Kinetics and Mechanism of Electron-transfer Reactions of Aqueous and Co-ordinated Thallium(III). Part X.† Kinetics of Reduction of Hexa-aquathallium(III) by Hydrogen Peroxide and Induction of the Reaction by Cerium(IV) and Iron(II) Ions

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Thallium(III) and H_2O_2 react in aqueous perchloric acid solution as in equation (i). The kinetics of reaction have

$$Tl^{III} + H_2O_2 \longrightarrow Tl^{I} + 2H^+ + O_2 \qquad (i)$$

been followed by estimating Tl^{III} iodometrically and the rate law for $[HClO_4] = 0{\cdot}5$—$2{\cdot}0$M and $I = 0{\cdot}5$—$2{\cdot}5$M is $-d[Tl^{III}]/dt = k'[Tl^{III}][H_2O_2]^2/(K_h + [H^+])$. Here k' is the apparent rate constant, which probably includes a formation constant also, and K_h is the acid dissociation constant of Tl^{3+}(aq); k' has the value $6{\cdot}7 \pm 0{\cdot}5$ l mol^{-1} s^{-1} at $I = 2{\cdot}0$M and 30 °C, and the energy of activation is $10{\cdot}3 \pm 0{\cdot}7$ kcal mol^{-1}. The reaction is independent of ionic strength in the range $0{\cdot}5$—$2{\cdot}5$M ($LiClO_4$). The reaction is induced by cerium(IV) ions through the intermediate radicals $H_2O_2^+$ and/or $HO_2^{\cdot}$, and the induction factor is unity. Iron(II) ions act as a strong initiator for the reaction, and hydrogen peroxide can be determined in their presence using thallium(III) as a primary standard.

ALTHOUGH the existence [1] of Tl^{II} is now beyond doubt, there is little direct kinetic evidence for its intermediacy in redox processes involving the Tl^{III}–Tl^{II} couple. Results on the oxidation of Fe^{II} (ref. 2) indicate intermediate formation of Tl^{II}, but in all other oxidations its existence is purely speculation. Hydrogen peroxide undergoes a two-electron change during oxidation and the intermediate product, $HO_2^{\cdot}$, has been assumed [3] and detected.[4] Thus in a redox process where the oxidant and reductant both undergo two-electron change, there is less probability of obtaining evidence for the intermediate products because in general the latter are reactive, at least in the reaction being considered. However, induction by Ce^{IV} and the chain-initiating role of Fe^{II} in the present reaction indirectly

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† Part IX is ref. 16.

[1] J. Jordon and H. A. Catherino, *J. Phys. Chem.*, 1963, **67**, 2241.

[2] B. Warnqvist and R. W. Dodson, *Inorg. Chem.*, 1971, **10**, 2624 and refs. therein.

[3] C. Czapski, B. H. J. Bielski, and N. Sutin, *J. Phys. Chem.*, 1963, **67**, 201.

[4] G. M. Coppinger, *J. Amer. Chem. Soc.*, 1957, **79**, 2758.

suggest the existence of intermediate products of reaction between Tl^{III} and H_2O_2. Other reactions with H_2O_2 which have been studied include those of Ce^{IV},[5] Mn^{III},[6,7] Co^{III},[8] Fe^{III},[9] and Cr^{III}. The first two are particularly fast and the last two are particularly slow. It is interesting to find that the reactivity of Tl^{III} towards H_2O_2 and its reduction potential lie between the two groups of metal ions mentioned above.

EXPERIMENTAL

Thallium(III) was prepared and standardized as reported earlier.[10] The stock solution of hydrogen peroxide was prepared by dilution of 20% w/v H_2O_2 (E. Merck). It was standardized [11] against a Ce^{IV} solution using Ferroin as indicator. Since stock solutions of hydrogen peroxide are somewhat unstable, they were always standardized immediately before use. Lithium perchlorate was prepared by dissolving lithium carbonate (Sojuzchimsxport, Moscow; pure, L.R.) in 60% perchloric acid. Carbon dioxide was removed by gentle heating and the pH of the solution was adjusted to 6·7—7·0. Sodium chloride, sodium sulphate, sodium nitrate, thallium(I) nitrate, and iron(II) sulphate were of B.D.H. AnalaR quality. Acrylamide (B.D.H.) was used as supplied. Solutions of cerium(IV) sulphate and perchlorate were prepared by dissolving ammonium cerium(IV) pentanitrate in 1·0M-sulphuric and 1·0M-perchloric acids respectively. These were standardized against diammonium iron(II) bis(sulphate) solution.* Doubly distilled water was used throughout the work.

Kinetics Procedure.—The experiments were conducted in stoppered Erlenmeyer flasks immersed in a thermostatted water-bath at 30 ± 0·1 °C, unless mentioned otherwise. The reaction was initiated by adding a known volume of thallium(III) perchlorate solution to a temperature-equilibrated mixture containing hydrogen peroxide and perchloric acid of desired concentrations. Aliquot portions (10 or 5 cm^3) were analysed for Tl^{III} iodometrically after suitable intervals. Constant and vigorous shaking of the solution was necessary during iodometric titration with thiosulphate ions. Since hydrogen peroxide also liberates iodine from iodide solutions, it was necessary to cool the reaction mixture with ice before adding potassium iodide. This effectively suppressed the reaction [12] between hydrogen peroxide and iodide ions. Under these conditions separate experiments without Tl^{III} showed that no iodine was liberated in 5 min if $[H_2O_2]$ was less than 7×10^{-3}M. However, the titration times were not greater than 2—3 min. The initial rates were calculated from a plot of $[Tl^{III}]$ against time. The results were reproducible to ±11%.

Some experiments were carried out by estimating H_2O_2 cerimetrically in the presence of chloride ions. Aliquot portions of the reaction mixture were added to a mixture of Ce^{IV} and sufficient chloride ions (10—15 times the concentration of Tl^{III} present in the reaction mixture), and excess of Ce^{IV} was determined with Fe^{II}.

RESULTS

Stoicheiometry.—For determination of the stoicheiometry, excess of Tl^{III} was determined as described in the kinetics procedure and ref. 10. Excess of H_2O_2 was determined cerimetrically [11] and the slight amount of decomposition (not more than 5%) of H_2O_2 was taken into account by running parallel experiments under identical conditions but without thallium(III). The results conformed to equation (1).

$$Tl^{III} + H_2O_2 \longrightarrow Tl^{I} + 2H^+ + O_2 \qquad (1)$$

Dependence on Tl^{III}.—The concentration of Tl^{III} was varied from 5×10^{-4} to 1×10^{-2}M with a fixed concentration (5×10^{-3}M) of H_2O_2 and a plot of log (initial rate) against log $[Tl^{III}]$ yielded a straight line passing through the origin.

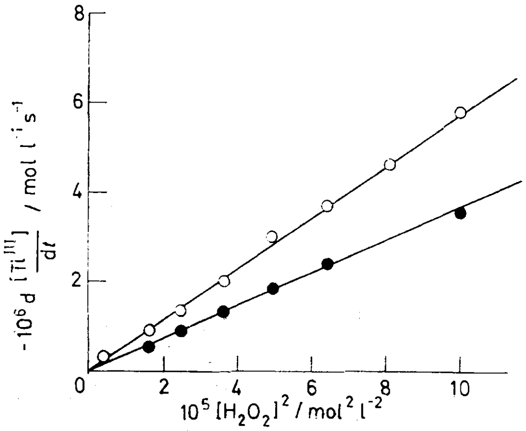

FIGURE 1 Plot of initial rate of reaction at $[HClO_4] = 0·5$M and 30 °C against (○), $[Tl^{III}] = 5·0 \times 10^3$M; (●), $[Tl^{III}] = 3·0 \times 10^{-3}$M

Dependence on H_2O_2.—The range of $[H_2O_2]$ investigated was 5×10^{-4}—1×10^{-2}M with fixed $[Tl^{III}] = 3 \times 10^{-3}$ or 5×10^{-3}M, and a plot of the initial rate against $[H_2O_2]^2$ is shown in Figure 1. The order in $[H_2O_2]$ is thus two, although the stoicheiometry is 1 mol H_2O_2 for 1 mol Tl^{III}.

The total order with respect to the main reactants is three. The average value of the third-order rate constant from the initial rates was 11·7 ± 0·9 l^2 mol^{-2} s^{-1} (at $[HClO_4]$ = 0·5M, I = 2·0M, and 30 °C). With stoicheiometric concentrations of Tl^{III} and H_2O_2, plots of $1/[Tl^{III}]^2$ or $1/[H_2O_2]^2$ against time yielded straight lines, from the gradients of which the third-order rate constant k'' was found to be 11·7 ± 0·8 l^2 mol^{-2} s^{-1} at $[HClO_4] = 0·5$M, I = 2·0M, and 30 °C. The rate law with $[Tl^{III}]$ and $[H_2O_2]$ dependences is as in equation (2), and this on integration

$$-d[Tl^{III}]/dt = k''[Tl^{III}][H_2O_2]^2 \qquad (2)$$

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* 1M = 1 mol dm^{-3}.

[5] S. Baer and G. Stein, *J. Chem. Soc.*, 1953, 3176.

[6] G. Davies, L. J. Kirschenbaum, and K. Kustin, *Inorg. Chem.*, 1968, **7**, 146.

[7] C. F. Wells and D. Mays, *J. Chem. Soc.*, 1968, 655.

[8] G. Davies and K. O. Watkins, *J. Phys. Chem.*, 1970, **74**, 3388.

[9] P. Jones, R. Kitching, M. L. Tobe, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1959, **55**, 79.

[10] K. S. Gupta and Y. K. Gupta, *J. Chem. Soc.* (*A*), 1970, 256.

[11] I. M. Kolthoff and R. Belcher, 'Volumetric Analysis,' Interscience, New York, 1957, vol. 3, p. 650.

[12] H. A. Liebhafsky and A. Mohammad, *J. Amer. Chem. Soc.*, 1933, **55**, 3977.

gives (3) where a and b are the concentrations of the two

$$k''t = \frac{1}{(a-b)^2}\left[\log\left(\frac{b-x}{a-x}\right) + \left(\frac{a-b}{b-x}\right)\right] + \frac{1}{(a-b)^2}\left[\log\left(\frac{b}{a}\right) + \left(\frac{a-b}{b}\right)\right] \quad (3)$$

reactants and the x the amount reacting in time t. A plot of $\left[\log\left(\frac{b-x}{a-x}\right) + \left(\frac{a-b}{b-x}\right)\right]$ against time yielded a straight line with $k'' = \text{gradient}/(a-b)^2$. Values of k'' were found to be 10—15 $l^2\ mol^{-2}\ s^{-1}$ in most cases, but in many other cases the values varied between 15 and 40 $l^2\ mol^{-2}\ s^{-1}$. In general it appears that where $(a - b)$ is small, the value of k'' is large irrespective of the fact that Tl^{III} or H_2O_2 is in excess. Some typical plots are shown in Figure 2.

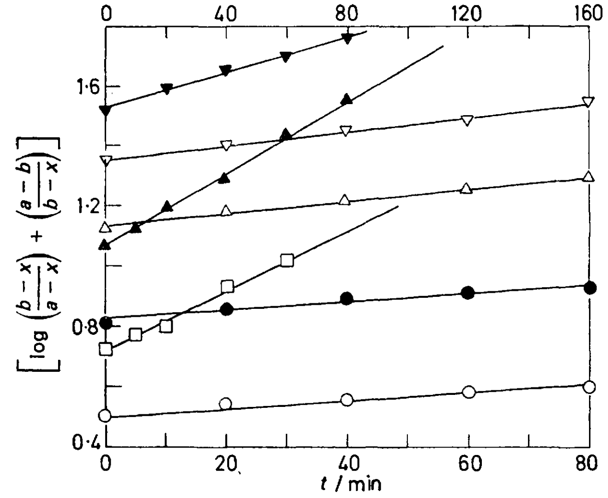

FIGURE 2 Third-order plots of the reaction between Tl^{III} and H_2O_2 at $[HClO_4]$ = 0·5M, I = 2·0M, and 30 °C

	$10^3[Tl^{III}]$/M	$10^3[H_2O_2]$/M	k''/$l^2\ mol^{-1}\ s^{-1}$
Upper time scale			
(○)	3·0	2·0	14
(●)	1·0	2·0	15
(△)	0·7	2·0	13
(▽)	0·5	2·0	10·5
Lower time scale			
(▼)	10·0	2·0	15·5
(▲)	2·0	5·5	14
(□)	3·0	5·5	20

Effect of Hydrogen Ions.—This effect was observed by varying the concentration of perchloric acid from 0·5 to 2·0M at fixed total 2·0M-perchlorate ion, adjusted with lithium perchlorate. The rate of reaction decreased with increasing perchloric acid concentration (Table 1) and plots of 1/rate against $[HClO_4]$ yielded straight lines with non-zero intercepts.

Effect of Ionic Strength.—Ionic strength was varied from 0·5 to 2·5M using lithium perchlorate ($[Tl^{III}] = 5 \times 10^{-3}$ and $[H_2O_2] = 5 \times 10^{-3}$M), but no change in the rate of reaction was observed.

Effect of Chloride Ions.—The behaviour of chloride ion in redox reactions involving Tl^{III} has been variously reported. It increases the rate of the Tl^{III}–Tl^{I} exchange reaction[13] and oxidations of Fe^{II},[2] hypophosphorous[10] and phosphorous[14] acids, and Sb^{III}.[15] On the other hand it is a strong inhibitor of the oxidations of hydrazine[16] and As^{III}.[17] Chloride ions strongly inhibit the oxidation of hydrogen peroxide also. The initial rate decreased from 43×10^{-7} (in absence of chloride) to $1{\cdot}2 \times 10^{-7}$ mol l^{-1} s^{-1} in the presence of 0·01M-chloride ($[Tl^{III}] = 5 \times 10^{-3}$, $[H_2O_2] = 8 \times 10^{-3}$, $[HClO_4]$ = 0·5M, and 30 °C).

TABLE 1

Third-order rate constants for the Tl^{III}–H_2O_2 reaction at different hydrogen-ion concentrations (ionic strength adjusted to 2·0M with $LiClO_4$): effects of $TlNO_3$, O_2, N_2, and acrylamide $[Tl^{III}] = 5 \times 10^{-3}$, and $[H_2O_2] = 6{\cdot}0 \times 10^{-3}$M

	k''/$l^2\ mol^{-2}\ s^{-1}$				
$[H^+]$/M	20	25	30	35	40 °C
0·5	7·0	9·0	11·8	16	21·4
0·75		6·1	8·0	10·4	
1·0		4·6	6·3	8·0	
1·25		3·7	5·1	6·6	
1·5		3·2	4·3	5·5	
1·75		2·8	3·7	4·8	
0·5 [a]			11·2		
0·5 [b]			11·5		
0·5 [c]			11·1		
0·5 [d]			11·2		
0·5 [e]			0·2		

[a] 0·001M-$TlNO_3$. [b] 0·01M-$TlNO_3$. [c] Dioxygen saturated. [d] Dinitrogen saturated. [e] 0·1M-Acrylamide.

Effect of Tl^{I} and Oxygen.—Variation of the concentration of thallium(I) nitrate from 0·001 to 0·01M had no effect on the rate of reaction. Carrying out the reaction in an atmosphere of nitrogen or oxygen also produced no change in the initial rate. This means that neither of the major products influences the rate of reaction. These results are shown in Table 1.

Effect of Acrylamide.—Acrylamide has been used previously to detect free radicals in redox reactions; it undergoes polymerization and the rate of redox reaction is reduced. The rate of the present reaction was strongly inhibited in the presence of acrylamide (Table 1).

DISCUSSION

Oxidation of H_2O_2 by metal ions occurs *via* intermediate-complex formation.[18,19] Some authors[20] propose the HO_2^- anion to be the co-ordinating species, but others[6,21] prefer H_2O_2. Since the acid dissociation constant of H_2O_2 is very small,[22] significant complexing

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[13] G. Harbottle and R. W. Dodson, *J. Amer. Chem. Soc.*, 1951, **73**, 2442.

[14] K. S. Gupta and Y. K. Gupta, *J. Chem. Soc. (A)*, 1971, 1180.

[15] P. D. Sharma and Y. K. Gupta, *Indian J. Chem.*, 1974, **12**, 100.

[16] B. M. Thakuria and Y. K. Gupta, preceding paper.

[17] P. D. Sharma and Y. K. Gupta, *J.C.S. Dalton*, 1972, 52.

[18] M. G. Evans, P. George, and N. Uri, *Trans. Faraday Soc.*, 1949, **45**, 230.

[19] M. Ardon and G. Stein, *J. Chem. Soc.*, 1956, 104.

[20] C. F. Wells and D. Mays, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 43.

[21] H. A. Mahlman, R. W. Mathews, and T. J. Sworski, *J. Phys. Chem.*, 1971, **75**, 250.

[22] 'Stability Constants of Metal–Ion Complexes,' eds. L. G. Sillén and A. E. Martell, Special Publ. No. 17, The Chemical Society, London, 1964, p. 210.

can occur only with H_2O_2. In any case the complex-formation constant does not appear to be large. Thallium(III) also has a tendency to form complexes with reductants before reduction takes place. Such behaviour was reported for the oxidation of hypophosphorous acid,[10] phosphorous acid,[14] and hydrazine.[16] It is thus obvious that any complex between Tl^{III} and H_2O_2 is likely to be formed prior to the redox step, although there is no evidence for such complex formation from the kinetics or other studies.

The inverse hydrogen-ion dependence of the rate of reaction in the $[HClO_4]$ range 0·5—2·0M can be correlated with the hydrolytic equilibrium of Tl^{3+} rather than any protonation [23] of H_2O_2. The hydrolysed species $[Tl(OH)]^{2+}$ may form a complex with H_2O_2. Since

$$Tl^{3+} + H_2O \overset{K_h}{\rightleftharpoons} [Tl(OH)]^{2+} + H^+ \qquad (4)$$

$$[Tl(OH)]^{2+} + H_2O_2 \overset{K_1}{\rightleftharpoons} (Tl,HO_2)^{2+} + H_2O \qquad (5)$$

the hydrolysis constant [24] of Tl^{3+} is only 0·073 mol l^{-1} at $I = 3$M and 25 °C, and the hydrogen-ion concentration employed in the present investigation is more than 0·5M, Tl^{III} exists mostly as Tl^{3+} and hence the hydrogen-ion effect can be alternatively represented by (6). The same complex is formed in steps (5) and

$$Tl^{3+} + H_2O_2 \overset{K_2}{\rightleftharpoons} (Tl,HO_2)^{2+} + H^+ \qquad (6)$$

(6) with the identical hydrogen-ion dependence and $K_2 = K_1K_h$. The slow-step leading to an order of two with respect to $[H_2O_2]$, probably occurs as in (7)

$$(Tl,HO_2)^{2+} + H_2O_2 \xrightarrow{k} \text{Products} \qquad (7)$$

if H_2O_2 is postulated [6] as a stabilizer for $H_2O_2^+$ (formed by protonation of HO_2). Alternatively, since there is evidence from Raman studies for dimerization [25] of H_2O_2 by hydrogen bonding in concentrated solutions, a complex of Tl^{3+} and the dimer may be formed [equation (8)] and which then decomposes to yield the final

$$Tl^{3+} + 2H_2O_2 \overset{K_1'}{\rightleftharpoons} (Tl,HO_2,H_2O_2)^{2+} + H^+ \qquad (8)$$

products (with $K_2k = K_1'k_1$).

$$(Tl,HO_2,H_2O_2)^{2+} \xrightarrow{k_1} \text{Products} \qquad (9)$$

Such a situation with indistinguishable rate laws has been found in the decomposition [26] of H_2O_2 by copper(II) 2,2′-bipyridyl complexes, although no dimer was postulated by the authors. Considering steps (4), (5), and (7) for the reaction between Tl^{III} and H_2O_2 and assuming $K_1 \ll K_h$, the decrease in the concentration of Tl^{III} is given by (10). A plot of

$$-d[Tl^{III}]/dt = kK_1[Tl^{III}][H_2O_2]^2/(K_h + [H^+]) = k''[Tl^{III}][H_2O_2]^2 \text{ (at constant } [H^+]) \qquad (10)$$

1/rate against $[HClO_4]$ gave a straight line with an intercept on the 1/rate axis from which K_h was calculated to be 0·076 ± 0·008, 0·087 ± 0·01, and 0·097 ± 0·01 mol l^{-1} at 25, 30, and 35 °C respectively. These values appear to overlap; however, the value at 25 °C is in good agreement with the reported [22] value of 0·073 mol l^{-1}. The quantity kK_1 was calculated as 5·0 ± 0·4, 6·9 ± 0·4, and 8·2 + 0·3 l^2 mol^{-2} s^{-1} at the above temperatures; the value of kK_1 calculated from the average k'' was 6·7 ± 0·5 l^2 mol^2 s^{-1} at 30 °C. The order of reactivity of various oxidizing ions towards H_2O_2 is thus $Ce^{IV} > Mn^{III} > Co^{III} > Tl^{III} > Fe^{III}$.

The overall energy of activation (10·3 ± 0·7 kcal mol^{-1}) is somewhat low.* Energies of activation lower than this were found in the oxidations of hydrogen peroxide [27] and hydrazoic acid [28] by Ce^{IV}. Since in the present system K_h is small compared to $[H^+]$, the energy of activation refers to kK_1. If the energy of activation for reduction of various complexes of Tl^{III} [with formic [29] (26·6), oxalic [30] (28·4), and phosphorous acid [14] (26·5 kcal mol^{-1})] is any guide to the energy of activation of step (7), ΔH_1 for step (5) is *ca.* −17 kcal mol^{-1}.

Reduction of Tl^{III} *induced by* Ce^{IV}.—An earlier attempt to follow the kinetics by estimating hydrogen peroxide cerimetrically [11] (without chloride) was unsuccessful due to interference from Tl^{III}. A systematic investigation of cerimetric estimation of hydrogen peroxide in the presence of thallium(III) perchlorate indicated that reduction of Tl^{III} by H_2O_2 is induced by Ce^{IV}.

Solutions of hydrogen peroxide were added to a mixture containing a known excess of Ce^{IV} and a fixed amount of Tl^{III}. Excess of Ce^{IV} was determined with Fe^{II}. The results in Figure 3 indicate that cerimetric estimation of hydrogen peroxide can be carried out even in the presence of Tl^{III} without any interference provided sufficient excess (more than ten times $[Tl^{III}]$) of Ce^{IV} is used. In the next set of experiments, a fixed amount of hydrogen peroxide was added to a mixture containing a fixed amount of Ce^{IV} and varying amounts of Tl^{III}. This time Tl^{III} was estimated iodometrically as mentioned in the kinetics procedure and these results are shown in Figure 4. This Figure shows that Tl^{III} is also reduced when a reaction between H_2O_2 and Ce^{IV} occurs and that the amount of Tl^{III} reduced is always half that of Ce^{IV} (when $[H_2O_2] > [Ce^{IV}]$ and $[Tl^{III}] > [Ce^{IV}]$). In the third set of experiments varying amounts of hydrogen peroxide were added to fixed amounts of Ce^{IV} and Tl^{III}. Excess of Tl^{III} was

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* 1 cal = 4·184 J.

[23] B. H. J. Bielski and E. Saito, *J. Phys. Chem.*, 1962, **66**, 2266.

[24] G. Biedermann, *Akiv Kemi*, 1964, **6(5)**, 527.

[25] R. C. Taylor and P. C. Cross, *J. Chem. Phys.*, 1956, **24**, 41.

[26] H. Sigel, C. Flierl, and R. Griesser, *J. Amer. Chem. Soc.*, 1969, **91**, 1061.

[27] C. F. Wells and M. Husain, *J. Chem. Soc. (A)*, 1970, 1013.

[28] C. F. Wells and M. Husain, *J. Chem. Soc. (A)*, 1969, 2981.

[29] H. N. Halvorson and J. Halpern, *J. Amer. Chem. Soc.*, 1956, **78**, 5562.

[30] L. B. Monsted, O. Monsted, and G. Nord (*née* Waind), *Trans. Faraday Soc.*, 1970, **66**, 936.

estimated iodometrically and the results are given in Table 2. Again if [Tl^{III}] > [Ce^{IV}], the amount of Tl^{III} consumed was always half that of Ce^{IV}. The results further showed that cerimetric estimation of hydrogen peroxide can be carried out even in the presence of Tl^{III} provided at least a ten-fold excess of chloride ion is also present.

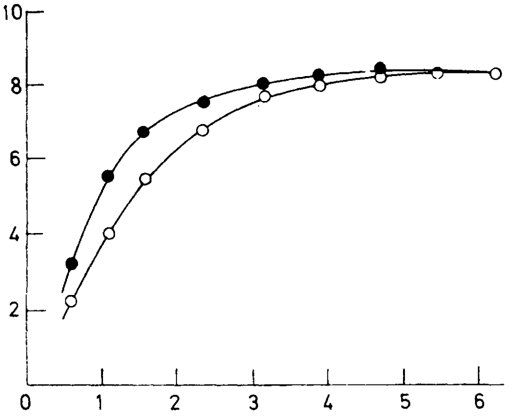

FIGURE 3 Estimation of H_2O_2 ($[H_2O_2]_0 = 4{\cdot}15 \times 10^{-3}$M) in the presence of Tl^{III} by determining the excess of Ce^{IV} with Fe^{II}: (●), [Tl^{III}] = 2·0 × 10^{-3}; (○), [Tl^{III}] = 4·0 × 10^{-3}M

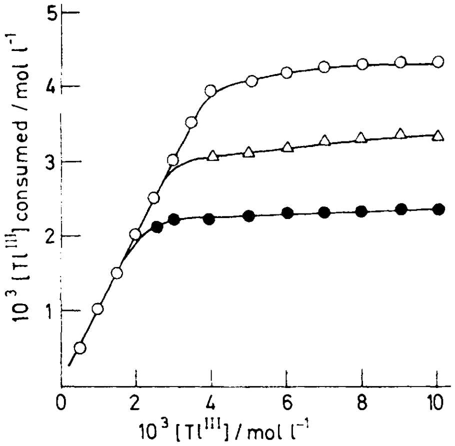

FIGURE 4 Reduction of Tl^{III} by H_2O_2 ($[H_2O_2]_0 = 1{\cdot}0 \times 10^{-2}$M) induced by Ce^{IV}. The excess of Tl^{III} was determined iodometrically. [Ce^{IV}] = 4·0 × 10^{-3} (●), 6·0 × 10^{-3} (△), and 8·0 × 10^{-3}M (○)

From the above results it follows that the reduction of Tl^{III} by H_2O_2 is induced by Ce^{IV}. Intermediate formation of HO_2 or $H_2O_2^+$ radicals[3,21,23] in the Ce^{IV}–H_2O_2 reaction is now beyond doubt. There is direct evidence[21,31] for it from e.s.r. spectroscopy. The reaction is fast and 2 mol Ce^{IV} react with 1 mol hydrogen peroxide according to reactions (11) and (12). In the

$$\mathrm{Ce^{IV}} + \mathrm{H_2O_2} \longrightarrow \mathrm{Ce^{III}} + \mathrm{H_2O_2^{+}} \qquad (11)$$

$$\mathrm{Ce^{IV}} + \mathrm{H_2O_2^{+}} \longrightarrow \mathrm{Ce^{III}} + 2\mathrm{H^{+}} + \mathrm{O_2} \qquad (12)$$

presence of Tl^{III} less than 2 mol Ce^{IV} are consumed and there appears to be an overall reaction (13) (with probable intermediate-complex formation) competing with (12).

$$\mathrm{Tl^{III}} + 2\mathrm{H_2O_2^{+}} \longrightarrow \mathrm{Tl^{I}} + 4\mathrm{H^{+}} + 2\mathrm{O_2} \qquad (13)$$

If the ratio [Ce^{IV}] : [Tl^{III}] is large, reaction (13) occurs to an insignificant extent and 2 mol Ce^{IV} are consumed for each of H_2O_2 as shown in Figure 3. However, if the concentration of Tl^{III} is larger than that of Ce^{IV}, reaction (13) predominates and for each mole of $H_2O_2^+$ produced by 1 mol Ce^{IV} in reaction (11), 0·5 mol Tl^{III} is consumed. This is obvious in Figure 4 for three different concentrations of Ce^{IV}. Thus, slow reduction of Tl^{III} by H_2O_2 is said to be induced by Ce^{IV} and the induction factor is 1. It is also found from Figure 4 that slightly more Tl^{III} than required is consumed because of the slow reaction between Tl^{III} and H_2O_2. Comparison of Figures 3 and 4 reveals that the ratio [Ce^{IV}] : [Tl^{III}] required to make reaction (12) predominant, is larger than the ratio [Tl^{III}] : [Ce^{IV}] required to make reaction (13) predominant. This suggests that reaction (13) is much faster than (12). Table 2 gives results for reactants with fixed concentrations of Ce^{IV} and Tl^{III} and varying amounts of H_2O_2 and further shows that the excess of Tl^{III} consumed increases with increasing H_2O_2.

TABLE 2

Estimation of H_2O_2 in the presence of Tl^{III}. The amounts of Tl^{III} and Ce^{IV} were fixed and that of H_2O_2 varied. [Ce^{IV}] = 2·0 × 10^{-3}M at 30 °C

10^3[Tl^{III}]/ M	10^3[H_2O_2]/ M	10^3[Tl^{III}]/ M [a]	10^3[H_2O_2]/ M [b]	10^3[Tl^{III}]/ M [c]
5·0	2·0	3·95		1·05
5·0	3·0	3·85	0·90	1·15
5·0	5·0	3·80	1·80	1·20
5·0	5·0	3·75	2·75	1·25
5·0	6·0	3·70	3·65	1·30
5·0	7·0	3·65	4·65	1·35
4·0	2·0	2·95		1·05
4·0	3·0	2·90	0·90	1·10
4·0	4·0	2·85	1·90	1·15
4·0	5·0	2·80	2·80	1·20
4·0	6·0	2·75	3·75	1·25
4·0	7·0	2·70	4·65	1·30
2·0	2·0	1·00		1·00
2·0	3·0	0·975	1·00	1·025
2·0	4·0	0·95	1·95	1·05
2·0	5·0	0·90	2·95	1·10
2·0	6·0	0·85	3·85	1·15
2·0	7·0	0·80	4·80	1·20

[a] Excess of Tl^{III} was determined iodometrically. [b] Excess of H_2O_2 was determined cerimetrically in the presence of chloride ion. [c] Amount consumed.

It has been mentioned that, in the presence of sufficient chloride ions, the amount of Ce^{IV} consumed is twice that of H_2O_2 in accordance with the stoicheiometry of 2 : 1 and reaction (13) does not occur. Chloride is known to form strong complexes[32] with Tl^{3+}. Reaction (13) probably occurs *via* an intermediate complex

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formed from Tl^{3+} and $H_2O_2^+$ as presumed in other oxidations.[9,18,19] In the present case, when the co-ordination sites of Tl^{3+} are effectively blocked by chloride ions, the reactive intermediate complex is not formed and Tl^{III} is not reduced. Effective blocking of co-ordination sites of Tl^{3+} occurs when the chloride-ion concentration is five to eight times that of Tl^{III}. When the kinetics of the main reaction between Tl^{III} and H_2O_2 are studied by determining H_2O_2 cerimetrically in the presence of chloride ions, the results are similar to those obtained by the iodometric method as mentioned earlier.

In kinetic experiments where no Ce^{IV} is employed, it has been found that the rate of reaction becomes almost negligible when the chloride-ion concentration is twice that of Tl^{III}, and hence it appears that higher chloro-complexes are not reactive and that reaction (1) must also occur *via* intermediate complex formation between Tl^{3+} and H_2O_2. Thus, from a study of the induced reduction of Tl^{III} and that of the chloride-ion effect, formation of a complex between Tl^{III} and H_2O_2 appears to precede the redox step.

Fe^{II} *as an Initiator or Prereductor.*—While carrying out the cerimetric titrations, a drop of Fe^{II} solution was accidentally introduced in the reaction mixture containing Tl^{III} and H_2O_2, and it was found that one of the reactants, whichever was not in excess, was immediately and completely consumed. A systematic investigation of the estimation of H_2O_2 by Tl^{III} in the presence of Fe^{II} was, therefore, carried out. Requisite quantities of solutions of excess of thallium(III) perchlorate, perchloric acid, and iron(II) sulphate were placed in an Erlenmeyer flask. A known quantity of hydrogen peroxide was added to this mixture and excess of Tl^{III} determined iodometrically. Quantitative results thus obtained are comparable to those obtained by cerimetry. Concentrations of Fe^{II} as low as 7×10^{-6}M were enough to complete the reaction between Tl^{III} and H_2O_2 within 10 s.

Iron(II) is reported[33] to increase the rate of oxidation of U^{IV} by H_2O_2, but the increase in rate is much larger in the Tl^{III}–H_2O_2 reaction. The increase is observed if Fe^{II} is added to a mixture of Tl^{III} and H_2O_2, or H_2O_2 is added to a mixture of Tl^{III} and Fe^{II}. If Tl^{III} is added to a mixture of Fe^{II} and H_2O_2 no increase in the rate of reaction is observed presumably because Fe^{III}, which is formed[34] in the reaction, has no effect. Iron(II), therefore, is not a catalyst but a prereductor or initiator and the process is explained by reactions (14)—(16).

$$Tl^{III} + Fe^{II} \rightleftharpoons Tl^{II} + Fe^{III} \qquad (14)$$

$$\left.\begin{aligned} Tl^{II} + H_2O_2 &\longrightarrow Tl^{I} + H_2O_2^+ \qquad (15)\\ Tl^{III} + H_2O_2^+ &\longrightarrow Tl^{II} + O_2 + 2H^+ \qquad (16)\end{aligned}\right\}\text{catalytic}$$

However, intermediate species other than $H_2O_2^+$ are also likely to participate in the above mechanism and oxide anion is one of them. Baker and Newton[33] postulated the formation of different radicals in the oxidation of U^{IV} by H_2O_2, in contrast to that by dissolved oxygen.[35] Formation of hyperoxide anion O_2^- is often reported[36] in association with Fe^{II} in oxidation by dissolved oxygen. Thallium(I), which is reported to be a scavenger[37] of OH free radicals, does not influence the rate of the present reaction. Similarly Fe^{III}, Cu^{II}, and Mn^{II}, whose role in a reaction is associated[38] with OH free radicals, have no effect on the Tl^{III}–H_2O_2 reaction and hence the Haber–Weiss mechanism[39] involving OH radicals is probably not operative in the present system.

[4/006 *Received, 2nd January,* 1974]

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