390. *The Kinetics of the Iodide-catalysed Reaction between Hydrogen Peroxide and Hydrazine in Acid, Aqueous Solution.*

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In dilute aqueous acid solution the oxidation of hydrazine by hydrogen peroxide is catalysed by iodide ions. Kinetic experiments show that hydrogen peroxide oxidises iodide to iodine which in turn oxidises hydrazine to nitrogen.

It is suggested that traces of transition-metal ion impurities are responsible for the reaction observed in the absence of deliberately added catalysts in neutral and alkaline solutions, and that there is no satisfactory evidence for a direct reaction between hydrogen peroxide and hydrazine under these conditions.

The kinetics of the uncatalysed reaction between hydrogen peroxide and hydrazine, $2H_2O_2 + N_2H_5^+ \longrightarrow 4H_2O + H^+ + N_2$, have been studied in aqueous solution by Gordon (Third Symposium on Combustion, Flame, and Explosion Phenomena, Univ. Wisconsin, 1948, p. 483). Our experiments have however led us to believe that with ordinary " pure " reagents the reaction is catalysed by traces of transition-metal ions, and we know of no convincing evidence for a direct reaction. The results of some of these experiments, referred to in detail by Davis (Thesis, Manchester, 1951), are briefly summarised in the Experimental section of this paper. In developing a method for the estimation of hydrogen peroxide and hydrazine present in the same sample, we found that the iodide ion was under certain conditions a good catalyst for the reaction between these substances, and this paper describes our investigation of this catalysis. In solutions of pH 0 to 1 the catalytic effect of trace-metal impurities when ordinary " pure " reagents are used is much lower than at higher pH values, and these conditions are suitable for a study of the catalytic effect of the iodide ion. Experiments were also done at pH 4, and here small concentrations of ethylenediaminetetra-acetate were used to minimise catalysis by traces of metal ions, a procedure found effective in the study of the direct reaction.

The iodide ion acts as a catalyst in the decomposition of hydrogen peroxide, and its effect has been ascribed to occurrence of the reactions :

$$2H^+ + H_2O_2 + 2I^- \longrightarrow 2H_2O + I_2$$
$$H_2O_2 + I_2 \longrightarrow 2H^+ + O_2 + 2I^-$$

(see, *e.g.*, Baxendale, " Advances in Catalysis," Academic Press Inc., New York, Vol. 4, p. 35). In a similar way the simplest interpretation of the catalytic effect of iodide in the hydrogen peroxide–hydrazine reaction would seem to be in terms of the separate reactions :

$$2H^+ + H_2O_2 + 2I^- \longrightarrow 2H_2O + I_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$
$$N_2H_5^+ + 2I_2 \longrightarrow 5H^+ + N_2 + 4I^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Under our conditions the rate of oxidation of hydrogen peroxide by iodine can be neglected in comparison with the rates of these two reactions. If equivalent initial concentrations of hydrogen peroxide and hydrazine are used and these reactions alone are important, a stationary concentration of iodine should be set up and, together with the corresponding reaction velocity constant, can be calculated if the rate laws for reactions (1) and (2) are known. For (1),

$$-\,d[H_2O_2]/dt = d[I_2]/dt = k_1[H_2O_2][I^-] + k_2[H_2O_2][I^-][H^+] = k'[H_2O_2],$$

and at the ionic strength (0·575) of our experiments, k_1 = 0·80 mole^{-1} l. min.$^{-1}$, and k_2 = 10·0 mole^{-2} l.^{2} min.$^{-1}$ (Bell, Gill, Holden, and Wynne-Jones, *J. Phys. Colloid Chem.*, **1951**, **55**, 874). The kinetics of the oxidation of hydrazine by iodine in acid solution have been studied by Berthoud and Porret (*Helv. Chim. Acta*, **1934**, **17**, 32), but their results are not applicable under our conditions. Using 0·002—0·020M-iodide ion, Mr. Marshall in this laboratory has found by similar methods that the rate equation for this reaction is :

$$-\frac{2\mathrm{d}[\mathrm{N_2H_5^+}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{Iodine}]}{\mathrm{d}t} = \frac{k_3[\mathrm{N_2H_5^+}][\mathrm{I_2}]}{[\mathrm{I^-}] + k_4} = k''[\mathrm{N_2H_5^+}],$$

Here [Iodine] = $[I_2] + [I_3^-]$, and $[I_2]$ is calculated from [Iodine] and $[I^-]$ by using the dissociation constant of I_3^-. Davis and Gwynne's work (*J. Amer. Chem. Soc.*, 1952, **74**, 2748) shows that this constant varies little with ionic strength, and accordingly a value of 0·00130 mole l.$^{-1}$ has been used. At 25°, and ionic strength = 0·575, and with $[H^+]$ = 0·479M, k_3 was found to equal 2·33 min.$^{-1}$, and k_4, 0·00071 mol l.$^{-1}$. For 0·16—0·50M-hydrogen ion, k_3 is inversely proportional to the hydrogen-ion concentration, while k_4 is independent of the latter.

When these constants are used, the following procedure gives the first-order constant for the catalysed reaction in terms of the total added iodide concentration, provided that the ratio of the hydrogen peroxide and the hydrazine concentration remains constant. For a given total added iodide concentration a value of the stationary iodide-ion concentration is assumed. The corresponding values of the stationary I_2 and I_3^- concentrations can then be found. From the values of $[I^-]$ and $[I_2]$, the rate constant, k'', for the disappearance of total iodine in the hydrazine–iodine reaction can be calculated. For the same total concentration of added iodide, different stationary concentrations of iodide are then assumed, and a plot of $k''/2$ against the stationary iodide concentration is constructed. The linear plot of the rate constant, k', for the formation of iodine in the hydrogen peroxide–iodide reaction, against the iodide concentration is then superimposed. The point at which the two plots intersect gives the rate constant for formation and disappearance of iodine caused by the hydrogen peroxide–iodide and the hydrazine–iodide reaction respectively. For the overall reaction $2H_2O_2 + N_2H_5^+ \longrightarrow 4H_2O + H^+ + N_2$, if $[H_2O_2]_{\mathrm{initial}} = 2[N_2H_5^+]_{\mathrm{initial}}$ and at iodide–iodine equilibrium,

$$-\frac{\mathrm{d}[\mathrm{I_2}]}{\mathrm{d}t}\,\begin{pmatrix}\mathrm{N_2H_5^+{-}I_2}\\ \text{reaction}\end{pmatrix} = \frac{\mathrm{d}[\mathrm{I_2}]}{\mathrm{d}t}\,\begin{pmatrix}\mathrm{H_2O_2{-}I^-}\\ \text{reaction}\end{pmatrix} = -\frac{\mathrm{d}[\mathrm{H_2O_2}]}{\mathrm{d}t} = \frac{2\mathrm{d}[\mathrm{N_2H_5^+}]}{\mathrm{d}t} = k'[\mathrm{H_2O_2}] = k''[\mathrm{N_2H_5^+}]$$

Hence is found the first-order rate constant $k = k' = \tfrac{1}{2}k''$ for the disappearance of hydrogen peroxide and hydrazine at the total added iodide concentration used in the calculation. The corresponding stationary concentration of iodine ($[I_2] + [I_3^-]$) is also known since $[I_2]$ and $[I_3^-]$ are evaluated in calculating the rate constant.

TABLE 1. $[H_2O_2]_{\mathrm{initial}}$ = 0·05M; $[N_2H_4,H_2SO_4]_{\mathrm{initial}}$ = 0·025M; $[H^+]$ = 0·479M.

Expt.	Added $[I^-]$ × 10^3M	$10^3k_{(\mathrm{obs.})}$ (min.$^{-1}$)	10^3k $_{(\mathrm{calc.})}$ (min.$^{-1}$)	$[\mathrm{Iodine}]_{(\mathrm{obs.})}$ × 10^2N	$[\mathrm{Iodine}]_{(\mathrm{calc.})}$ × 10^2N
1	0·0667	0·443	0·372	<0·05	<0·01
2	0·167	1·10	0·930	<0·05	<0·01
3	0·333	2·15	1·80	<0·05	<0·01
4	0·667	4·26	3·65	<0·05	<0·01
5	1·67	9·04	8·76	<0·05	0·01
6	3·33	12·1	16·0	<0·10	0·03
7	5·00	16·0	22·2	<0·15	0·07
8	6·67	17·7	27·4	<0·20	0·13
9	8·33	21·2	31·7	<0·35	0·19
10	10·0	25·4	35·5	<0·45	0·26
11	13·3	31·6	42·1	<0·60	0·41
12	16·7	35·9	47·5	<0·75	0·56
13	25·0	45·2	58·2	<1·30	1·00
14	33·3	53·0	66·5	<1·60	1·47

In Table 1 calculated and observed values of k, defined above, and of the stationary iodine concentration are tabulated with the corresponding concentration of added iodide for experiments at 0·479M-hydrogen ion. In Table 2 are tabulated similar data at 0·312, 0·160, and 10^{-4} M-hydrogen ion. For these experiments the stationary iodine concentrations were too small to be measured with reasonable accuracy and hence the calculated values are not recorded. At 10^{-4} M-hydrogen ion the solutions remained colourless, showing a very low stationary iodine concentration. Agreement between calculated and experimental values is fairly good, and we conclude therefore that iodide acts as a redox catalyst in that it is oxidised by the hydrogen peroxide to iodine which in its turn oxidises the hydrazine. It is not possible to be more specific since the detailed mechanisms of the contributing reactions, (1) and (2), are unknown.

TABLE 2. $[H_2O_2]_{initial} = 0{\cdot}05$M; $[N_2H_4,H_2SO_4]_{initial} = 0{\cdot}025$M.

$[H^+]$ M	Added $[I^-]$ $\times 10^3$M	$10^3k_{(obs.)}$ (min.$^{-1}$)	$10^3k_{(calc.)}$ (min.$^{-1}$)	$[H^+]$ M	Added $[I^-]$ $\times 10^3$M	$10^3k_{(obs.)}$ (min.$^{-1}$)	$10^3k_{(calc.)}$ (min.$^{-1}$)
0·312	0·25	1·19	0·98	0·160	6·67	15·0	14·4
0·312	0·50	2·32	1·95	10^{-4}	0·33	0·247	0·254
0·312	2·50	9·88	9·30	10^{-4}	1·67	1·25	1·33
0·312	5·00	14·8	17·3	10^{-4}	3·33	2·42	2·66
0·160	0·33	0·99	0·80	10^{-4}	6·67	4·94	5·32
0·160	1·00	2·89	2·39	10^{-4}	13·3	9·92	10·6
0·160	1·67	4·77	3·98				

The discrepancies between calculated and experimental values may arise partly because the rate constants used were determined under different concentration conditions from those obtaining in the catalysis experiments. Also, for the hydrazine–iodine reaction the predominating anion was chloride, as distinct from perchlorate in the hydrogen peroxide–iodide and the catalysis experiments. In the experiments at low iodide concentrations in 0·160, 0·312, and 0·479M-hydrogen ion, the observed rate constants are somewhat larger than those for the hydrogen peroxide–iodide reaction at the same acidities. At low iodide concentrations the rate constants for the catalysis experiments should closely approach, but should not exceed, those for the hydrogen peroxide–iodide reaction. However, the reaction rates are small and it is possible that this anomaly may be caused by the presence of catalytically active impurities.

In strongly acid solutions iodide is an effective catalyst only at low concentrations, and, with regard to the evolution of nitrogen, the reaction virtually ceases at added iodide concentrations about three times the hydrogen peroxide concentration. Under these conditions the hydrogen peroxide is quantitatively reduced while the iodine so formed reacts very slowly with hydrazine. The analytical method used for determining hydrogen peroxide in the presence of hydrazine depends in part upon these circumstances.

EXPERIMENTAL

Materials.—Hydrogen peroxide stock solutions were prepared by dilution of the Laporte, stabiliser-free product; sodium iodide was of B.P. recryst. quality; sodium perchlorate was Hopkin and Williams' recrystallised product. Ethylenediaminetetra-acetic acid (disodium salt) was obtained from Siegfried, Zofingen; other reagents were of B.D.H. "AnalaR" quality. Demineralised water, of conductivity not greater than $1{\cdot}5 \times 10^{-7}$ mhos when prepared, was obtained by passing distilled water through a column of "Bio-deminrolit F" mixed exchange resin (Permutit Co.).

Analysis.—All stock oxidising and reducing solutions used, including the sodium iodide solutions, were ultimately referred to potassium iodate as primary standard Hydrogen peroxide was estimated in the reaction mixture by adding a sample to sufficient 3M-sulphuric acid to make the solution approx. molar in hydrogen ion. Solid potassium iodide was immediately added to give 0·5—1·0M-iodide ion, and the iodine liberated was titrated with 0·1N-sodium thiosulphate, the solution being agitated throughout the titration. 0·1N-Iodine, in small excess over the amount equivalent to the hydrazine present, was then added and the mixture buffered to approximately pH 5 by addition of the appropriate amount of concentrated sodium acetate solution. After 2 min., the excess of iodine was back-titrated against 0·1N-sodium thiosulphate. By this procedure hydrogen peroxide and hydrazine concentrations could be determined with an accuracy of ±0·0004M and ±0·0002M respectively, as shown by experiments with catalyst-free solutions under similar conditions. To obtain the true hydrogen peroxide concentration in the experiments at high iodide concentration in 0·479M-acid it was necessary to subtract the concentration of iodine already present in the reaction mixture from the hydrogen peroxide concentration found by the above method. When the reactants were mixed at the beginning of a kinetic experiment the iodine concentration increased for *ca.* 3 min. and then, within a random error of about ±10%, was constant for the remainder of the reaction. The comparative slowness with which the stationary concentration was established enabled a fairly close upper limit to be obtained by rapid titration of a sample of reaction mixture with 0·1N-sodium thiosulphate. Since the stationary iodine concentrations were much smaller than the initial hydrogen peroxide concentration, the errors introduced in correcting to the true hydrogen peroxide concentration were unimportant except towards the end of the reaction. Concentrations of reactants were not determined after reaction was about 85% complete.

Kinetic Experiments.—Experiments were done at 25° under nitrogen in a vessel fitted with a mercury-sealed stirrer. Samples for analysis were withdrawn by pipette. All stock solutions used in making up the reaction mixture were prepared with demineralised water. Initial concentrations of hydrogen peroxide and hydrazine were 0·05M and 0·025M respectively, except for experiments 9 to 14 (Table 1) where extra hydrogen peroxide, approximately equivalent to the stationary iodine concentration, was used. Hydrazine was added as monohydrazine sulphate, N_2H_4,H_2SO_4. In calculations of the hydrogen-ion concentration, 0·08 mole $l.^{-1}$ was used for the second dissociation constant of sulphuric acid at an ionic strength of 0·575. This value was obtained by a short extrapolation from Bray and Liebhafsky's results (*J. Amer. Chem. Soc.*, 1935, **57**, 51). In the reaction solution, sodium iodide was preferred to potassium iodide since potassium perchlorate precipitates were obtained with the latter. In the experiments at pH 4 an acetic acid–sodium acetate buffer was used and the reaction solutions contained 0·002M-ethylenediaminetetra-acetate to minimise catalysis by traces of metal ions (see below). For all the kinetic experiments the stoicheiometry was within the limits $\Delta[H_2O_2]/\Delta[N_2H_5^+] = 2{\cdot}00 \pm 0{\cdot}04$. For most of the kinetic experiments eight determinations of reactant concentrations were made at suitable time intervals.

The Direct Reaction between Hydrogen Peroxide and Hydrazine in Aqueous Solution.—Before studying the iodide-catalysed reaction we had investigated the possibility of a direct reaction between hydrogen peroxide and hydrazine. The method of analysis described above was used. In experiments at pH 9·5 and 13 we found that the rate of disappearance of both reactants was of the first order with respect to hydrogen peroxide if the hydrazine was in similar concentration to the hydrogen peroxide ($\simeq$ 0·05M), or was in 20—40-fold excess. With hydrogen peroxide in 20-fold excess (0·80M) the rate was constant for the first 50% reaction but then slowly diminished. Repurification of the reagents and the use of demineralised water gave lower rates of reaction, but consistent results could not be obtained except when experiments were repeated with the same stock solutions. The order of reaction was again as described above. These observations suggest that the rate-determining step involves reaction between hydrogen peroxide and an impurity. At pH 9·5 the addition of small amounts of copper(II) caused a very large increase in the rate of reaction; at this pH, 10^{-7}M-copper(II) would be sufficient to account for the rates observed with "pure" reagents. Other transition-metal ions were effective, but much less so than copper(II).

In the presence of small amounts of ethylenediaminetetra-acetate, generally 2% of the initial concentrations of the reactants, and in one case 0·05%, the rate of reaction was very much lower than that obtained with purified reagents under otherwise similar conditions (see Table 3). We conclude that traces of transition-metal ions were not removed in our purification procedures, and that the ethylenediaminetetra-acetate ion greatly reduced the concentration of these catalytically active species in forming the corresponding inactive or much less active complex ions. We regard this as a more likely explanation than that the effect of the complex-forming reagent is to decrease the length of reaction chains by reaction with radical intermediates.

TABLE 3.

pH	9·05	9·5	9·5	9·5	10·3	10·7	11·6	13	13
10^3k (min.$^{-1}$) (Gordon)	2·75	—	—	—	4·76	9·27	2·75	—	—
10^3k (min.$^{-1}$) (this work)	—	6·7	0·09	0·08	—	—	—	1·17	0·138
10^3[enta] (M)	—	—	0·05	2·0	—	—	—	—	2·0

In Table 3 are tabulated typical rate constants found in the presence and absence of ethylenediaminetetra-acetate (enta), together with first-order rate constants, also at 25°, calculated from Gordon's work (*loc. cit.*). Our first-order rate constants are defined as $-k = d(\ln[H_2O_2])/dt = d(\ln[N_2H_5^+])/dt$, as for the iodide-catalysed reaction; concentrations were H_2O_2 = 0·100M, $N_2H_5^+$ = 0·050M. The rate constants from Gordon's work are equivalent, and are found from the expression $d[N_2]/dt = k[N_2H_5^+]$, though no indication of the order of the reaction is given. In his experiments, in which the initial reactant concentrations were both 1·5M, presumably only the initial rates of nitrogen formation were measured. It can be seen that at similar hydrogen-ion concentrations our rate constants in the absence of ethylenediaminetetra-acetate are similar to Gordon's, but that in the presence of this reagent we obtained substantially lower values. Since in our experiments the residual reaction in the presence of the complexing reagent still showed first-order kinetics, we consider that a direct reaction between hydrogen peroxide and hydrazine in dilute aqueous solution can account for a small proportion only of the total reaction rate normally observed unless special measures are taken to remove catalytically active impurities. Thus we think it possible that Gordon was studying the reaction catalysed by traces of metal ions, though the relatively high concentrations of reactants he used are admittedly more favourable to the occurrence of the direct (second-order) reaction than are our conditions. We conclude therefore that his results do not provide unequivocal evidence for an uncatalysed reaction between hydrogen peroxide and hydrazine in aqueous solution.

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