Kinetics and Mechanism of Reduction of Bromothallium(III) Complexes by Hydrogen Peroxide in Perchloric Acid Media

Muvvala Sanni Prasada Rao,* Adari Rama Mohan Rao, Rachamadugu Kalavathi, Tirukkovalluri Siva Rao and Parvateneni Vani
Inorganic Chemistry Laboratories, Andhra University, Visakhapatnam 530 003, India

The thallium(III)–H_2O_2 reaction was found to be catalysed by bromide ion and the maximum rate observed at a bromide to thallium(III) ratio, R, of 2:1; the rate decreased at higher values of R. The reactivity of various bromothallium(III) species follows the order $[TlBr]^{2+} < [TlBr_2]^+ > TlBr_3 > [TlBr_4]^-$. The complicated rate law of the reaction is as in equation (i) where k_1, k_2, k_3 and k_4 are the rate constants for

$$-d[Tl^{III}]/dt = (kK[Tl^{3+}][H_2O_2] + k_1K_1[TlBr^{2+}] + k_2K_2[TlBr_2{}^+] + k_3K_3[TlBr_3] + k_4K_4[TlBr_4{}^-])[H_2O_2]/[H^+] \quad (i)$$

the steps involving $[TlBr(O_2H)]^+$, $[TlBr_2(O_2H)]$, $[TlBr_3(O_2H)]^-$ and $[TlBr_4(O_2H)]^{2-}$ and K_1, K_2, K_3 and K_4 the respective formation constants, and k and K are the rate and formation constants for the steps representing the bromide-ion independent path.

Many photochemical redox reactions involving thallium(III) are catalysed in the presence of small concentrations of chloride and/or bromide ions.[1–7] The effect of chloride ion on the kinetic and mechanistic patterns of thallium(III) reductions with different substrates has been thoroughly investigated.[8–15]

The reduction of thallium(III) by hydrogen peroxide[16,17] was investigated but conflicting reports were made. Rao *et al.*[18] have reinvestigated the reaction; their results coincided with those of Sharma and Gupta[16] and the mechanism in equations (1)–(3)

$$Tl^{3+} + H_2O \xrightleftharpoons{k_h} [Tl(OH)]^{2+} + H^+ \quad (1)$$

$$Tl^{3+} + H_2O_2 \xrightleftharpoons{K} [Tl(HO_2)]^{2+} + H^+ \quad (2)$$

$$[Tl(HO_2)]^{2+} + H_2O_2 \xrightarrow{k} \text{Products} \quad (3)$$

was proposed. This leads to the rate law (4). Further, whereas

$$\text{Rate} = -d[Tl^{III}]/dt = kK[Tl^{III}][H_2O_2]^2/[H^+] \quad (4)$$

this reaction is inhibited by chloride ions, bromide ions at low concentrations[18] have catalytic activity. Surprisingly, no attempt seems to have been made, so far, to study the effect of bromide ion on the kinetics and mechanism of reduction of thallium(III). Hence, we have made such a study using hydrogen peroxide as reductant, so as to get a better insight into the mechanism of thallimetric oxidations.

Experimental

The thallium(III) solution was prepared and standardised as reported earlier[19] and the thallium content determined iodometrically.[20,21] The stock solution of hydrogen peroxide was prepared by dilution of 30% (w/v) hydrogen peroxide (E. Merck) and standardised against cerium(IV).[22] The dilute solutions of hydrogen peroxide were standardised just before starting the kinetic runs. Lithium perchlorate solution was prepared by dissolving lithium carbonate (BDH, LR) in 70% perchloric acid. AnalaR grade (BDH) sodium chloride and sodium bromide were used. Thallium(I) perchlorate was prepared by dissolving thallium(I) carbonate (BDH, LR) in 70% perchloric acid. All kinetic runs were carried out at a constant temperature of 30 ± 0.1 °C, unless otherwise mentioned. Rate measurements were made with equal concentrations of hydrogen peroxide and thallium(III).

Aliquots of the reaction mixture were taken at known intervals of time and run into 0.5 mol dm^{-3} hydrochloric acid to quench the reaction. The thallium(I) formed was determined bromatometrically.[23] If the titres at times zero, t and ∞ are denoted by T_0, T_t and T_∞ respectively, $(T_\infty - T_t)$ gives an estimate of the concentration of thallium(III) at time t. As the reaction proceeds the concentration of thallium(III) in the reaction mixture decreases whereas the concentration of bromide remains constant. This gradually changes the bromide to thallium ratio (R) and the relative concentrations of the bromothallium(III) species. To account for this discrepancy, the initial rates method was employed. Initial rates were determined from concentration *versus* time plots by employing the plane-mirror method[24] and found to be reproducible within ±10%.

Results

Stoichiometry.—The analytical aspects of the reaction have been thoroughly investigated earlier[5,6] and the stoichiometry was found to correspond to equation (5).

$$Tl^{III} + H_2O_2 \longrightarrow Tl^{I} + 2H^+ + O_2 \quad (5)$$

Product Dependence.—The effect of the product, thallium(I), on the rate of the reaction in the presence of bromide ion was studied by keeping the concentrations of thallium(III) (2.0×10^{-3} mol dm^{-3}), hydrogen peroxide (2.0×10^{-3} mol dm^{-3}) and hydrogen ions (0.5 mol dm^{-3}) constant, but varying the concentration of thallium(I) (1.0×10^{-3}–3.0×10^{-3} mol dm^{-3}) and was found to have no effect on the initial rate, showing that the rate-determining step has no pre-equilibrium steps involving thallium(I).

Ionic Strength Dependence.—The ionic strength was varied by using lithium perchlorate (0.25–1.25 mol dm^{-3}), keeping the concentrations of thallium(III) and hydrogen peroxide constant at different Tl^{III} to Br^- ratios. The initial rate of the reaction was independent of ionic strength. This probably indicates that neutral H_2O_2 is the reactive species.

Table 1 Effect of thallium(III) concentration on the initial rates; $[H_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 0.5$ mol dm^{-3}, 30 °C ± 0.1 °C

Experiment no.	10^3 [Tl^{III}]/ mol dm^{-3}	10^3 [Br$^-$]/ mol dm^{-3}	R	10^7 Initial rate/ mol dm^{-3} s^{-1}	k_{obs} */ s^{-1}
1	1.0	0.20	0.2	3.8	0.84
2	1.5	0.30	0.2	5.0	0.73
3	2.0	0.40	0.2	6.3	0.69
4	2.5	0.50	0.2	7.7	0.68
5	3.0	0.60	0.2	9.3	0.68
6	1.0	0.50	0.5	4.2	0.36
7	1.5	0.75	0.5	6.3	0.36
8	2.0	1.00	0.5	8.1	0.35
9	2.5	1.25	0.5	10.4	0.36
10	3.0	1.50	0.5	11.6	0.34
11	1.0	1.00	1.0	4.3	0.11
12	1.5	1.50	1.0	6.0	0.10
13	2.0	2.00	1.0	8.7	0.11
14	2.5	2.50	1.0	11.7	0.11
15	3.0	3.00	1.0	14.5	0.12
16	1.0	2.00	2.0	8.0	0.20
17	1.5	3.00	2.0	12.0	0.20
18	2.0	4.00	2.0	14.0	0.17
19	2.5	5.00	2.0	18.0	0.18
20	3.0	6.00	2.0	24.0	0.20
21	1.0	3.00	3.0	2.3	0.06
22	1.5	4.50	3.0	3.5	0.06
23	2.0	6.00	3.0	5.0	0.06
24	2.5	7.50	3.0	6.3	0.06
25	3.0	9.00	3.0	7.2	0.06
26	1.0	5.00	5.0	2.2	0.06
27	1.5	7.50	5.0	3.3	0.06
28	2.0	10.00	5.0	4.3	0.05
29	2.5	12.50	5.0	5.6	0.06
30	3.0	15.00	5.0	7.0	0.06

* k_{obs} Values recorded in Tables 1–3 were calculated by assuming the order with respect to $[H_2O_2]$ to be 1.35, 1.20 and 1.0 at $R = 0.2$, 0.5 and $\geqslant 1$ respectively.

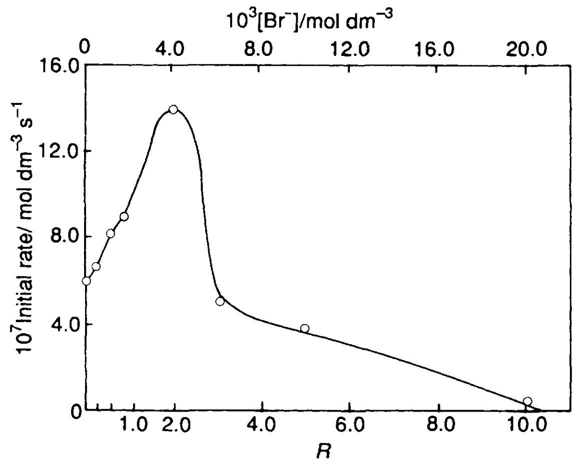

Fig. 1 Plot of initial rate *versus* [Br$^-$] or R at [Tl^{III}] = 2.0×10^{-3} mol dm^{-3}, $[H_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 0.5$ mol dm^{-3} and 30 ± 0.1 °C

Thallium(III) *Dependence*.—The effect of bromide-ion concentration on the rate of the reaction was studied and a plot of initial rate against [Br$^-$]/[Tl^{3+}] *i.e.* R, is shown in Fig. 1. The maximum rate occurs when $R = 2$. A simple order in thallium(III) is not obvious because thallium(III) forms a number of complexes having different reactivities the proportions of which vary with R. Hence, the bromide-ion concentration was also varied with thallium(III) and the order with respect to thallium(III) determined in 0.5 mol dm^{-3} perchloric acid medium, keeping the metal concentration in the range 1.0×10^{-3}–3.0×10^{-3} mol dm^{-3} and the bromide-ion concentration 0.2×10^{-3}–15×10^{-3} mol dm^{-3}. Plots of log initial rates *versus* log [Tl^{III}] at different ratios [Br$^-$]/[Tl^{III}] = R were linear with slopes 1.0 ± 0.05, confirming a first-order dependence on the concentration of thallium(III). The data obtained are given in Table 1.

Hydrogen Peroxide Dependence.—In order to determine the order with respect to hydrogen peroxide, kinetic runs were carried out in 0.5 mol dm^{-3} perchloric acid medium at different ratios [Br$^-$]/[Tl^{III}] (R) and varying the concentration of hydrogen peroxide from 1.0×10^{-3} to 3.0×10^{-3} mol dm^{-3}. The initial rates obtained from the slopes of plots of $(T_\infty - T_t)$ *versus* time are given in Table 2. When the bromide concentration is maintained such that $R = 0.2$ and 0.5 the plots of log initial rate against log $[H_2O_2]$ are linear with slopes of 1.35 and 1.20 indicating the order with respect to hydrogen peroxide concentration to be between 1 and 2 (Fig. 2) when $R < 1$. However, when the initial rates are plotted against the concentration of hydrogen peroxide at $R = 1$, 2, 3 and 5, straight lines passing through the origin are obtained (Fig. 3) thereby indicating the order with respect to hydrogen peroxide concentration to be unity.

Hydrogen-ion Dependence.—The effect of hydrogen-ion concentration on the rate of the reaction was studied from 0.5 to 1.25 mol dm^{-3} using perchloric acid, at $R = 0.2$, 0.5, 1, 2, 3 and 5. The reaction shows a marked decrease in rate with increase in perchloric acid concentration. The data obtained are given in Table 3. Further, plots of initial rate *versus* 1/[H$^+$] are straight lines passing through the origin at different ratios R (Fig. 4).

Temperature Dependence.—Kinetic experiments were made at 30, 35, 40 and 45 °C and the initial rates were found to be 14.0×10^{-7}, 20.60×10^{-7}, 26.60×10^{-7} and 31.3×10^{-7} mol dm^{-3} s^{-1} respectively, at [Tl^{III}] = 2.0×10^{-3}, $[H_2O_2] = 2.0 \times 10^{-3}$, [Br$^-$] = 4.0×10^{-3} and $[HClO_4] = 0.5$ mol

Table 2 Effect of hydrogen peroxide concentration on the initial rates; $[Tl^{III}] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 0.5$ mol dm^{-3}, $R = [Br^-]/[Tl^{III}]$, 30 ± 0.1 °C

Experiment no.	$10^3 [H_2O_2]$/ mol dm^{-3}	R	10^7 Initial rate/mol dm^{-3} s^{-1}	k_{obs}/s^{-1}
1	1.0	0.2	3.2	0.88
2	1.5	0.2	5.6	0.90
3	2.0	0.2	7.6	0.70
4	2.5	0.2	10.6	0.86
5	3.0	0.2	13.7	0.87
6	1.0	0.5	4.6	0.46
7	1.5	0.5	6.3	0.38
8	2.0	0.5	8.3	0.36
9	2.5	0.5	11.6	0.38
10	3.0	0.5	14.1	0.37
11	1.0	1.0	4.7	0.12
12	1.5	1.0	7.0	0.12
13	2.0	1.0	9.0	0.11
14	2.5	1.0	12.3	0.12
15	3.0	1.0	14.6	0.12
16	1.0	2.0	8.0	0.20
17	1.5	2.0	11.0	0.18
18	2.0	2.0	15.3	0.19
19	2.5	2.0	19.3	0.19
20	3.0	2.0	21.3	0.17
21	1.0	3.0	2.4	0.06
22	1.5	3.0	3.5	0.06
23	2.0	3.0	5.6	0.07
24	2.5	3.0	6.3	0.06
25	3.0	3.0	7.1	0.06
26	1.0	5.0	2.2	0.05
27	1.5	5.0	3.3	0.05
28	2.0	5.0	4.3	0.05
29	2.5	5.0	5.6	0.06
30	3.0	5.0	7.0	0.06

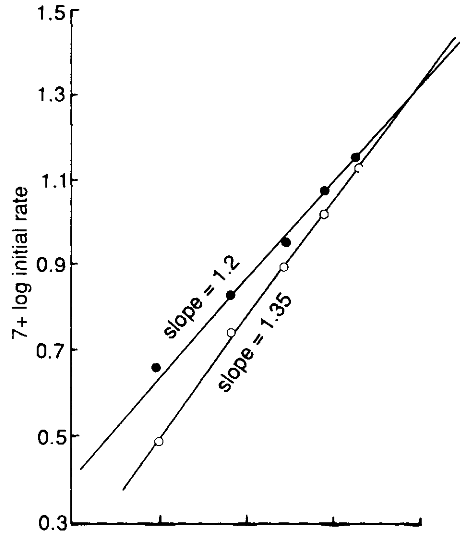

Fig. 2 Plots of log initial rate *versus* log$[H_2O_2]$ at R = 0.2 (○) and 0.5 (●), $[Tl^{III}] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 0.5$ mol dm^{-3} and 30 ± 0.1 °C

dm^{-3}. The energy of activation E_a was calculated to be 42.6 ± 2.5 kJ mol^{-1} and the entropy of activation $\Delta S^‡ = -127.1 \pm 7.7$ J K^{-1} mol^{-1}.

Reactive Species, Mechanism and Rate Constants.—In reactions involving hydrogen peroxide some authors[25] considered HO_2^- anion to be the co-ordinating species, others[26,27] preferred H_2O_2. The acid dissociation constant of hydrogen peroxide being very small, Sharma and Gupta[16] proposed complex formation with hydrogen peroxide, as the ionised species is less likely to occur in more acidic media.

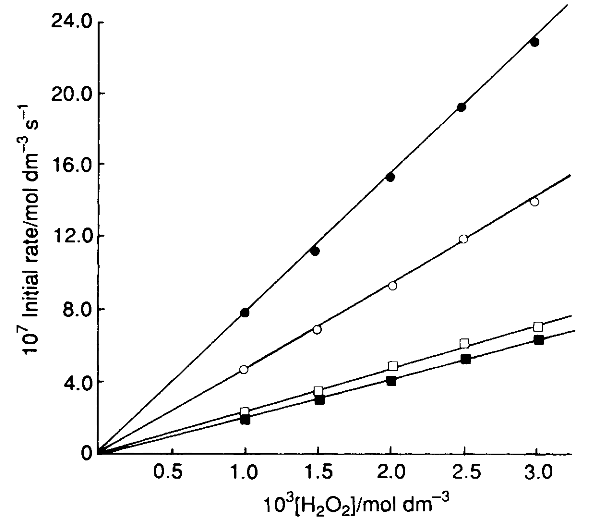

Fig. 3 Plots of initial rate *versus* $[H_2O_2]$ at R = 1.0 (○), 2.0 (●), 3.0 (□), 5.0 (■). Other conditions as in Fig. 2

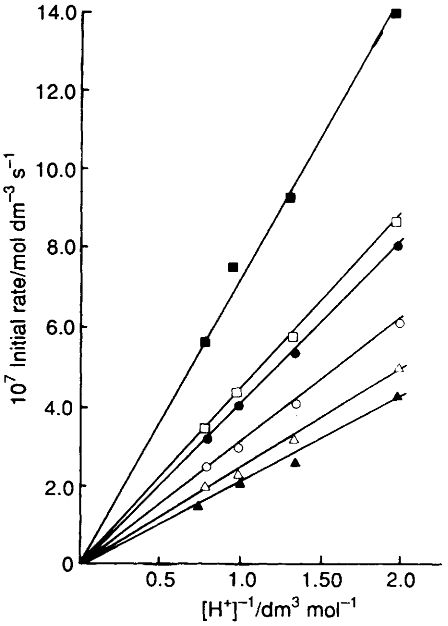

Fig. 4 Plots of initial rate *versus* $1/[H^+]$ at R = 0.2 (○), 0.5 (●), 1.0 (□), 2.0 (■), 3.0 (△), 5.0 (▲), $[Tl^{III}] = [H_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, and 30 ± 0.1 °C

In a kinetic study of the reduction of chloro complexes of thallium(III) by various reductants, Gupta and Gupta[13,14] observed chloride-ion catalysis and proposed different chloro complexes like $[TlCl_2]^+$, $TlCl_3$ and $[TlCl_4]^-$ to be the reactive species. However, the present reaction between hydrogen peroxide and thallium(III) is inhibited by chloride ions, whereas bromide ions in low concentrations are found to catalyse the reaction.

The simplest interpretation of these results is that thallium(III) ion forms various bromo complexes which differ in their reactivities and that the overall rate is a function of the concentrations of these complexes. The interconversion between hydrated thallium(III) species and the various complexes is rapid compared to the rates of reactions involved in the present work. Hence, a detailed consideration of these complexes is necessary before suggesting the rate law.

Table 3 Effect of hydrogen-ion concentration on the initial rates; $[Tl^{III}] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[H_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, 30 ± 0.1 °C, $R = [Br^-]/[Tl^{III}]$

Experiment no.	$[H^+]$/mol dm^{-3}	R	10^7 Initial rate/mol dm^{-3} s^{-1}	k_{obs}/s^{-1}
1	0.50	0.2	6.2	0.68
2	0.75	0.2	4.1	0.68
3	1.00	0.2	3.1	0.68
4	1.25	0.2	2.5	0.69
5	0.50	0.5	8.1	0.35
6	0.75	0.5	5.4	0.35
7	1.00	0.5	4.0	0.35
8	1.25	0.5	3.2	0.35
9	0.50	1.0	8.7	0.11
10	0.75	1.0	5.8	0.11
11	1.00	1.0	4.4	0.11
12	1.25	1.0	3.4	0.11
13	0.50	2.0	14.0	0.17
14	0.75	2.0	9.3	0.17
15	1.00	2.0	7.5	0.18
16	1.25	2.0	6.3	0.19
17	0.50	3.0	5.0	0.06
18	0.75	3.0	3.2	0.06
19	1.00	3.0	2.3	0.06
20	1.25	3.0	2.1	0.06
21	0.50	5.0	4.3	0.05
22	0.75	5.0	2.6	0.05
23	1.00	5.0	2.1	0.05
24	1.25	5.0	1.6	0.05

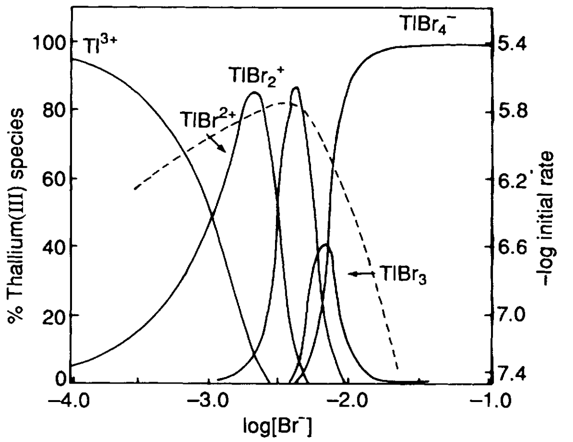

Fig. 5 The rates (– – – –) and distribution (——) of thallium(III) species at various bromide concentrations for the Tl^{III}–H_2O_2 reaction at $[Tl^{III}] = [H_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 0.5$ mol dm^{-3} and 30 ± 0.1 °C

There are various reports regarding the number of bromo complexes formed.[28] Carpenter *et al.*[29] made a detailed study of the complexes and reported the stepwise formation constants to be 4.0×10^8, 2.5×10^6, 1.0×10^4 and 0.5×10^4 dm^3 mol^{-1} at 25 ± 1 °C for the species $[TlBr]^{2+}$, $[TlBr_2]^+$, $TlBr_3$ and $[TlBr_4]^-$ respectively. These values are utilised to calculate the relative concentrations of the Tl^{3+}, $[TlBr]^{2+}$, $[TlBr_2]^+$, $TlBr_3$ and $[TlBr_4]^-$ species by the computer-simulation program DISPLOT.[30] The percentage fractions of thallium(III) present as these species are plotted against $\log[Br^-]$ in Fig. 5. A log plot of initial rate *versus* $[Br^-]$ is also shown in the same figure. It may be seen that the concentrations of the various species and their reactivities may be readily correlated, the relative order of reactivity being $[TlBr]^{2+} < [TlBr_2]^+ > TlBr_3 > [TlBr_4]^-$. Hence, the general mechanism in equations (6) and (7) (n = 1–4) may be proposed for the reduction of bromothallium(III) with H_2O_2.

$$[TlBr_n]^{3-n} + H_2O_2 \overset{K_n}{\rightleftharpoons} [TlBr_n{\cdot}OH_2]^{2-n} + H^+ \quad (6)$$

$$[TlBr_n{\cdot}OH_2]^{2-n} \xrightarrow{k_n} \text{products} \quad (7)$$

$$K_n = \frac{[TlBr_n{\cdot}OH_2{}^{2-n}][H^+]}{[TlBr_n{}^{3-n}][H_2O_2]} \quad (8)$$

Considering a parallel path involving free Tl^{3+} also contributing to the rate of the reaction [equations (1)–(3)], the rate equation (9) in the presence of bromide ions ($R < 1$) can be

$$\text{Rate} = -d[Tl^{III}]/dt = k[Tl(HO_2)^{2+}][H_2O_2] + \Sigma k_n[TlBr_n{\cdot}OH_2{}^{2-n}] = kK[Tl^{3+}][H_2O_2]^2[H^+]^{-1} + \Sigma k_nK_n[TlBr_n{}^{3-n}][H_2O_2][H^+]^{-1} \quad (9)$$

written. This explains the experimental observations such as the first-order dependence on the concentration of bromothallium(III) species and decrease in rate with increase in $[H^+]$. It also predicts the order with respect to hydrogen peroxide concentration to be fractional (between one and two). However, experimentally a first-order dependence on $[H_2O_2]$ has been observed when $[Br^-]/[Tl^{III}]$ is $\geqslant 1$ and a fractional order between 1 and 2 when < 1 (Fig. 2). This observation indicates that in the presence of bromide ion corresponding to $R \geqslant 1$ there is no free Tl^{3+} available in the solution. However, at $R < 1$, Tl^{3+} is not completely converted into a bromo species and both $[TlBr]^{2+}$ and Tl^{3+} exist in the reaction mixture. Hence, the presence of both species simultaneously accounts for the observed order between 1 and 2 with respect to $[H_2O_2]$. At $[Br^-]/[Tl^{III}]$ = 1–5 only the bromo complexes of thallium(III) exist and the rate equation (9) reduces to (10). Hence, a complete

$$-d[Tl^{III}]/dt = \Sigma k_nK_n[TlBr_n{}^{3-n}][H_2O_2]/[H^+] \quad (10)$$

rate law for the reduction of bromo complexes of thallium(III) by hydrogen peroxide under the present conditions (R = 1–5) may be written as in equation (11) where k_1, k_2, k_3 and k_4 are

$$-d[Tl^{III}]/dt = (k_1K_1[TlBr^{2+}] + k_2K_2[TlBr_2{}^+] + k_3K_3[TlBr_3] + k_4K_4[TlBr_4{}^-])[H_2O_2]/[H^+] \quad (11)$$

the rate constants for the steps involving $[TlBr(O_2H)]^+$, $[TlBr_2(O_2H)]$, $[TlBr_3(O_2H)]^-$ and $[TlBr_4(O_2H)]^{2-}$ and K_1, K_2, K_3 and K_4 are the respective formation constants. However, no kinetic or spectrophotometric evidence has been obtained for the formation of complexes between $TlBr_n{}^{3-n}$ species and H_2O_2, probably because of their small formation constants.

Further, the rate equation (11) predicts that plots of initial rate *versus* $1/[H^+]$ at different $[Br^-]/[Tl^{III}]$ ratios should be straight lines passing through the origin. The plots shown in Fig. 3 clearly substantiate this.

Discussion

In perchlorate solution[28] Tl^{III} exists as $[Tl(H_2O)_6]^{3+}$ with the two water molecules in axial positions of a distorted octahedron being more strongly bound than the four equatorial ones. In the formation of mono- and di-halogeno species the axial waters are successively replaced, finally giving a linear structure again possibly surrounded by four loosely bound waters in the equatorial plane.[28] Further addition of chloride or bromide ions results in partial disproportionation of the TlX_3 formed, to linear $[TlX_2]^+$ and tetrahedral $[TlX_4]^-$.[31] Solvent-extraction studies of thallium(III) from hydrochloric and hydrobromic acid solutions have confirmed[32,33] that the $[TlX_4]^-$ species remains intact and neither water nor the organic solvent enters the inner co-ordination sphere of thallium(III).

On the basis of the chloride effect Gupta and Gupta[14] divided reductions of thallium(III) into two classes. The first involves formation of a complex between thallium(III) ion and the substrate and chloride ions are presumed to block the coordination sites on Tl^{3+} inhibiting the formation of an intermediate complex. In the second class chloride ion accelerates the rate of the reaction and the catalysis is explained by a bridge-activated mechanism.

In the present investigation chloride ions are found to inhibit the reduction of thallium(III) with hydrogen peroxide and a similar observation was made by the earlier workers.[16-18] However, bromide ions are found to catalyse the reduction of thallium(III) with hydrogen peroxide.

The bromide-ion catalysis of the present reaction can be explained by assuming a bridge-activated mechanism similar to that proposed for the reduction of thallium(III) by phosphite or hypophosphite in the presence of chloride. Thus, the transition state may be presumed to involve the attachment of H_2O_2 to the highly positive thallium(III) centre through bromide ion, thus facilitating electron transfer from H_2O_2 to the metal ion [equation (12)].

$$Br_{n-1}\text{–}TlBr^{3-n}\cdots O_2H^- \longrightarrow Tl^+ + O_2 + H^+ + n\mathrm{Br}^- \quad (12)$$

The relative reactivity of the bromothallium(III) species can be explained on the basis of decreasing electrophilicity of the higher bromothallium(III) species. The electrophilic nature decreases in the order $[TlBr_4]^- < TlBr_3 < [TlBr_2]^+ < [TlBr]^{2+}$ thereby decreasing the affinity for H_2O_2. The higher reactivity of $[TlBr_2]^+$ compared to $[TlBr]^{2+}$ may be attributed to the statistical factor. Obviously $[TlBr_2]^+$ provides an extra site for attack by the substrate molecule compared to $[TlBr]^{2+}$.

The absence of catalytic activity in the case of chloride ions may be due to the fact that chloride is a less effective bridging ligand compared to bromide in facilitating electron transfer. In general, the electrophilicity of the halogenothallium(III) complexes is less than that of aquathallium(III) because of the decrease in the positive charge on the complex ion. When bromide is the bridging ligand this decrease in electrophilicity is more than compensated by the greater ease of electron transfer through the bridging ligand, while in the case of chloride the loss in electrophilicity dominates. This is substantiated by the fact that, even in the case of bromide ion at higher concentrations, when less electrophilic, higher bromo complexes are formed, there is a decrease in the rate of the reaction compared to that involving aquathallium(III) species, probably because further loss in electrophilicity cannot be compensated by the other favourable factor.

Acknowledgements

The authors thank Professor L. S. A. Dikshitulu and P. V. Subba Rao, School of Chemistry, Andhra University, Visakhapatnam for their valuable suggestions. A. Rama Mohan Rao and T. Siva Rao thank the Council of Scientific and Industrial Research and University Grants Commission, New Delhi, India for the award of senior and junior Research Fellowships respectively.

References

1 S. R. Sagi, K. Appa Rao and M. S. Prasada Rao, *Talanta*, 1982, **29**, 413.
2 S. R. Sagi, K. Appa Rao and M. S. Prasada Rao, *Talanta*, 1983, **30**, 292.
3 S. R. Sagi, K. Appa Rao and M. S. Prasada Rao, *Can J. Chem.*, 1983, **61**, 2795.
4 S. R. Sagi, K. Appa Rao and M. S. Prasada Rao, *Analyst* (*London*), 1984, **109**, 53.
5 A. Rama Mohan Rao, M. S. Prasada Rao, K. V. Ramana and S. R. Sagi, *Talanta*, 1989, **36**, 686.
6 M. S. Prasada Rao, A. Rama Mohan Rao, K. V. Ramana and S. R. Sagi, *Talanta*, 1990, **37**, 753.
7 M. S. Prasada Rao, A. Rama Mohan Rao, K. V. Ramana and S. R. Sagi, *Talanta*, 1991, **38**, 937.
8 B. M. Thakuria and Y. K. Gupta, *J. Chem. Soc.*, *Dalton Trans.*, 1975, 2541.
9 H. N. Halvorson and J. Halpern, *J. Am. Chem. Soc.*, 1956, **78**, 5562.
10 P. D. Sharma and Y. K. Gupta, *J. Chem. Soc.*, *Dalton Trans.*, 1972, 52.
11 F. R. Duke and B. Bornog, *J. Phys. Chem.*, 1956, **60**, 1015.
12 P. D. Sharma and Y. K. Gupta, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 789.
13 K. S. Gupta and Y. K. Gupta, *Inorg. Chem.*, 1974, **13**, 851.
14 K. S. Gupta and Y. K. Gupta, *Inorg. Chem.*, 1975, **14**, 2000.
15 G. M. Waind, *Discuss Faraday Soc.*, 1960, **29**, 136.
16 P. D. Sharma and Y. K. Gupta, *J. Chem. Soc.*, *Dalton Trans.*, 1975, 81.
17 Z. Böti, H. Istvan, Z. Szil and L. J. Isanyi, *J. Chem. Soc.*, *Dalton Trans.*, 1978, 1012.
18 M. S. Prasada Rao, A. Rama Mohan Rao and P. Vani, *React. Kinet.*, *Catal. Lett.*, 1992, **48**, 519.
19 S. R. Sagi and K. V. Ramana, *Talanta*, 1969, **16**, 1217.
20 J. Prozt, *Z. Anal. Chem.*, 1928, **73**, 401.
21 I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Interscience, New York, 1957, vol. 3, p. 370.
22 I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Interscience, New York, 1957, vol. 3, p. 143.
23 I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Interscience, New York, 1957, vol. 3, p. 519.
24 M. Latshaw, *J. Am. Chem. Soc.*, 1925, **47**, 793.
25 C. F. Wells and D. Mays, *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 43.
26 G. Davis, L. J. Kirschenbaum and K. Kustin, *Inorg. Chem.*, 1968, **7**, 146.
27 H. A. Mahlman, R. W. Mathews and T. J. Sworski, *J. Phys. Chem.*, 1971, **75**, 250.
28 A. G. Lee, *The Chemistry of Thallium*, Elsevier, London, 1971.
29 L. G. Carpenter, H. M. Ford-Smith, R. D. Bell and R. W. Dodson, *Discuss. Faraday Soc.*, 1960, **29**, 92.
30 G. Nageswara Rao, A. Ravindra Babu, S. V. V. Satyanarayana, A. Satyanarayana, K. V. Ramana and R. Sambasiva Rao, *Acta Cien. Indica*, 1989, **15**, 321.
31 F. Ya Kulba, V. E. Minonov, A. V. Barsukov and B. I. Lobov, *Zh. Neorg. Khim.*, 1969, **14**, 140.
32 L. K. Chuchalin, I. A. Kuzon, K. F. Obzherina, T. T. Omarov and L. S. Chuchalina, *Zh. Neorg. Khim.*, 1967, **12**, 751.
33 L. K. Chuchalin, I. A. Kuzin, K. F. Obzherina, T. T. Omarov and L. S. Chuchalina, *Zh. Neorg. Khim.*, 1967, **12**, 1175.

Received 26*th January* 1993; *Paper* 3/00501A