H^+} were obtained by use of the phosphate buffer data given by Cohn;[5] the effect of the presence of other salts on the buffer was neglected. (A discussion of the salt effects in this reaction system is given in I.) The average concentrations computed in this way and the specific rates calculated from Equations 14 and 15 are summarized in Table I.

TABLE I

k_1 AND k_2' AT 25° AND AT DIFFERENT VALUES OF THE RATIO OX/RED

No.[a]	$\Sigma_f I_2$[b]	$\Delta\Sigma I_2$[b]	O_2[b]	$10^7(\alpha_{H^+})$[c]	(I^-)[c]	$10^4(I_2)$[c]	Ox/Red	k	k_1^0	$10^{12}k_2'$
	Ox/Red ≪ 1; *i. e.*, at a distance from the steady state on the iodide side									
	Accepted value from Reference 2.								0.69	...
	Ox/Red < 1; *i. e.*, in the approach to the steady state from the iodide side									
37	39.60	+7.34	1.78	1.27	0.4450	1.13	0.20	0.210	0.40	2.2
13[e]	19.40	+5.89	1.51	1.61	.2524	0.91	.26	.150	.49	1.8
32[e]	16.00	+2.96	1.23	0.88	.2650	.76	.29	.190	.55	1.2
12	13.51	+2.30	1.13	1.73	.2076	.92	.33	.134	.49	2.2
31	13.18	+2.55	1.30	1.10	.2037	.81	.34	.147	.54	1.1
30	11.23	+1.90	1.64	1.52	.1405	1.02	.46	.100	.49	1.0
29	9.69	+1.17	1.36	1.89	.1092	1.15	.54	.078	.46	1.1
33	17.61	+1.59	1.83	0.73	.2570	0.91	.54	.222	.56	1.2
11	11.71	+1.43	2.04	1.73	.1582	1.04	.59	.110	.44	1.9
34	16.42	+1.33	1.95	0.466	.3360	0.655	.59	.293	.55	1.2
10	10.49	+0.99	2.37	1.75	.1339	1.10	.71	.104	.46	1.6
	Average values								.49	1.50
	Ox/Red = 1; *i. e.*, at the steady state									
	Average values from I, Table I(b) and Fig. 3								0.69	1.92[d]
8	9.69	0.00	2.88	1.71	0.1066	1.26	1.00	0.134	.63	1.7
28	9.10	0.00	1.92	2.20	.0740	1.69	1.00	.078	.53	0.8
	Ox/Red > 1; *i. e.*, in the approach to the steady state from the iodine side									
24	8.53	−0.11	1.78	3.16	0.0636	1.85	1.07	0.094	0.72	1.7
16	22.70	− .50	1.46	1.72	.1370	2.31	1.52	.177	.51	1.9
14	13.56	− .52	1.50	1.67	.1161	1.64	1.53	.159	.54	1.9
15	17.30	− .50	1.15	1.65	.1268	1.89	1.77	.172	.49	2.0
20	47.30	−1.05	1.40	1.98	.1122	5.80	4.00	.256	.46	1.6
23	11.59	−1.23	1.58	2.33	.0541	3.08	4.52	.175	.59	1.4
19	48.40	−1.20	1.45	1.81	.1086	6.22	5.80	.300	.41	1.5
22[e]	13.21	−1.49	1.73	2.10	.0498	3.81	7.22	.233	.57	1.2
21	14.90	−1.71	1.76	1.84	.0448	4.79	35.2	.326	.2[f]	1.0
	Average values								.48	1.58
	Ox/Red ≫ 1; *i. e.*, at a distance from the steady state on the iodine side									
	Accepted value from II, Equation 8a								...	1.2

[a] Experiments with numbers below 20 have total phosphate 0.2 *M;* for the others total phosphate is 0.1 *M*.

[b] This quantity is expressed in millimoles for a liter of reaction mixture.

[c] An average value, expressed in moles/liter, is given for this quantity. $\Sigma_f I_2$ denotes its value at the end of the experiment.

[d] Average value of k_2' calculated from average values for k_1^0 and the steady state function, F: $k_2' = Fk_1^0$ (*cf.* I).

[e] This experiment showed curvature in the log $a - x$ *vs.* t plot; k corresponds to line through center.

[f] Approximate value only; not included in the average.

An inspection of the last two columns of Table I will reveal that k_1^0 and k_2' are both independent of Ox/Red: that is, the two rate laws, Equations 14 and 15, with their (virtually) constant specific

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(4) Jones and Kaplan, THIS JOURNAL, **50**, 1485 (1928).

(5) Cohn, *ibid.*, **49**, 173 (1927).

rates, suffice to describe the reaction system in all its phases. This point seems conclusively established even though the concordance of the individual results leaves something to be desired. Since the experimental method employed is only an approximate one at best, no discussion of the divers sources of error will be given. The object of this investigation—to prove that the reaction system is no more complex in the approach to than at the steady state or at a distance from it—seems accomplished beyond all reasonable doubt.

The approach to the steady state has been studied previously by Abel[6] in the course of an extensive investigation, in which the experimental conditions were not always so simple as ours. Consequently his method of evaluating the results is more complex than ours, although the two are similar in many respects (thus Abel's χ is the reciprocal of our Ox/Cons). The character of his results led him to conclude,[6c] however, that iodine hydrolyzes at a moderate rate ($k_h = 0.25$), so that this reaction must be regarded as an additional rate-determining step in the iodine–iodide–hydrogen peroxide reaction system. This conclusion, already shown to be in conflict with certain related experimental results,[7] is rendered untenable by the data in Table I.

It may be emphasized, finally, that the new experimental evidence in Table I provides little, if any, further verification of the *mechanisms* of the rate-determining steps involved in the reaction system—Reaction 2 may be used to illustrate this point. What has been proved is that one rate law (Equation 15) applies to this reaction at the steady state (I), at a distance from the steady state (II), and in the approach to it (IV). The corroboration in II and IV of the rate law established in I proves the reaction system to be essentially simple, but it affords no further insight into the actual mechanism of the rate-determining step (or steps) to which this rate law corresponds. The most reasonable mechanism is the one which has been adopted; namely

$$IO^- + H_2O_2 \xrightarrow{k_2} H_2O + O_2 + I^- \qquad (16)$$

but, as has been pointed out in II and III,[8] this interpretation is subject to an uncertainty inherent in the interpretations of many complex rate laws. If hypoiodite ion were actually isolated and found to react with peroxide at a rate much slower (a much faster rate seems inconceivable) than what one would predict from Equation 15, or if an equally serious discrepancy came to be established, it would then be necessary to consider an alternative mechanism—perhaps one involving the direct interaction of peroxide and iodine.[8] These considerations apply, *mutatis mutandis*, also to a reaction system in which a measurable equilibrium is reached.

Conclusion

The extensive re-investigation of the reaction system involving the interaction at 25° of hydrogen peroxide with the iodine–iodide couple is now complete, and leads to the conclusion that the mechanism postulated by Abel for the catalytic decomposition at the steady state is fully capable of explaining results that have been obtained under all experimental conditions. None of the new experimental results taken alone or in conjunction with the others, necessitates the assumption that iodine hydrolyzes at a rate comparable with the absolute rate at which it oxidizes hydrogen peroxide (Reaction 2).

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[6] Abel, (a) *Z. Elektrochem.*, **37**, 598 (1908); (b) *Z. physik. Chem.*, **96**, 1 (1920); (c) *ibid.*, **136**, 161 (1928).

[7] *Cf.* II and III; and Liebhafsky, *Z. physik. Chem.*, **155A**, 289 (1931).

[8] II and III, page 3507. In this connection, *cf.* also Makower and Liebhafsky, *Trans. Faraday Soc.*, **29**, 597 (1933), where the mechanism of a reaction involving a reactive intermediate compound (the oxidation of oxalate by hypobromous acid) has been verified.