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KINETICS AND MECHANISM OF ELECTRON TRANSFER REACTIONS OF AQUO-THALLIUM(III) AND COORDINATED THALLIUM(III). REDUCTION OF THALLIUM(III) AND CHLOROTHALLIUM(III) COMPLEXES BY L-ASCORBIC ACID IN AQUEOUS ACID MEDIUM

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The stoichiometry of the reaction of Tl^{III} with ascorbic acid (H_2A) in the presence and absence of chloride ion conforms to

$$Tl^{III} + H_2A \xrightarrow{Cl} Tl^{I} + 2H^+ + A,$$

where A is dehydroascorbic acid. The reaction exhibits complex kinetics and the reactivity of various chlorothallium (III) species decreases in the order of $[TlOH]^{2+} > Tl^{3+} > [TlCl]^{2+} > [TlCl_2]^+ > TlCl_3 > [TlCl_4]^-$. The mass balance relationship was employed to calculate the equilibrium concentration of the chloride ion for evaluation of the rate constants.

INTRODUCTION

Tl^{III}, being a potential oxidant, has been widely exploited as an important synthetic[1,2] and analytical[3] reagent in aqueous acid medium. The oxidant undergoes two-electron reduction in two steps of one electron each and the intermediate Tl^{II} has been detected[4] and employed[5] to reveal useful reaction events of Tl^{III} which otherwise escape detection.

Tl^{III} reactions, in general, occur via an intermediate complex as the occupation of the coordination sites by oxidizable substrate usually provides a facile pathway.[6] A few papers on the reactivity pattern of chloro–Tl^{III} complexes have appeared.[7,8] The role of chloride ion as an inert ligand is not yet well established, despite the known formation constants of chlorothallium(III) species.[9] The reactions of Tl^{III} with H_3PO_2,[10] H_3PO_3,[10] antimony (III)[11] and iron (II)[12] are known to be accelerated by chloride ion, whereas reactions of As(III),[13] $N_2H_5^+$,[14] NH_3OH^+,[15] H_2O_2[16] and organic acids[17] are decelerated. However, the reasons for such a dual behaviour of chloride ions have not been established. Nevertheless, the decelerating effect of chloride ions can be exploited in studying reactions of Tl^{III} where conventional techniques fail. The reaction of Tl^{III} with ascorbic acid is one such reaction, and the deceleration by Cl^- can be useful in revealing certain important features of the reaction. Moreover, any conventional technique can be employed to ascertain the kinetic features in such systems which otherwise require a fast technique. These factors prompted us to undertake the present study to achieve a better insight into the reaction events.

EXPERIMENTAL

Materials. Thallium(III) perchlorate solution was prepared by dissolving thallium(III) oxide (BDH, AnalaR) in 70% perchloric acid (Merck) and was standardized iodimetrically.[18] L-Ascorbic acid (H_2A) solution was prepared by dissolving the requisite amount of the acid in deionized water and was standarized iodimetrically.[19] All other reagents were either of BDH AnalaR or Merck general-reagent quality and used as received.

Doubly distilled water was employed throughout, the second distillation being from alkaline permanganate solution in an all-glass still. Triply distilled water was

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also employed in a few reactions, the third distillation being from EDTA solution.

Kinetic procedure. Measured amounts of the substrate, perchloric acid, chloride ion and other reaction ingredients except Tl^{III} were placed in stoppered Erlenmeyer flasks immersed in a water-bath thermostated at 10 ± 0·1 °C unless stated otherwise. Reactions were initiated by adding temperature pre-equilibrated solutions of either Tl^{III} or ascorbic acid as the order of mixing had no effect. Aliquot portions ($5\ cm^3$) were withdrawn periodically and were discharged into an ice-cold solution of cerium(IV). Unused cerium(IV) was titrated against ammonium iron(II) sulphate solution employing ferroin as an indicator. However, other components of the reaction mixture did not interfere in the cerimetric determination of the substrate.[4,16] Since a few reactions were also carried out in triply distilled water with reproducible results, any possibility of trace metal ion catalysis was therefore eliminated.[20]

Treatment of the kinetic data was based on the initial rates[21] computed by the plane mirror method. Triplicate rate measurements were reproducible to within ±5%.

Stoichiometry. Stoichiometry was determined by taking either of the reactants in excess in the reactions and were carried out in a thermostated water-bath at 25 ± 0·1 °C (Table 1). The results in Table 1 correspond to the stoichiometry of the reaction as represented by

$$Tl^{III} + H_2A \rightarrow Tl^{I} + 2H^{+} + A \qquad (1)$$

Similar stoichiometry has also been reported earlier[22] for the title reaction.

Table 1. Stoichiometry of the reaction of ascorbic acid and thallium(III) with $[H^+] = 1\cdot0\ mol\ dm^{-3}$

$10^4[H_2A]$ (mol dm^{-3})	$10^4[Tl^{III}]$ (mol dm^{-3})	$10^3[Cl^-]$ (mol dm^{-3})	$\Delta[H_2A]/\Delta[Tl^{III}]$
2·00	6·00	6·00	1·05
3·00	6·00	6·00	1·07
4·00	6·00	6·00	1·01
6·00	2·00	2·00	1·00
6·00	3·00	3·00	1·00
6·00	4·00	4·00	0·98
2·00	5·00	5·00	1·02
3·00	5·00	5·00	1·03
4·00	10·00	10·00	1·04
5·00	2·00	2·00	0·98
6·00	3·00	3·00	0·96
10·00	4·00	4·00	0·99

RESULTS

Thallium(III) dependence

Certain difficulties were encountered in managing the kinetics, which restricted wider variations of Tl^{III}. However, the chlorothallium(III) species are formed quantitatively and thus help in establishing a procedure for the determination of the order with respect to thallium(III). Therefore, $[Tl^{III}]$ and $[Cl^-]$ were varied at $R = 2$, 3 and 4 ($R = [Cl^-]/[Tl^{III}]$) and fixed concentrations of other reaction components. The plot of the initial rate (R_0) versus $[Tl^{III}]$ in all these conditions yielded straight lines passing through the origin commensurate with a first-order reaction with respect to the oxidant. Further, $[Tl^{III}]$ was also varied at $R > 10$ and the plot of initial rate (R_0) versus $[Tl^{III}]$ also yielded a straight line passing through the origin.

Ascorbic acid dependence

The concentration of ascorbic acid was varied from $2\cdot0 \times 10^{-4}$ to $8\cdot0 \times 10^{-4}\ mol\ dm^{-3}$ at $[Tl^{III}] = 4\cdot0 \times 10^{-4}\ mol\ dm^{-3}$ and $5\cdot0 \times 10^{-4}\ mol\ dm^{-3}$, $[HClO_4] = 1\cdot0\ mol\ dm^{-3}$ and $[Cl^-] = 5\cdot0 \times 10^{-3}$ and $1\cdot0 \times 10^{-2}\ mol\ dm^{-3}$. A plot of initial rate (R_0) versus $[H_2A]$ yielded a straight line passing through the origin, indicating a first-order reaction with respect to the organic acid. The second-order rate constants were also derived from the second-order plots for comparable and stoichiometric concentrations of thallium(III) and ascorbic acid. However, the second-order rate constants calculated under these conditions were in agreement to within ±5% with the second-order rate constants calculated from the initial rate (Table 2).

Hydrogen ion dependence

The hydrogen ion concentration was varied from 0·2 to $1\cdot0\ mol\ dm^{-3}$ at $[Tl^{III}] = 5\cdot0 \times 10^{-4}\ mol\ dm^{-3}$, $[H_2A] = 5\cdot0 \times 10^{-4}\ mol\ dm^{-3}$, ionic strength $I = 1\cdot0$ $mol\ dm^{-3}$ and three different concentrations of Cl^-, viz. $5\cdot0 \times 10^{-3}$, $1\cdot0 \times 10^{-2}$ and $1\cdot5 \times 10^{-2}\ mol\ dm^{-3}$. The rate decreased with increasing $[H^+]$ (Table 3).

Ionic strength dependence

The ionic strength effect was studied by varying the concentration of sodium perchlorate at $[H_2A] = 5\cdot0 \times 10^{-4}\ mol\ dm^{-3}$, $[Tl^{III}] = 5\cdot0 \times 10^{-4}\ mol\ dm^{-3}$, $[HClO_4] = 0\cdot3\ mol\ dm^{-3}$ and $[Cl^-] = 5\cdot0 \times 10^{-3}$ $mol\ dm^{-3}$. The rate was independent of the ionic strength even with a fivefold increase in ionic strength.

Chloride ion dependence

Sodium chloride was employed for the variation of the chloride ion concentration at $[H_2A] = 5\cdot0 \times 10^{-4}$

Table 2. Second-order rate constants for the reaction of ascorbic acid and thallium(III) in aqueous acid solution with $[HClO_4] = 1\cdot0$ mol dm^{-3}

$10^4[H_2A]$ (mol dm^{-3})	$10^4[Tl^{III}]$ (mol dm^{-3})	$10^3[Cl^-]$ (mol dm^{-3})	$10^6 R_0$ (mol dm^{-3} s^{-1})[a]	k (dm^3 mol^{-1} s^{-1})[b]
5·0	2·0	0·6	6·0	60·0
5·0	3·0	0·9	9·0	60·0
5·0	4·0	1·2	12·0	60·0
5·0	5·0	1·5	14·5	58·0
5·0	6·0	1·8	18·0	60·0
5·0	2·0	0·8	5·0	50·0
5·0	3·0	1·2	7·5	50·0
5·0	4·0	1·6	10·0	50·0
5·0	5·0	2·0	12·5	50·0
5·0	6·0	2·4	15·0	50·0
4·0	2·0	10·0	1·9	23·7(23·0)
4·0	3·0	10·0	2·9	24·2(23·0)
4·0	4·0	10·0	3·8	23·9(23·0)
4·0	5·0	10·0	4·66	23·3(23·0)
4·0	6·0	10·0	5·66	23·5(24·5)
4·0	7·0	10·0	6·66	23·7(24·3)
4·0	8·0	10·0	7·66	23·9(23·0)
2·0	5·0	5·0	3·20	32·0
3·0	5·0	5·0	4·20	28·0
4·0	5·0	5·0	5·50	27·5
5·0	5·0	5·0	6·90	27·6
6·0	5·0	5·0	8·30	27·6
7·5	5·0	5·0	10·00	26·6
2·0	4·0	10·0	1·83	22·9(23·0)
3·0	4·0	10·0	2·80	23·3(23·0)
4·0	4·0	10·0	3·83	23·9(22·5)
5·0	4·0	10·0	4·66	23·9(23·4)
6·0	4·0	10·0	5·66	23·6(23·0)
7·1	4·0	10·0	6·66	23·8(24·6)
8·1	4·0	10·0	7·50	23·4(23·4)
3·0	3·0	10·0	–	23·3[c]
4·0	4·0	10·0	–	23·0[c]
5·0	5·0	10·0	–	23·3[c]
6·0	6·0	10·0	–	23·3[c]
7·0	7·0	10·0	–	24·0[c]
8·0	8·0	10·0	–	24·1[c]

[a] R_0 = initial rate.

[b] The values of the rate constants obtained from the second order plots are given in parentheses.

[c] Calculated from the stoichiometric plots.

mol dm^{-3}, $[Tl^{III}] = 5\cdot0\times10^{-4}$ mol dm^{-3}, $I = 1\cdot0$ mol dm^{-3} and four hydrogen ion concentrations. The rate increased with increasing $[Cl^-]$. However, chloride ion concentrations at $R < 2$ were not employed as the kinetics were not manageable by the technique employed.

Thallium(I) dependence

The Tl^I concentration was varied from $1\cdot0\times10^{-4}$ to $1\cdot0\times10^{-3}$ mol dm^{-3} at $[H_2A] = 5\cdot0\times10^{-4}$ mol dm^{-3}, $[Tl(III)] = 5\cdot0\times10^{-4}$ mol dm^{-3}, $[HClO_4] = 1\cdot0$ mol dm^{-3} and $[Cl^-] = 5\cdot0\times10^{-3}$ mol dm^{-3}. Since the rate is not affected by chloride ion, the possibility of any fast equilibrium involving thallium(I) or proceeding by a rate-limiting step is ruled out.

DISCUSSION

The reactions of the chlorothallium(III) complexes usually exhibit substrate-dependent reactivity.[8–16] Woods *et al.*[9] determined the formation constants of four successive chlorothallium(III) complexes, viz. $[TlCl]^{2+}$, $[TlCl_2]^+$, $TlCl_3$ and $[TlCl_4]^-$, to be $5\cdot22\times10^6$ (K_1), $1\cdot25\times10^5$ (K_2), $4\cdot82\times10^2$ (K_3) and $65\cdot3$ (K_4) dm^3 mol^{-1}, respectively, at

Table 3. Hydrogen ion variation at different concentrations of chloride ion in the reaction of thallium(III) and ascorbic acid, with $[H_2A] = 5{\cdot}0 \times 10^{-4}$ mol dm^{-3}, $[Tl^{III}] = 5{\cdot}0 \times 10^{-4}$ mol dm^{-3}, $I = 1{\cdot}0$ mol dm^{-3} and 10 °C

$10^3[Cl^-]$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	$10^5(R_0)$ (mol dm^{-3} s^{-1})
5·00	0·20	2·50
	0·25	2·06
	0·30	1·75
	0·40	1·40
	0·60	0·97
	0·70	0·90
	0·80	0·80
	1·00	0·67
10·0	0·20	2·15
	0·30	1·55
	0·40	1·20
	0·60	0·83
	0·80	0·70
	1·00	0·57
15·00	0·20	1·90
	0·25	1·55
	0·30	1·33
	0·40	1·05
	0·60	0·72
	0·80	0·60
	1·00	0·53

$I = 0{\cdot}5$ mol dm^{-3} and 25 °C:

$$Tl^{3+} + Cl^- \rightleftharpoons [TlCl]^{2+} \quad K_1 \qquad (2)$$

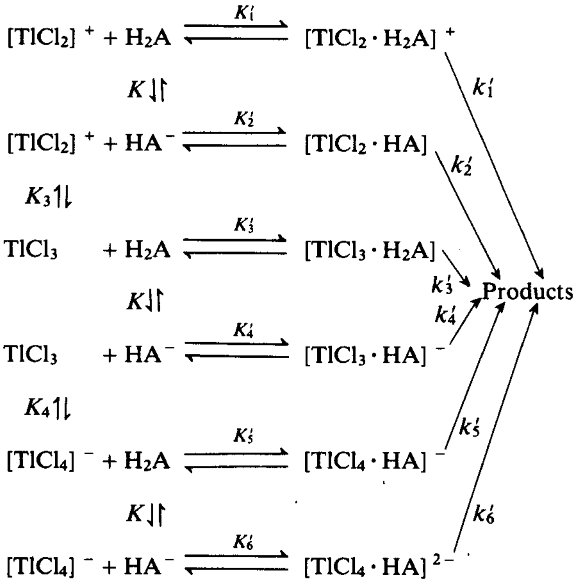
$$[TlCl]^{2+} + Cl^- \rightleftharpoons [TlCl_2]^+ \quad K_2 \qquad (3)$$

$$[TlCl_2]^+ + Cl^- \rightleftharpoons TlCl_3 \quad K_3 \qquad (4)$$

$$TlCl_3 + Cl^- \rightleftharpoons [TlCl_4]^- \quad K_4 \qquad (5)$$

Higher complexes such as $TlCl_5^{2-}$ and $TlCl_6^{3-}$ have also been reported,[23] but their reactivity patterns are not well known. The chlorothallium(III)[7,8] complexes only involve four chlorine atoms coordinated to each thallium(III). Therefore, the formation constants of these complexes were recalculated at 10 °C and $I = 1{\cdot}0$ mol dm^{-3} to be $5{\cdot}93 \times 10^6$ (K_1), $1{\cdot}39 \times 10^5$ (K_2), $5{\cdot}39 \times 10^2$ (K_3) and 65·3 (K_4) dm^3 mol^{-1}, respectively, by employing the mean activity coefficient of sodium chloride at $I = 1{\cdot}0$ mol dm^{-3} and the enthalpy value reported by Woods *et al.*[9] However, Thakuria and Gupta[14] reported a variation in the value of K_4 of only 2% for each 10 °C rise in temperature.

These recalculated equilibrium constants were employed to calculate the equilibrium concentrations of Cl^- by the method of successive approximation and mass balance relations.[24,25] However, the correlation of the rate with the equilibrium concentration of chloride ion indicates that the reactivity pattern of the chlorothallium(III) species decreases in the order $Tl^{3+} > [TlCl]^{2+} > [TlCl_2]^+ > TlCl_3 > [TlCl_4]^-$. Ascorbic acid is a dibasic acid with pK_1 and pK_2 values of *ca* 4·03 and 12, respectively.[26] The concentration of A^{2-} species can be neglected in view of the higher hydrogen ion concentrations employed in the title reaction. Therefore, the reactive species of ascorbic acid are H_2A and HA^-, and the species HA^- is more reactive. Since the chloride ion concentration employed in the reaction is in the range $R > 2$, the chlorothallium(III) species that participate in the reaction should be $[TlCl_2]^+$, $TlCl_3$ and $[TlCl_4]^-$. Therefore, considering these reactive species of thallium(III) and ascorbic acid, the following reaction mechanism can be envisaged:



Hence the loss of thallium (III) leads to the rate law

$$R_0 = \{k_1'K_1' + k_2'K_2'K/[H^+]) + (k'K_3'K_3[Cl^-] + k_5'K_5'K_3K_4[Cl^-]^2) + (k_4'K_4'KK_3[Cl^-] + k_6'K_6'KK_3K_4[Cl^-]^2)/[H^+]\}/\{(1 + K_3[Cl^-] + K_3K_4[Cl^-]^2)\}\,[Tl(III)]\,[H_2A] \qquad (4)$$

where $[Tl^{III}]$ and $[H_2A]$ are the gross analytical concentrations of chlorothallium(III) species and ascorbic acid, respectively. Since K_1', K_2', K_3', K_4', K_5' and K_6' are small equilibrium constants, the rate law (4) reduces to

$$k = \{(k_1 + k_2K/[H^+]) + (k_3K_3[Cl^-] + k_5K_3K_4[Cl^-]^2) + (k_4KK_3[Cl^-] + k_6KK_3K_4[Cl^-]^2)/[H^+]/(1 + K_3[Cl^-] + K_3K_4[Cl^-]^2) \qquad (5)$$

where $k_1 = k_1'K_1'$, $k_2 = k_2'K_2'$, $k_3 = k_3'K_3'$, $k_4 = k_4'K_4'$, $k_5 = k_5'K_5'$ and $k_6 = k_6'K_6'$. The value of k was calculated to be 23·6 ± 0·3 dm^3 mol^{-1} s^{-1} at $[Cl^-] = 1{\cdot}0 \times 10^{-2}$ mol dm^{-3}, $I = 1{\cdot}0$ mol dm^{-3} and 10 °C as the observed second-order rate constant.

Considering the lower range of Cl^- concentrations ($R < 6$), $[TlCl_2]^+$ and $TlCl_3$ are the reactive chlorothallium(III) species and the higher species $[TlCl_4]^-$ can be neglected. This reduces the rate law (5) to

$$k = (k_1 + k_2K/[H^+]) + (k_3K_3 + k_4KK_3/[H^+])[Cl^-]/(1 + K_3[Cl^-]) \quad (6)$$

A plot of $k\ (1 + K_3[Cl^-])$ versus $[Cl^-]$ from equation (6) was constructed that yielded a straight line with a non-zero intercept. The intercept (Y) and gradient (G) were represented by the following equations:

$$Y = k_1 + k_2K/[H^+] \quad (7)$$

$$G = k_3K_3 + k_4KK_3/[H^+] \quad (8)$$

Plots of Y versus $[H^+]^{-1}$ from equation (7) and G versus $[H^+]^{-1}$ from equation (8) were constructed (Figure 1) and the values of k_1, k_2K, k_3K_3 and k_4KK_3 were calculated (Table 4).

Since the species $TlCl_3$ and $[TlCl_4]^-$ are predominant in the higher range of $[Cl^-]$ ($R > 10$), the rate law (5) reduces to

$$k = \{(k_3K_3 + k_4KK_3/[H^+]) + (k_5K_3K_4 + k_6KK_3K_4/[H^+])[Cl^-]\}/(k_3 + K_3K_4[Cl^-]) \quad (9)$$

A plot of $k(K_3 + K_3K_4[Cl^-])$ versus $[Cl^-]$ from equation (9) was constructed that also yielded a straight line with non-zero intercept. The intercept (Y') and gradient (G') were represented by the following equations:

$$Y' = k_3K_3 + k_4KK_3/[H^+] \quad (10)$$

$$G' = k_5K_3K_4 + k_6KK_3K_4/[H^+] \quad (11)$$

Plots of Y' versus $[H^+]^{-1}$ from equation (10) and G' versus $[H^+]^{-1}$ from equation (11) were also constructed and straight lines with non-zero intercepts were obtained in both instances. The intercepts and gradients of these plots yielded the values of k_3K_4, k_4KK_3, $k_5K_3K_4$ and $k_6KK_3K_4$ (Table 4).

Since $[H^+]$ was varied only in the range of higher Cl^- concentration ($R > 10$), a plot of $k(K_3[Cl^-] + K_3K_4[Cl^-]^2)$ versus $[H^+]^{-1}$ from equation (9) also yielded a straight line with a non-zero intercept (Figure 2). The intercept Y'' and gradient (G'') calculated from Figure 2 can be represented by the following equations:

$$Y'' = k_3K_3[Cl^-] + k_5K_3K_4[Cl^-]^2 \quad (12)$$

$$G'' = k_4KK_3[Cl^-] + k_6KK_3K_4[Cl^-]^2 \quad (13)$$

Plots of $Y''/[Cl^-]$ versus $[Cl^-]$ from equation (12) and $G''/[Cl^-]$ versus $[Cl^-]$ from equation (13) were con-

Table 4. Values of different rate constants for the reaction of Tl^{III} and H_2A in presence of chloride ion at 10 °C, $I = 1\cdot0$ mol dm^{-3}

Rate constants	Value
k_1	$30\cdot0$ dm^3 mol^{-1} s^{-1}
k_2K	$30\cdot0$ s^{-1}
k_3	$3\cdot7$ dm^3 mol^{-1} s^{-1}
k_4K	$2\cdot2$ s^{-1}
k_5	$1\cdot1$ dm^3 mol^{-1} s^{-1}
k_6K	$0\cdot55$ s^{-1}

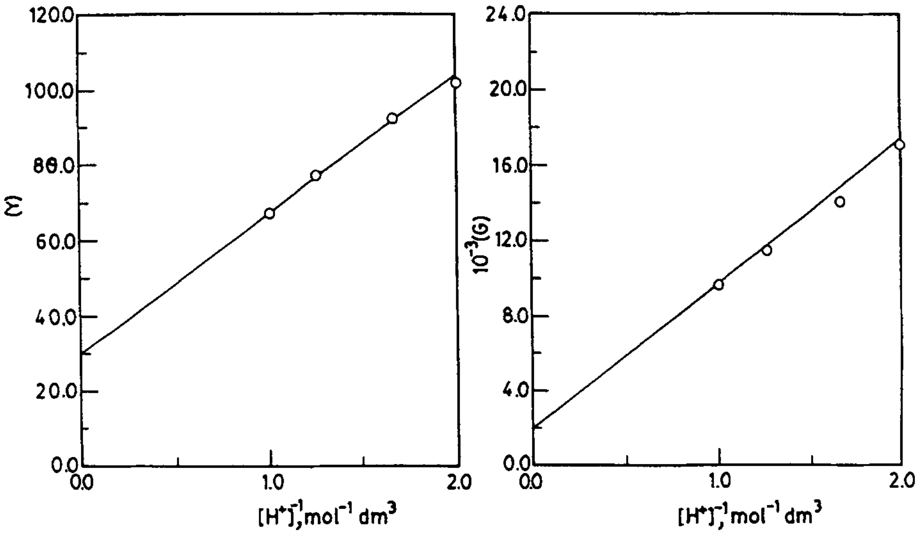


Figure 1. Plots of Y and G versus $[H^+]^{-1}$

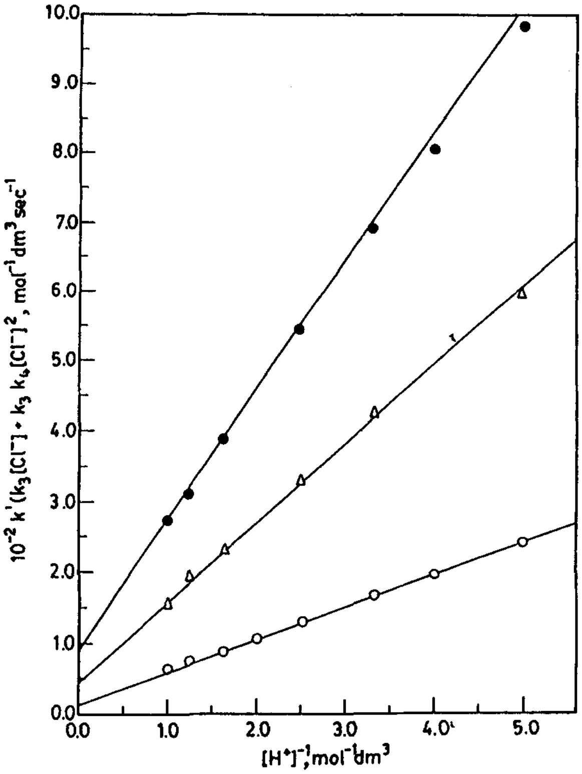


Figure 2. Effect of variation of hydrogen ion concentration. $[H_2A] = 5{\cdot}0 \times 10^{-4}$ mol dm^{-3}; $[Tl^{III}] = 5{\cdot}0 \times 10^{-4}$ mol dm^{-3}; $[Cl^-]_f =$ (○) $0{\cdot}36 \times 10^{-3}$ mol dm^{-3}, (△) $8{\cdot}3 \times 10^{-3}$ mol dm^{-3} and (●) $1{\cdot}3 \times 10^{-2}$ mol dm^{-3}; temperature = 10 °C

structed and straight lines with non-zero intercepts were obtained in both instances. The values of k_3K_3, $k_5K_3K_4$, k_4KK_3 and $k_6KK_3K_4$ were calculated from these plots (Table 4) and these were in agreement with the values of these constants calculated earlier with chloride ion variation. These values of composite rate constants were further substituted in the rate law (5) and the values of k_{cal} were in agreement with those of k_{exp} to within ± 12%. Such an agreement between k_{cal} and k_{exp} values is more than satisfactory in such a system.

Since the catalysis by chloride ion of the reactions of thallium(III) is ascribed[7] to the stabilization of the substrate oxidation products by the chloride ion, no such possibility appears in Cl^--inhibited reactions. However, inhibition of Tl^{III} reactions by Cl^- provides indirect evidence for an intermediate complex of thallium(III) and the substrate. Obviously, chloride ions block coordination sites of $Tl^{3+}_{(aq)}$ and thus inhibit incorporation of the organic acid in the coordination shell of the oxidant. The inverse hydrogen ion dependence, the reactivity of both the molecular and anionic species of ascorbic acid and neither kinetic nor spectral evidence for intermediate complexes between chlorothallium(III) species and ascorbic acid are observations which account for an outer-sphere mode of electron transfer.[27] However, the inhibition of the reaction by chloride ions is contrary to an outer-sphere model and indirectly supports complexation between the metal ion and the substrate. Although the chloride ion inhibition could arise from a progressive decrease in the E^0 values for $[TlCl_x]^{n+}$ complexes as x increases, such a proposition was abandoned in view of the rapid reaction of the lower chlorothallium(III) species and ascorbic acid.

Since the hydrolysis of thallium(III) is significantly suppressed by chloride ion, the hydrolysis constant (K_h) cannot be neglected for the hydrogen ion concentrations employed in the reaction. K_h had been reported[28] to be $0{\cdot}073$ mol dm^{-3} at $I = 3{\cdot}0$ mol dm^{-3} and 25 °C, and also[29] $0{\cdot}086$ mol dm^{-3} at $I = 1{\cdot}5$ mol dm^{-3} and 25 °C. However, $K_h = 0{\cdot}073$ mol dm^{-3} was widely employed in the thallium(III) reactions. If the enthalpy change[30] of hydrolysis ($69{\cdot}4$ kJ mol^{-1}) is employed, K_h is estimated to *ca* $0{\cdot}019$ mol dm^{-3} at 10 °C.

Further, as the rate decreases with increasing $[H^+]$, the species $[TlOH]^{2+}$ should be more reactive than $Tl^{3+}_{(aq)}$. $[TlOH]^{2+}$ has also been considered in other reactions of thallium(III) with Hg_2^{2+},[31,32] U^{IV},[33] formic acid,[34] α-hyroxy acids[17] and hydroxylamine.[15] Therefore, the hydrogen ion dependence should be related to the oxidant as K_h cannot be neglected under the experimental conditions. Similarly, $MnOH^{2+}$ and $CoOH^{2+}$ were also found to be reactive species in the reactions, viz. Mn^{III}–H_2A[35] and Co^{III}–H_2A,[36] respectively.

Although the formation of an intermediate complex between thallium(III) and ascorbic acid is not indicated kinetically, the possibility of such a complex in view of the ligand properties of the organic acid and the tendency of $Tl^{3+}_{(aq)}$ to act as a coordinating centre cannot be ruled out. Thus, considering both $Tl^{3+}_{(aq)}$ and $[TlOH]^{2+}$ to be the reactive species of thallium(III) and the molecular form (H_2A) to be that of ascorbic acid, a reaction mechanism consistent with the observed hydrogen ion dependence can be envisaged as follows:

$$Tl^{3+} + H_2O \overset{K_h}{\rightleftharpoons} [TlOH]^{2+} + H^+ \tag{14}$$

$$Tl^{3+} + H_2A \overset{K'}{\rightleftharpoons} [Tl \cdot H_2A]^{3+} \xrightarrow{k'} Tl^+ + 2H^+ + A \tag{15}$$

$$[TlOH]^{2+} + H_2A \overset{K''}{\rightleftharpoons} [TlOH \cdot H_2A]^{2+} \xrightarrow{k''} Tl^+ + H^+ + A + H_2O \tag{16}$$

Since the Cl^--inhibited reactions of thallium(III) reportedly occur via an intermediate complex between the oxidant and the substrate,[7,37] and fast interaction between Tl^{III} and H_2A is ascribed to the formation of the intermediate complex. An intermediate complex is also supported by the fact that the rate in the presence of sulphate ions[3] is faster than that observed in the presence of chloride and acetate ions. Presumably, the faster rate in the presence of sulphate ions can be accounted for by the weak sulphatothallium(III) complexes. Therefore, the proposed mechanism appears reasonable in view of these observations and the loss of Tl^{III} leads to the rate law

$$k^{Tl} = (k'K'[H^+] + k''K''K_h)/(K_h + [H^+]) \qquad (17)$$

or

$$k^{Tl} = (k_1^{Tl}[H^+] + k_2^{Tl}K_h)/(K_h + [H^+]) \qquad (18)$$

where $k_1^{Tl} = k'K'$ and $k_2^{Tl} = k''K''$ are the composite rate constants as the equilibrium constants K' and K'' are small.

A plot of $k^{Tl}(K_h + [H^+])$ versus $[H^+]$ from equation (18) was constructed that yielded a straight line with a non-zero intercept (Figure 3). The values of $k_2^{Tl}K_h$ from the intercept and k_1^{Tl} from the gradient were calculated to be 64·0 s^{-1} and 27·0 $dm^3\,mol^{-1}\,s^{-1}$, respectively, at $I = 1{\cdot}0$ mol dm^{-3} and 10 °C (Table 5).

Since no evidence for free radicals was obtained, the possibility of the intermediate species Tl^{2+} reacting with ascorbate free radical in the solvent cage before diffusing out cannot be completely ruled out. The higher oxidation potential[38] of the Tl^{2+}/Tl^{+} couple (1·5 V) than that of the Tl^{3+}/Tl^{+} couple (1·25 V)[39] also accounts for the fast interaction between Tl^{2+} and H_2A species in the solvent cage.

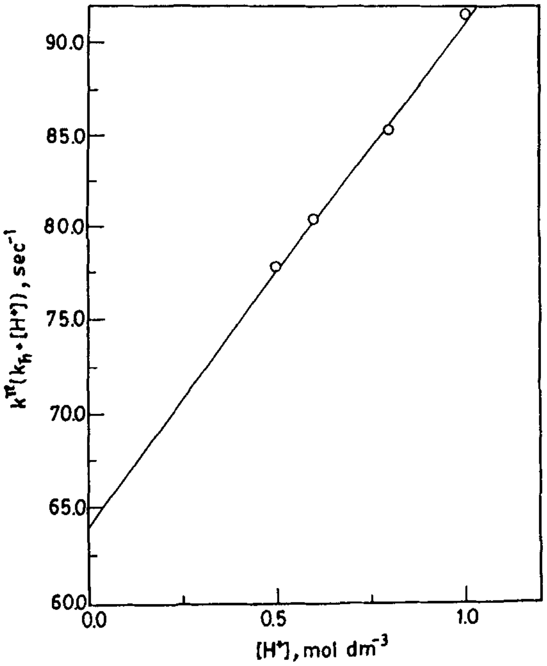


Figure 3. Plot of $k^{Tl}(k_h + [H^+])$ versus $[H^+]$

Table 5. Second-order rate constants

$[H^+]$ (mol dm^{-3})	0·5	0·6	0·8	1·0
10^2k^{Tl} ($dm^3\,mol^{-1}\,s^{-1}$)	1·5	1·3	1·04	0·9

Alternatively, the possibility of the $Tl^{3+}_{(aq)}$–H_2A reaction occurring via the activation processes ($Tl^{3+} + H_2A$) and ($Tl^{3+} + HA^-$) was also envisaged, particularly in view of the fact that a straight line with a non-zero intercept was obtained in a plot of k^{Tl} versus $[H^+]^{-1}$. However, this proposal was abandoned on two counts, viz. the hydrolysis constant (K_h) of thallium(III) for the hydrogen ion concentration employed in the reaction cannot be neglected, and the rate does not depend on the ionic strength. Had it not been for this situation, the rate would have decreased with increasing ionic strength owing to the predominant (Tl^{3+}–HA^-) pathway.

REFERENCES

1. K. B. Wiberg (Ed.), *Oxidation in Organic Chemistry, Part A*, p. 234. Academic Press, New York (1965).
2. A. G. Lee, *The Chemistry of Thallium.* Elsevier, Amsterdam (1971).
3. P. D. Sharma and Y. K. Gupta, *Talanta* **20**, 903 (1973); **21**, 168 (1974).
4. W. C. E. Higginson and K. G. Ashurst, *J. Chem. Soc.* 3044 (1953); C. E. Johnson, *J. Am. Chem. Soc.* **74**, 959 (1952).
5. B. Faleinella, P. D. Felgate and G. S. Laurence, *J. Chem. Soc.* 1367 (1974).
6. B. M. Thakuria and Y. K. Gupta, *Inorg. Chem.* **16**, 1401 (1977); E. Penna-Eranca and R. W. Dodsen, *J. Am. Chem. Soc.* **77**, 2651 (1955); A. G. Harkness and J. Halpern, *J. Am. Chem. Soc.* **81**, 3526 (1959); C. M. Loue, L. P. Quinn and C. H. Brubaber, Jr, *J. Inorg. Nucl. Chem.* **27**, 2119 (1965); K. S. Gupta and Y. K. Gupta, *J. Chem. Soc. A* 256 (1970); H. N. Halvorsen and S. M. Taylor, *Discuss. Faraday Soc.* **29**, 174 (1950); R. Lortik and M. Zader, *Can. J. Chem.* **58**, 1305 (1980); P. D. Sharma and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.* 54 (1972); I. Rao, S. K. Mishra and P. D. Sharma, *Indian J. Chem.* **30A**, 773 (1991).
7. K. S. Gupta and Y. K. Gupta, *Inorg. Chem.* **13**, 951; (1974); **14**, 2000 (1975).
8. P. D. Sharma and Y. K. Gupta, *Aust. J. Chem.* **26**, 2115 (1973).
9. J. M. Woods, P. K. Gallaghar, Z. Z. Hugus, Jr, and E. L. King, *Inorg. Chem.* **3**, 1313 (1964).
10. K. S. Gupta and Y. K. Gupta, *J. Chem. Soc A* 256 (1970); 1180 (1971).
11. P. D. Sharma and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.* 789 (1973).
12. G. Harbottle and R. W. Dodson, *J. Am. Chem. Soc.* **73**, 2442 (1951).

13. P. D. Sharma and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.* 52 (1972).
14. B. M. Thakuria and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.* 2541 (1975).
15. B. M. Thakuria and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.* 77 (1975).
16. P. D. Sharma and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.* 81 (1975).
17. P. Gupta, P. D. Sharma and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.* 1867 (1984); I. Rao, S. K. Mishra and P. D. Sharma, *Indian J. Chem.* **30A**, 773 (1991).
18. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III, p. 370. Interscience, New York (1957).
19. I. M. Kolthoff, R. Belcher, R. Stanger and G. Matsayan, *Volumetric Analysis*, Vol. III, p. 212. Interscience (1957).
20. D. K. Mishra, T. P. A. Dhas, P. D. Sharma, A. P. Bhargava and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.* 1265 (1990).
21. M. Latshaw, *J. Am. Chem. Soc.* **47**, 793 (1925).
22. A. Berka, J. Volterin and J. Zyka, *Newer Redox Titrants*, p. 169. Pergamon Press, Oxford (1963).
23. T. G. Spiro, *Inorg. Chem.* **4**, 1290 (1965); **4**, 731 (1965).
24. G. M. Waind, in *Proceedings of Symposium on Coordination Chemistry, Tihany Hungary.* (1964).
25. L. G. Carpenter, M. H. Fordsmith, R. P. Bell and R. W. Dodson, *Discuss. Faraday Soc.* **29**, 92 (1960).
26. M. Kimura, A. Kobayashi and K. Boku, *Bull. Chem. Soc. Jpn.* **55**, 2068 (1982).
27. A. Agrawal, S. K. Mishra and P. D. Sharma, *Rasayan Samiksha, Hindi Granth Academy* **1**, 12, (1990) and references cited therein.
28. G. Biedermann, *Ark. Kemi* **6**, 527 (1964),
29. T. E. Rogers and G. M. Waind, *Trans. Faraday Soc.* **57**, 1360 (1961).
30. Yu. B. Yokolev, F. Ya. Kulba and L. N. Thu, *Zh. Fiz. Khim.* **41**, 1168 (1967).
31. A. M. Armstrong and J. Halpern, *Can. J. Chem.* **35**, 1020 (1957).
32. A. M. Armstrong, J. Halpern and W. C. E. Higginson, *J. Phys. Chem.* **60**, 1661 (1956).
33. J. O. Wear, *J. Chem. Soc.* 5596 (1965).
34. H. N. Halvorson and J. Halpern, *J. Am. Chem. Soc.* **78**, 5562 (1956).
35. E. Pellizzetti, E. Mentasti and E. Pramauro, *J. Chem. Soc., Dalton Trans.* 61 (1978).
36. R. A. Rickman, R. L. Sorenson, K. U. Watkins and G. Davies, *Inorg. Chem.* **16**, 1570 (1977).
37. V. V. Vebsin, N. I. Pecharova and V. I. Spitsyn, *Zh. Neorg. Khim* **22**, 3044 (1977); N. I. Pechurova, V. V. Vebsin, L. A. Zhabordova and V. I. Spitsyn, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1977 (1972).
38. N. Hush, *Trans. Faraday Soc.* **57**, 557 (1961).
39. W. M. Latimer, *Oxidation Potentials*, 2nd ed. Prentice Hall, New York (1952).