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The Mechanism of Decomposition of Hydrogen Peroxide by Iodine in Acid Solutions. The Rates of Associated Reactions

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For the purpose of isolating elementary reactions responsible for the decomposition of hydrogen peroxide by iodine and its compounds, the reaction at 50°C of acid solutions containing I_2, I^-, HIO, *etc.* with $[I^-]$ and $[I_2]$ controlled by use of TlI(s) and I_2(s) was studied. The rates of the evolution of oxygen, consumption of hydrogen peroxide and production of H^+ were subjected to measurement and led to a formulation of a complex mechanism consisting of the following reactions: $HIO_2+H_2O_2 \longrightarrow HIO+H_2O+O_2$; $H_2OI^++H_2O_2 \longrightarrow HIO_2+H^++H_2O$; $HIO+H_2O_2 \longrightarrow H^++I^-+H_2O+O_2$; $HIO_2+H^++I^- \longrightarrow 2HIO$; $H_2OI^+ \rightleftharpoons HIO+H^+$; $I^-+H^++H_2O_2 \longrightarrow HIO+H_2O$; and $I_2+H_2O \rightleftharpoons HIO+H^++I^-$. Absolute or relative rate constants for the first four reactions were evaluated by using equilibrium and rate constants of the others.

A series of preliminary investigations[3-6] has been made at 50°C toward clarifying the mechanism of the decomposition of hydrogen peroxide by iodine and its compounds, the only known completely inorganic oscillating reaction. It has been suggested that the following step might have much to do with the oxygen evolution in the pulses:

$$\text{Step 10: } HIO + H_2O_2 \longrightarrow H^+ + I^- + H_2O + O_2$$ [7]

The purpose of the present investigation is to determine the value of the rate constant, which would help us understand to what degree Step 10 contributes to the pulsed oxygen evolution. The step is found to be responsible for most oxygen produced when hydrogen peroxide is oxidized by iodine at 25°C in acid solutions[8] in the virtual absence of iodate ion, which should be present to achieve oscillating decomposition.

Step 10 is difficult to study even in acid solutions because it is always accompanied by other reactions such as

$$\text{Step 11: } I^- + H^+ + H_2O_2 \longrightarrow HIO + H_2O$$

$$\text{Step 13: } IO^- + H_2O_2 \longrightarrow I^- + H_2O + O_2$$

$$I_2 + 5H_2O_2 = 2IO_3^- + 2H^+ + 4H_2O \quad (1)$$

$$3I_2 + 3H_2O = IO_3^- + 5I^- + 6H^+ \quad (2)$$

By using TlI(s) to control the iodide concentration, Liebhafsky[8] accomplished what appeared to be a satisfactory isolation of Step 10 at 25°C in acid solutions saturated with iodine so that oxygen evolution could be measured *as a constant rate* and its rate law deduced. Under these conditions, the overall reaction was assumed to be

$$I_2(s) + 2Tl^+ + H_2O_2 = 2TlI(s) + 2H^+ + O_2 \quad (3)$$

The rate of oxygen evolution at 50°C was studied by the method outlined above. Under certain conditions, the amount of H_2O_2 consumed was considerably greater than that called for by the stoichiometry of (3), and the H^+ produced was considerably less. It accordingly became necessary to investigate the additional reactions. They have been confirmed, and the result will contribute to the eventual understanding of the oscillating decomposition.

Experimental

Materials and Apparatus. Hydrogen peroxide of 30% content without inhibitor from J. T. Baker Chemical Co. and from Mallinckrodt Chemical Works was determined iodometrically before each experiment as follows. After dilution of 0.2 m*l* 30% H_2O_2 to 25 m*l*, 20 m*l* of 2N H_2SO_4, 2 g KI and 3 drops of 3% $(NH_4)_6Mo_7O_{24}$ (to expedite reaction) were successively added. After 3 min, the liberated iodine was titrated with 0.1M $Na_2S_2O_3$, starch indicator being added near the end of the titration.

Perchloric acid of analytical grade (J. T. Baker Chemical Co., 60 or 70% by weight) was used in preparing dilute (0.1N and less) solutions standardized against Na_2CO_3 with bromocresol green as indicator.

Iodine of analytical grade (J. T. Baker Chemical Co.) was pulverized before use.

A stick of highly pure thallium (Fisher Scientific Co.) was shaved as needed for the preparation of thallous perchlorate. The shavings were dissolved in excess strong perchloric acid at 105°C. The precipitated perchlorate was filtered and washed at 5°C with water until the washings were neutral.

Thallous nitrate of analytical grade (K & K Laboratories and Fisher Scientific Co.) was used in the reaction mixtures and also to prepare the slightly soluble thallous iodide by addition of potassium iodide. The precipitate was thoroughly washed with water.

The reaction vessel (Fig. 1), a 125 m*l* Erlenmeyer flask, sharply indented to promote mixing, had a rubber-capped side arm for the addition of reagents and for the withdrawing

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[3] J. H. Woodson and H. A. Liebhafsky, *Nature*, **224**, 690 (1969).

[4] J. H. Woodson and H. A. Liebhafsky, *Anal. Chem.*, **41**, 1894 (1969).

[5] I. Matsuzaki, J. H. Woodson, and H. A. Liebhafsky, This Bulletin, **43**, 3317 (1970).

[6] I. Matsuzaki, R. B. Alexander, and H. A. Liebhafsky, *Anal. Chem.*, **42**, 1690 (1970).

[7] Reactions that are probable steps in the oscillating decomposition will be identified by the numbers assigned to them in the tentative complete mechanism formulated here for the very complex overall reaction. Rates of these steps will be represented by V with the appropriate subscript: *e.g.*, V_{10}.

[8] H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **54**, 3504 (1932).

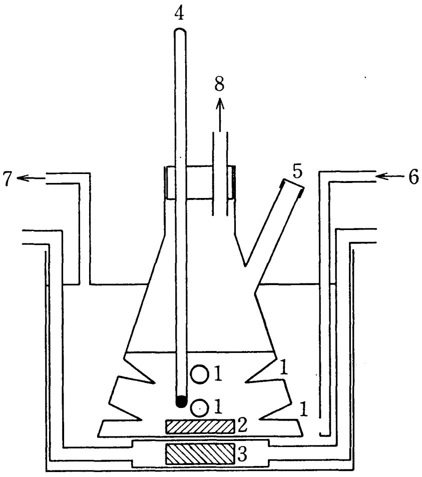

Fig. 1. Apparatus used.
1: Indent, 2: Magnetic stirrer, 3: Air-driven magnet, 4: Thermometer, 5: Rubber cap, 6: Water from thermostat, 7: Water to thermostat, 8: Gas buret.

of samples by means of a syringe. It was connected to a 100 m*l* gas buret for the measurement of evolved oxygen.

Procedure. Water pre-saturated with oxygen, perchloric acid, 0.05 g of TlI(s), thallous perchlorate solution and 2 g of I_2(s) were added successively to the reaction vessel at room temperature to make a liquid volume near 60 m*l*. After thermal equilibrium was reached in the thermostat at 50°C, the prescribed amount of hydrogen peroxide at thermostat temperature was injected from the syringe to start the reaction ($t=0$). Two minutes later the first sample (1.6 m*l*) was withdrawn. Further samples, the same in volume, were taken at recorded intervals of time. Gas-buret readings were made every 2 or 3 min. From these, rates of oxygen evolution were calculated, correction for the partial pressure of water vapor being made for 25°C, the assumed gas temperature.

The reaction was stopped in the samples as follows. From the 1.6 m*l* of reaction mixture in a 50 m*l* beaker, 1 m*l* was withdrawn with a pipet and discharged into 2 m*l* of carbon tetrachloride and 25 m*l* of water. The mixture was then shaken vigorously to extract iodine. Acid was then determined on one 10 m*l* portion of the aqueous phase by titration with NaOH, and H_2O_2 iodometrically on another by titration with thiosulfate. Blank tests showed that the formation of TlI and of TlI_3, which occurred on the addition of KI prior to titration, did not interfere with the iodine determination. Values of $\Delta[H_2O_2]$ and $\Delta[H^+]$ were calculated for the

TABLE 1. RESULTS OF THREE COMPREHENSIVE EXPERIMENTS AT 50°C

	Exp't No.	1	2	3
Data at time=0[a]	Volume of react. mixt. (m*l*)	58.4	58.4	58.4
	$[I_2]_0 \times 10^3$ (M)[b]	3.08	3.08	3.08
	$[Tl^+]_0$ (M)[c]	0.225	0.225	0.225
	$[I^-]_0 \times 10^6$ (M)[d]	1.86	1.86	1.86
	$[H^+]_0$ (M)[e]	0.141	0.413	1.182
	$[H_2O_2]_0$ (M)[e]	0.234	0.484	0.955
	Measured Rates			
	$(dO_2/dt)_0 \times 10^4$ (mol/*l*/min)	1.02	1.09	1.22
	$(-d[H_2O_2]/dt)_0 \times 10^4$ (M/min)	1.20	2.19	4.21
	$(d[H^+]/dt)_0 \times 10^4$ (M/min)	1.20	1.34	0.76
	Rate Quotients			
	$(-dO_2/d[H_2O_2])_0$ (O_2 in mol/*l*)	0.85	0.49	0.29
	$(-d[H^+]/d[H_2O_2])_0$	1.0	0.61	0.18
Data at the end of run	Stoichiometric Data			
	React. time (min)	460	383	268
	Volume of react. mixt. (m*l*)	52.0	55.2	52.0
	ΔO_2 (Total amount of O_2 evolved) $\times 10^3$ (mol)	2.085	2.405	2.120
	ΔTlI (TlI formed) $\times 10^3$ (mol)	2.74	2.246	−0.15[f]
	$TlIO_3$ formed $\times 10^3$ (mol)	0	0	0.046
	Rate Quotient			
	$\Delta TlI/\Delta O_2$	1.31	0.893	−0.071[f]

a) Subscripts 0 in $[H^+]_0$, $(d[H^+]/dt)_0$, *etc.*, specify quantities at time=0.

b) The value of 3.08×10^{-3}M is the solubility of I_2 at 50°C. Two grams of I_2, *i.e.*, 7.9×10^{-3} mol, was added to saturate the reaction mixtures (60 m*l* before the first sampling), so that it may be regarded as saturated with I_2.

c) The value of $[Tl^+]_0$ was obtained by multiplying the amount in mole of $TlClO_4$ added to the reaction mixture (60 m*l*) by 1000/60.

d) The solubility product for TlI is 4.2×10^{-7}M^2 at 50°C as determined by interpolation of the data[9]; this value, on division by $[Tl^+]_0$, gives $[I^-]_0$. Experimentally, in order to ensure the establishment of the dissolution equilibrium of TlI, 0.05 g ($=1.5 \times 10^{-4}$ mol) of TlI was added to each reaction mixture (60 m*l* before the first sampling).

e) The values shown were obtained by extrapolating the concentrations of the withdrawn samples to time=0. They were practically in agreement with those calculated for the amounts of reagents mixed.

f) Lower limit.

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[9] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, Burlington House, London (1964), pp. 339 and 350.

1 m*l* of reaction mixture by taking the volume ratio 26/10 into account.

At the end of the reaction, information on TlI(s) and $TlIO_3$(s), both sparingly soluble, was obtained from the weighed, filtered residue after removal of I_2(s) by sublimation. Cubic thallous iodide is red at sublimation temperature and changes to a yellow, rhombic form as it is cooled to room temperature. The iodate is white and its presence was confirmed qualitatively by iodine liberation in Experiment 3 (Table 1). No iodate was formed in Experiments 1 and 2 (Table 1).

Results of Comprehensive Experiments. We begin by examining the relative importance of several reactions in this system.

For V_{13}, we have[10)]

$$V_{13} \equiv dO_2/dt = -d[H_2O_2]/dt = k_{13}[H_2O_2][IO^-] = k'_{13}[H_2O_2][I_2]/[H^+]^2[I^-] \quad (4)$$

with $k'_{13}=5.62\times 10^{-11}$(M²/min) according to Fig. 1, Ref. 10. This corresponds to $(V_{13})_0=1.09\times 10^{-6}$, 2.64×10^{-7}, and 6.35×10^{-8}M/min for Experiments 1, 2, and 3, respectively. Comparison with the measured rates in Table 1 shows that V_{13} can be neglected.

For V_{11}, we have[11)]

$$V_{11} \equiv -d[H_2O_2]/dt = -d[H^+]/dt = k_{11}[H_2O_2][I^-] + k'_{11}[H_2O_2][I^-][H^+]$$

$$k_{11} = 4.91\times 10^9\ e^{-13400/RT}(\text{M}^{-1}\cdot\text{min}^{-1})$$

$$k'_{11} = 4.58\times 10^8\ e^{-10450/RT}(\text{M}^{-2}\cdot\text{min}^{-1})$$

from which we obtain at 50°C

$$V_{11}(\text{M/min}) = (4.18+38.9[H^+])[I^-][H_2O_2] \quad (5)$$

For a comparison with the measured rates in Table 1 as above, we calculate $(V_{11})_0=0.042\times 10^{-4}$, 0.182×10^{-4}, and 0.891×10^{-4}M/min for Experiments 1, 2, and 3, respectively. These rates are not negligible relative to the corresponding rates in Table 1.

Formation of I_3^- was neglected in computing $[I^-]_0$ values for Table 1. We have for the tri-iodide equilibrium

$$K_{15} = [I_2][I^-]/[I_3^-] = 2.67\times 10^{-3}\text{M}$$

the numerical value having been obtained by extrapolating experimental data.[12)] For the conditions of Table 1, the equilibrium value of $[I_3^-]$ is 1.28×10^{-7}mol, which is negligible relative to the amount (0.05 g or 1.5×10^{-4}mol) of TlI added and justifies the calculation of $[I^-]_0$ as made.

$TlIO_3$ was formed only in Experiment 3 and in a negligible amount. Reactions (1) and (2) may therefore be disregarded in discussing mechanism.

Schematic Representation of Mechanism: We formulated and tested various mechanisms for their capability of accounting for the results. Of these a plausible one has been found. Because of its complexity the mechanism is shown schematically (Fig. 2). The figure shows only the interaction of the various iodine species. Steps are represented by single arrows; equilibria, by double arrows; H_2O_2, H^+, and H_2O are omitted. The complete equations are

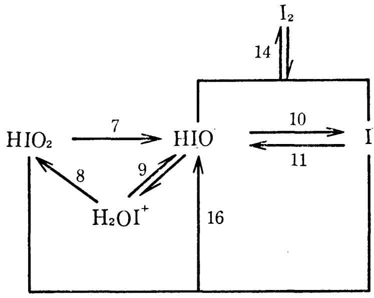

Fig. 2. Schematic representation of the mechanism.

Step 7 $HIO_2 + H_2O_2 \longrightarrow HIO + H_2O + O_2$

Step 8 $H_2OI^+ + H_2O_2 \longrightarrow HIO_2 + H^+ + H_2O$

Equilibrium 9 $H_2OI^+ \overset{K_9}{\rightleftharpoons} HIO + H^+$

Step 10 $HIO + H_2O_2 \longrightarrow H^+ + I^- + H_2O + O_2$

Step 11 $I^- + H^+ + H_2O_2 \longrightarrow HIO + H_2O$

Equilibrium 14 $I_2 + H_2O \overset{K_{14}}{\rightleftharpoons} HIO + H^+ + I^-$

Step 16 $HIO_2 + H^+ + I^- \longrightarrow 2HIO$

The solubility equilibria for I_2(s) and TlI(s) have not been included. Of the intermediate iodine species, HIO and H_2OI^+ exist at equilibrium concentrations; HIO_2 is at a steady-state concentration and is amenable to treatment by the Bodenstein steady-state approximation. The use of this approximation is on a firm basis as the rates in the reaction system are constant.

Analyses of Results According to the Mechanism: The steady-state approximation gives

$$d[HIO_2]/dt = V_8 - V_7 - V_{16} = (k_8/K_9)[HIO][H^+][H_2O_2] - k_7[HIO_2][H_2O_2] - k_{16}[HIO_2][H^+][I^-] = 0 \quad (6)$$

and hence

$$[HIO_2] = (k_8/K_9)[HIO][H^+][H_2O_2]/(k_7[H_2O_2] + k_{16}[H^+][I^-]) \quad (7)$$

The rate of oxygen evolution is

$$dO_2/dt = V_{10} + V_7 = k_{10}[HIO][H_2O_2] + k_7[HIO_2][H_2O_2] \quad (8)$$

By insertion of K_{14} and of $[HIO_2]$, Eq. (8) is transformed into

$$(dO_2/dt)([H^+][I^-]/[I_2][H_2O_2]) = k_{10}K_{14} + (k_8/K_9)K_{14}[H^+]/\{1+(k_{16}/k_7) \times ([I^-][H^+]/[H_2O_2])\} \quad (9)$$

For the sake of brevity the left side of Eq. (9) will be denoted by A, and the right side by A′.

The quantity A is convenient for obtaining k_{10}, k_8/K_9, and k_{16}/k_7 from the experimental results. Let us plot A as a function of $[H^+]$ as abscissa for the experiments in Table 1, in which $[I^-]$ is constant, and denote the intercept on the ordinate axis by A^0. Then, we have by Eq. (9)

$$A^0 = k_{10}K_{14} \quad (10)$$

$$(dA/d[H^+])_{[H^+]=0} = (k_8/K_9)K_{14} \quad (11)$$

The products of constants shown above can be evaluated graphically from the experimentally established variation of A with $[H^+]$. By use[13)] of $K_{14}=4.12\times 10^{-12}$M² and $K_9=6\times 10^2$M at 50°C, and of the graphically evaluated results, the following constants were calculated:

$$\left.\begin{aligned} k_{10} &= 2.68\times 10^{-8}/4.12\times 10^{-12} = 6.5\times 10^3(\text{M}^{-1}\cdot\text{min}^{-1}) \\ k_8/K_9 &= 9.4\times 10^{-8}/4.12\times 10^{-12} = 2.28\times 10^4(\text{M}^{-2}\cdot\text{min}^{-1}) \\ k_8 &= 2.28\times 10^4\times 6\times 10^2 = 1.37\times 10^7(\text{M}^{-1}\cdot\text{min}^{-1}) \\ k_{16}/k_7 &= 2.14\times 10^5(\text{M}^{-1}) \end{aligned}\right\} \quad (12)$$

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10) H. A. Liebhafsky, *Chem. Rev.*, **17**, No. 1, August, 89 (1935).

11) H. A. Liebhafsky and A. Mohammad, *J. Amer. Chem. Soc.*, **55**, 3977 (1933).

12) A. D. Awtrey and R. E. Connick, *ibid.*, **73**, 1842 (1951).

13) J. D. Burger and H. A. Liebhafsky, unpublished work.

The value of k_{16}/k_7 was calculated from Eq. (9). That the results listed above are satisfactory for all experiments in Table 1 is evident from a comparison of the following values of A and A':

$A \times 10^8$ (mol/l) ··· 3.82(Exp. 1), 5.76(Exp. 2), 9.36(Exp. 3)

$A' \times 10^8$ (mol/l) ··· 3.82(Exp. 1), 5.45(Exp. 2), 10.12(Exp. 3)

The specific rates in Eq. (12) are based on values of dO_2/dt only. A severe test of their reliability is to see whether a mechanism that uses these specific rates can yield the three experimentally determined rate quotients listed in Table 1. For this purpose, the rates V_7, V_8, V_{10}, V_{11}, and V_{16} must be expressed in suitable form.

We begin with

$$\begin{aligned} V_8 &= k_8[\mathrm{H_2OI^+}][\mathrm{H_2O_2}] = (k_8/K_9)[\mathrm{HIO}][\mathrm{H^+}][\mathrm{H_2O_2}] \\ &= (k_8/K_9)(K_{14}[\mathrm{I_2}]/[\mathrm{H^+}][\mathrm{I^-}])[\mathrm{H^+}][\mathrm{H_2O_2}] \\ &= (k_8/K_9)K_{14}([\mathrm{I_2}][\mathrm{H_2O_2}]/[\mathrm{I^-}]) \end{aligned} \tag{13}$$

We then proceed to obtain V_7, V_{10}, and V_{16} by the relations

$$\begin{aligned} V_{10}/V_8 &= k_{10}[\mathrm{HIO}][\mathrm{H_2O_2}]/(k_8/K_9)[\mathrm{HIO}][\mathrm{H^+}][\mathrm{H_2O_2}] \\ &= k_{10}/(k_8/K_9)[\mathrm{H^+}] \end{aligned}$$

$$\therefore \quad V_{10} = \{k_{10}/(k_8/K_9)[\mathrm{H^+}]\} \times V_8 \tag{14}$$

$$\begin{aligned} V_7/V_{16} &= k_7[\mathrm{HIO_2}][\mathrm{H_2O_2}]/k_{16}[\mathrm{HIO_2}][\mathrm{H^+}][\mathrm{I^-}] \\ &= (k_7/k_{16})([\mathrm{H_2O_2}]/[\mathrm{H^+}][\mathrm{I^-}]) \end{aligned}$$

$$V_7 + V_{16} = V_8$$

the last of which is derived from the Bodenstein steady-state approximation applied to HIO_2.

By solving the last two equations simultaneously, we find

$$V_{16} = V_8/\{(k_7/k_{16})([\mathrm{H_2O_2}]/[\mathrm{H^+}][\mathrm{I^-}])+1\} \tag{15}$$

which leads to V_7 because

$$V_7 = V_8 - V_{16} \tag{16}$$

Expressed in terms of the individual rates, the three rate quotients in Table 1 are

$$\begin{aligned} -\mathrm{d}O_2/\mathrm{d}[\mathrm{H_2O_2}] &= (\mathrm{d}O_2/\mathrm{d}t)/(-\mathrm{d}[\mathrm{H_2O_2}]/\mathrm{d}t) \\ &= (V_7+V_{10})/(V_7+V_{10}+V_8+V_{11}) \end{aligned} \tag{17}$$

$$\begin{aligned} -\mathrm{d}[\mathrm{H^+}]/\mathrm{d}[\mathrm{H_2O_2}] &= (\mathrm{d}[\mathrm{H^+}]/\mathrm{d}t)/(-\mathrm{d}[\mathrm{H_2O_2}]/\mathrm{d}t) \\ &= \frac{(V_{10}+V_8-V_{16}-V_{11})-(V_{11}+2V_{16}+V_7-V_{10}-V_8)^{14)}}{V_7+V_{10}+V_8+V_{11}} \\ &= (2V_{10}+2V_8-3V_{16}-2V_{11}-V_7)/(V_7+V_{10}+V_8+V_{11}) \end{aligned} \tag{18}$$

$$\begin{aligned} \Delta \mathrm{TlI}/\Delta O_2 &\doteqdot \mathrm{dTlI}/\mathrm{d}O_2 \\ &= \{(V_{10}-V_{16}-V_{11})-(V_{11}+2V_{16}+V_7-V_{10}-V_8)\}^{15)}/ \\ &\quad (V_7+V_{10}) \\ &= (2V_{10}-2V_{11}-3V_{16}-V_7+V_8)/(V_7+V_{10}) \end{aligned} \tag{19}$$

TABLE 2. COMPARISON OF CALCULATED RATE QUOTIENTS WITH EXPERIMENTAL RATE QUOTIENTS FROM TABLE 1

Exp't No.	1	2	3
$V_7 \times 10^5$ (M/min)	2.92	5.59	9.93
$V_8 \times 10^5$ (M/min)	3.62	7.50	14.80
$V_{10} \times 10^5$ (M/min)	7.35	5.18	3.58
$V_{11} \times 10^5$ (M/min)	0.42	1.82	8.91
$V_{16} \times 10^5$ (M/min)	0.698	1.90	4.87
$(-\mathrm{d}O_2/\mathrm{d}[\mathrm{H_2O_2}])_0$[a)]	0.717 (0.85)	0.536 (0.49)	0.363 (0.29)
$(-\mathrm{d}[\mathrm{H^+}]/\mathrm{d}[\mathrm{H_2O_2}])_0$[a)]	1.12 (1.0)	0.519 (0.61)	−0.151 (0.18)
$(\mathrm{dTlI}/\mathrm{d}O_2)_0$[b)]	1.21 (1.31)	0.272 (0.893)	−1.51 (−0.071)

a) Experimental values from Table 1 in parentheses, the inaccuracies of which are estimated to be less than ±2.5%.

b) Experimental values for $\Delta \mathrm{TlI}/\Delta O_2$ from Table 1 in parentheses.

A comparison of experimental and calculated rate quotients is given in Table 2. In light of the complexity of the reaction system and the difficulty of analytical work, we consider the comparison satisfactory.

TABLE 3. DATA FOR SUPPORTING MEASUREMENTS AT 50°C OF OXYGEN EVOLUTION RATE

Exp't No.	4	5	6	7
$[\mathrm{I_2}]_0 \times 10^3$ (M)	3.08	3.08	3.08	3.08
$[\mathrm{I^-}]_0 \times 10^6$ (M)	1.86	1.12	0.93	1.42
$[\mathrm{H^+}]_0$ (M)	0.393	0.112	0.449	0.224
$[\mathrm{H_2O_2}]_0$ (M)	1.724	1.722	1.91	2.58
$A \times 10^8$ (mol/l)	5.34	3.40	6.02	5.00
$A' \times 10^8$ (mol/l)	6.07	3.72	6.71	4.72

Supporting Measurements of Oxygen Evolution Rate. To confirm the validity of Eq. (9), and to establish a basis for estimating the reliability of the various specific rates, measurements of the rate of oxygen evolution were carried out at various $[\mathrm{I^-}]$ and $[\mathrm{H^+}]$. Values of A and A' for these experiments are listed in Table 3. The agreement between each A and the corresponding A' is good enough, in view of the complexity of Eq. (9).

Relation to Previous Work

What began as a simple temperature-coefficient measurement for a reaction previously investigated[8)] at 25°C had to be expanded into a complete kinetic investigation because evidence was obtained at 50°C to show that Eq. (3), assumed by Liebhafsky,[8)] did not describe what actually took place. An attempt was made to interpret his results at 25°C in terms of the new mechanism. The attempt was partially successful. It gave consistent results and showed in particular that his value of k_{10} must be too high. Because his rate measurements were for calculated *average* (not *initial*) concentrations, they must be repeated if reliable values of the specific rates at 25°C are to be obtained.

The new work has a bearing on the *reduction*[16)] of hydrogen peroxide by iodine. One difficulty with this

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14) Under the experimental conditions, Equilibrium 14 is maintained, and $[\mathrm{H^+}]$, $[\mathrm{Tl^+}]$ —and hence $[\mathrm{I^-}]$— are virtually constant; consequently so is [HIO]. Therefore, the net rate of HIO production in the reaction system must equal the net rate of HIO consumption in the reverse reaction in Equilibrium 14. This net rate of HIO production is given by the terms in the second parentheses; owing to Equilibrium 9, H_2OI^+ counts as HIO. As one H^+ is consumed for each HIO in the reverse reaction of Equilibrium 14, the terms in the parentheses in question also give the rate of H^+ consumption in this reverse reaction. The terms in the first parentheses give the net rate of H^+ production in all reactions other than the forward reaction of Equilibrium 14.

15) The reasoning here parallels that given in 14) except that I^- (or TlI) and not H^+ is involved.

16) H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **53**, 2074 (1931).

reaction was the need to find some species related to iodine that could *reduce* H_2O_2. HIO seemed to be excluded because it oxidizes H_2O_2 in Step 10. The existence of $H_2I_2O_3$ was consequently postulated. Subsequently Bell and Gelles[17] proved the existence of H_2OI^+, which makes the assumption of Step 8 seem a better way out of the difficulty.

The complexity of the new results shows that the present reaction system is closely related to that in which the oscillating decomposition of peroxide occurs; an important difference is that $[IO_3^-]$ is appreciable in the second system. The new specific rates (k_8, k_{10}, and the ratio k_{16}/k_7) should eventually be useful for describing the oscillating decomposition.

In the previous work, it was assumed that HIO_2 reduces H_2O_2 to form IO_3^-, which contradicts Step 7 if HIO_2 can react with H_2O_2 in only one way. Unfortunately, HIO_2 cannot be isolated under our conditions for a direct test of its reactivity with H_2O_2. The evidence for Step 7 is as strong as indirect evidence of this kind can be.

Summary

An investigation of the oxidation by iodine of hydrogen peroxide in acid solutions at 50°C has shown the reaction to be more complex than had been expected.

Comprehensive experiments in which $[I^-]$ was controlled by use of TlI(s) gave a mechanism in which the four steps

Step 7 $HIO_2 + H_2O_2 \longrightarrow HIO + H_2O + O_2$
Step 8 $H_2OI^+ + H_2O_2 \longrightarrow HIO_2 + H^+ + H_2O$
Step 10 $HIO + H_2O_2 \longrightarrow H^+ + I^- + O_2 + H_2O$
Step 16 $HIO_2 + H^+ + I^- \longrightarrow 2HIO$

are involved as constituent elementary steps. Numerical values for 50°C: $k_8 = 1.37 \times 10^7 \text{M}^{-1}\cdot\text{min}^{-1}$; $k_{10} = 6.5 \times 10^3 \text{M}^{-1}\cdot\text{min}^{-1}$; $k_{16}/k_7 = 2.14 \times 10^5 \text{M}^{-1}$. The last two specific rates appear as a ratio because $[HIO_2]$ is unknown.

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[17] R. P. Bell and E. Gelles, *J. Chem. Soc.*, **1951**, 2734.