Stoicheiometry and Kinetics of the Reaction between Thallium(III) and Antimony(III) Ions in Perchloric Acid Solution

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The rate of the reaction between Tl^{III} and Sb^{III} ions in perchloric acid solution (stoicheiometry 1 : 1) is measurable by conventional methods at 60 °C. After *ca.* 70—80% reaction, a precipitate is obtained consisting mainly of Sb^{V} ions, with small amounts of Tl^{I}, and adsorbed Tl^{III} and Sb^{III} ions. The rate of reaction is independent of the ionic strength, and reaction appears to occur *via* two transition states, $[TlOH,HSbO_2]^{2+}$ and $[Tl,HSbO_2]^{3+}$, the first path accounting for *ca.* 85% reaction. The tentative rate law is as in (i), where K_1 and K_2 are hydrolytic constants

$$\frac{-d[Sb^{III}]}{dt} = \frac{[Tl^{III}][Sb^{III}]}{([H^+] + K_1)}\left(\frac{k_3K_1K_2}{[H^+]} + k_3'K_2\right) \qquad \text{(i)}$$

for the ions Tl^{3+} and SbO^+ respectively. The quantities k_3K_2 and $k_3'K_2$ were found to be 2·66 and 0·30 s^{-1} respectively at 60 °C, and the overall energy and entropy of activation were 16·0 ± 0·4 kcal mol^{-1} and −13·1 ± 1·8 cal K^{-1} mol^{-1} respectively. In the presence of chloride ions, the reaction is complex because of the formation of various chloro-complexes with the ions Tl^{III}, Sb^{III}, and Sb^{V}.

HALPERN [1] has previously shown that the principle [2] of equivalence change has limited validity because of factors, such as the entropy of activation, pertaining to redox systems. Reductions of the ion Tl^{III} present somewhat interesting features. Thus whereas non-complementary reactions with the ions Fe^{II},[3,4] Hg_2^+,[5,6] V^{III},[7] *etc.* are much faster than complementary reactions with U^{IV},[8,9] H_3PO_2,[10] and H_3PO_3,[11] the complementary reaction of the ion As^{III} (ref. 12) is faster than the non-complementary reaction of Fe^{II}.[6] No kinetic evidence for the formation of the intermediate ions Tl^{II} and As^{IV} was found in the oxidation of As^{III}, although the non-complementary oxidations of the ions Fe^{II} (ref. 6) and V^{III} (ref. 7) suggest the formation of Tl^{II}. The oxidation [5] of the ion Hg_2^{2+} provides evidence for intermediate formation of Hg^0. The present study of the reaction between the ions Tl^{III} and Sb^{III} was carried out in order to compare the observed rate constants with those for the corresponding reaction with As^{III}, and to determine whether there is any kinetic evidence for the intermediate ions Tl^{II} and Sb^{II}. The oxidation of triphenylstibine by thallium(III) chloride has been studied previously,[13,14] but no kinetic details are available.

EXPERIMENTAL

Stock solutions of thallium(III) perchlorate were prepared and standardised [15,16] as described previously.[12] A solution of antimony(III) perchlorate, prepared [17] by dissolving antimony trioxide (E. Merck, Guaranteed Reagent) in hot perchloric acid (60%), standardised [18] with bromate-ion solution using Methyl Orange as indicator, and with an excess of Ce^{IV}, back titrating the latter with Fe^{II} to a Ferroin end point.[19] Fresh solutions of antimony(III) perchlorate were prepared daily, since such solutions deteriorate over a period of time.

A solution of cerium(IV) perchlorate was prepared by dissolving cerium(IV) ammonium nitrate (B.D.H., AnalaR) in perchloric acid (60%) and standardised [19] against iron(II) ammonium sulphate to the Ferroin end point. Lithium perchlorate solution was prepared by neutralising perchloric acid with lithium carbonate to pH 6·5—7. All solutions were prepared in doubly distilled water, the second distillation being from potassium permanganate.

Determination of the Stoicheiometry.—Reactants of suitable concentrations were mixed in a measuring flask (250 ml) and allowed to react on a water-bath at 60 °C for *ca.* 2 h. A precipitate was obtained, the colour of which varied from green (excess of Tl^{III}) to yellowish-white (excess of Sb^{III}). The remaining liquid in the flask was made up (to 250 ml) with distilled water and the precipitate allowed to settle completely. The precipitate was then filtered off and washed three or four times with water. The filtrate and the washings were collected in a measuring flask and made up to 250 ml with water [solution (A)]. The precipitate was dissolved in 5M-HCl on heating and the resulting solution made up to 250 ml with water so as to yield a solution 2·5M in HCl [(B)]. The concentrations of the various species in (A) and (B) were determined separately as follows.

(A). (*a*) The ion Sb^{III} was determined using cerium(IV) ions as described under Kinetic Procedure. (*b*) The ions Sb^{III} and Tl^{I} together were determined bromometrically [18] in 2·5—3·5M-HCl using Methyl Orange as indicator. (*c*) The ions Tl^{III} and Sb^{V} were reduced by sulphite ions [20]

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and the excess of the latter then removed as sulphur dioxide by boiling the solution. The total amount of Sb^{III} (that present initially plus that obtained by reduction of Sb^{V} ions) was determined using cerium(IV) ions as in (*a*). (*d*) The total amount of Tl^{I} and Sb^{III} in the reduced solution (*c*) was determined bromometrically.[18]

(B). (*e*) The total amount of the ions Sb^{III} and Tl^{I} was determined bromometrically [18] without interference from the ions Tl^{III} and Sb^{V}. (*f*) The ion Sb^{V} was reduced by sulphite ions and the excess of the latter removed by boiling the solution. The total amount of the ion Sb^{III} thus obtained was determined iodimetrically [21] in a hydrogencarbonate-ion medium. (*g*) The ion Tl^{III} was also reduced in (*f*) and hence the total amount of the ions Sb^{III} and Tl^{I}, which is equivalent to the initial total amount of the ions Sb^{III}, Sb^{V}, Tl^{III}, and Tl^{I}, was determined bromometrically.[18] (*h*) The ion Tl^{III} was precipitated as thallium(III) oxide by sodium hydroxide, centrifuged, washed, and determined iodometrically.[15,16] It was not possible to determine the ion Sb^{III} in solution (B) using cerium(IV) ions, because the reaction between Ce^{IV} and Tl^{I} ions is catalysed [22] by chloride ions.

TABLE 1

Concentrations * of the species Tl^{I}, Tl^{III}, Sb^{III}, and Sb^{V} obtained in the filtrate (A) and precipitate (B) on reaction of the ions Tl^{III} and Sb^{III}

$[Tl^{III}]_0$ / mmol l⁻¹	$[Sb^{III}]_0$ / mmol l⁻¹	(A)				(B)			
		Tl^{III}	Sb^{III}	Tl^{I}	Sb^{V}	Tl^{III}	Sb^{III}	Tl^{I}	Sb^{V}
2·00	1·00	2·50		47·5	10·0	42·5		7·50	85·0
3·00	2·00	2·66		61·7	10·0	27·5		8·33	87·5
4·00	3·00	6·25		72·5	8·33	17·5		3·75	90·0
5·00	4·00	6·00		75·0	8·75	12·0		4·00	92·5
1·00	2·00		37·5	80·0	12·5		5·0	10·0	35·0
2·00	3·00		26·6	87·5	15·0		4·2	5·25	50·0
3·00	4·00		21·2	91·7	12·5		3·12	8·33	61·2
4·00	5·00		15·0	91·50	11·2		3·1	8·50	65·0
2·00	2·00			90·0	7·50			12·50	90·0
3·00	3·00			88·3	11·6			7·50	87·0
4·00	4·00			93·8	10·0			6·00	91·2
5·00	5·00			97·0	10·0			4·50	89·0

* Expressed as a percentage of the concentrations of the reactants Tl^{III} and Sb^{III}.

Kinetic Procedure.—Most kinetic experiments were carried out at 60 °C in stoppered flasks of Corning glass. The reaction was followed by determining the Sb^{III} ion in the reaction mixture at various times in the following way, which is based on the reaction [22] between Sb^{III} and Ce^{IV} ions in perchloric acid. Aliquot portions (5 or 10 ml) of the reaction mixture were added to a known excess of cerium(IV) perchlorate solution, diluted to yield $[H^+] = 0{\cdot}15$—$0{\cdot}2$M, and set aside for 8—10 min. The excess of Ce^{IV} was back titrated against a standard solution of iron(II) ammonium sulphate to the Ferroin end point; H_2SO_4 was added (0·5—1M) to improve the end point. The ions Fe^{II} and Tl^{III} do not interfere with this method.[23] The method is not suitable in the presence of chloride-ion concentrations $>0{\cdot}1$M for the very slow reaction between Ce^{IV} and Tl^{I} ions is catalysed [24] by chloride ions, and a slow reaction [25] between Ce^{IV} and chloride ions occurs yielding a complex which decomposes to give chlorine.

All kinetic runs were carried out under such concentrations of the reactants that no precipitate appeared, or appeared only when more than 70% reaction had occurred. The order of mixing of the reactants had no effect on the rate of the reaction. Rate constants for identical runs were reproducible within ±1—4% depending on the error in the analyses of the aliquot portions.

RESULTS

Stoicheiometry.—Although stoicheiometric experiments were complicated by formation of the precipitate and adsorption of Tl^{III} and Tl^{I} ions, all the four species Tl^{I}, Tl^{III}, Sb^{III}, and Sb^{V} could be determined and the results (with a maximum deviation of ±10%) show that 1 mole of Sb^{III} reacts with 1 mole of Tl^{III} to form 1 mole of Sb^{V} and 1 mole of Tl^{I}. The concentration of the different species in the filtrate and precipitate were calculated as follows

Filtrate (A)	Precipitate (B)
$[Sb^{III}] = a$	$[Tl^{III}] = h$
$[Tl^{I}] = b - a$	$[Tl^{I}] = g - f - h$
$[Sb^{V}] = c - a$	$[Sb^{III}] = e - g + f + h$
$[Tl^{III}] = d - c - b + a$	$[Sb^{V}] = g - e - h$

(results are shown in Table 1). In view of the complicated way in which the determinations have been made, the stoicheiometric results are more than satisfactory. It is obvious that the precipitate consists mainly of the ion Sb^{V} with a small quantity of Tl^{I}. It also has adsorbed Tl^{III} or Sb^{III} ions, whichever was in excess in the original mixture. It may be of interest to report that simple mixing of the ions Sb^{III} and Sb^{V} in perchloric acid solutions results in a white turbidity as is also found [26] in the exchange reaction.

Kinetics.—The reaction was found to be first order in $[Sb^{III}]$ and $[Tl^{III}]$ from the log–log plots of rate against concentration. Second-order rate constants (Table 2) were calculated from conventional $\log[Tl^{III}]/[Sb^{III}]$ against time plots (Figure 1). In a few cases, second-order rate constants were calculated from pseudo-first-order rate constants obtained from linear plots of log $[Sb^{III}]$ against time with an excess of Tl^{III} ions.

The hydrogen-ion concentration was varied with perchloric acid at a constant ionic strength of 3M ($LiClO_4$).

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The rate of reaction decreased with increasing hydrogen-ion concentration. Results at 50, 55, and 60 °C and $I = 3{\cdot}0$M are shown in Table 3. A log–log plot of rate against hydrogen-ion concentration yielded a negative order of *ca.* 1·3 with respect to [H$^+$]. Although the ionic strength was changed from 0·8 to 3·0M (LiClO$_4$), no change in the rate of reaction was observed. The products of reaction, Tl$^{\text{I}}$ ($\leqslant$0·005M) and Sb$^{\text{V}}$ ($\leqslant$0·002M), were also found to have no effect on the rate of reaction.

TABLE 2

Second-order rate constants for the reaction between Tl$^{\text{III}}$ and Sb$^{\text{III}}$ ions at 60 °C, [H$^+$] = 1·5M, and I = 1·5M

10^3[Tl$^{\text{III}}$]/M	10^3[Sb$^{\text{III}}$]/M	k/l mol^{-1} s^{-1}
1·00	1·00	0·77
1·50	1·50	0·80
2·00	1·35	0·76
2·00	1·50	0·77
2·00	2·50	0·77
2·00	3·00	0·77
2·00	4·50	0·81
2·00	5·00	0·81
2·50	1·35	0·76
3·00	1·35	0·76
3·00	2·00	0·77
3·00	2·50	0·77
3·50	2·50	0·83
3·50	3·50	0·80
4·00	1·35	0·76
4·00	4·00	0·80
4·50	2·50	0·77
5·00	0·50	0·77 *
5·00	2·00	0·80
5·00	2·50	0·78
5·50	0·50	0·76 *
6·00	0·50	0·77 *
6·50	0·50	0·81 *
7·00	2·00	0·77
		Average 0·78 ± 0·02

* Obtained from pseudo-first-order rate constants in runs in which Tl$^{\text{III}}$ was in excess.

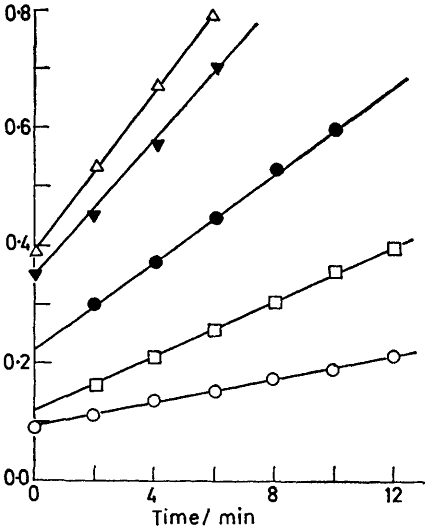

FIGURE 1 Second-order plots at 60 °C for the Tl$^{\text{III}}$–Sb$^{\text{III}}$ reaction: (△), [Tl$^{\text{III}}$] = 0·005M, [Sb$^{\text{III}}$] = 0·002M; (▼), [Tl$^{\text{III}}$] = 0·0045M, [Sb$^{\text{III}}$] = 0·002M; (●), [Tl$^{\text{III}}$] = 0·0045M, [Sb$^{\text{III}}$] = 0·0025M; (□), [Tl$^{\text{III}}$] = 0·0035M, [Sb$^{\text{III}}$] = 0·0025M; (○), [Tl$^{\text{III}}$] = 0·002M, [Sb$^{\text{III}}$] = 0·0025M

The energy and entropy of activation of reaction were calculated to be 16·0 ± 0·4 kcal mol^{-1} and $-13{\cdot}1 \pm 1{\cdot}8$ cal K^{-1} mol^{-1} respectively.

TABLE 3

Second-order rate constants for the reaction between Tl$^{\text{III}}$ and Sb$^{\text{III}}$ ions at different hydrogen-ion concentrations and temperatures. I = 3·0M, [Tl$^{\text{III}}$] = [Sb$^{\text{III}}$] = 2 × 10^{-3}M

Temp./°C	[HClO$_4$]/M	k/l mol^{-1} s^{-1}
60	1·25	0·84
	1·50	0·74
	1·75	0·50
	2·00	0·42
	2·25	0·355
	2·50	0·303
	2·75	0·260
55	1·00	0·67
	1·25	0·50
	1·50	0·40
	1·75	0·316
	2·00	0·260
	2·25	0·210
50	1·00	0·500
	1·25	0·366
	1·50	0·290
	2·00	0·191
	2·50	0·133
	2·75	0·117

DISCUSSION

The hydrolysed species TlOH^{2+} has been considered to be reactive in most kinetic studies [9,27] involving the Tl$^{\text{III}}$ ion. Daugherty [7] assumed that the second hydrolysed species Tl(OH)$_2^+$ was the reactive one in the oxidation of V$^{\text{III}}$ ion but there is no evidence for this species in the present investigation. The ion Sb$^{\text{III}}$ predominantly exists as SbO$^+$ in perchloric acid solutions as indicated [28] by high-voltage ionophoresis, ion-exchange studies, and diffusion measurements. The oxide Sb$_2$O$_3$ or its hydrated form HSbO$_2$ may also exist [29,30] in such solutions, but not to the extent of more than 5% in 1·5M-HClO$_4$.

Equilibria (1) and (2) generally determine the hydrogen-ion dependence of reactions involving the ions Tl$^{\text{III}}$ and Sb$^{\text{III}}$. Although various values of K_1 have

$$\text{Tl}^{3+} + \text{H}_2\text{O} \overset{K_1}{\rightleftharpoons} \text{TlOH}^{2+} + \text{H}^+ \qquad (1)$$

$$\text{SbO}^{+} + \text{H}_2\text{O} \overset{K_2}{\rightleftharpoons} \text{HSbO}_2 + \text{H}^+ \qquad (2)$$

been reported,[31,32] the most accepted value based on e.m.f. measurements [33] is 0·073 mol l^{-1} at 25 °C and I = 3·0M. Since the enthalpy [34,35] of hydrolysis is 11·0 kcal

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mol^{-1}, K_1 has the values 0·516, 0·39, and 0·295 mol l^{-1} at 60, 55, and 50 °C respectively. The hydrolysis constant [29] for the ion SbO$^+$ is *ca.* 0·02 mol l^{-1} at 25 °C, and hence Sb^{III} largely exists in this form in the acid solutions of the present investigation.

With Tl^{3+} or TlOH^{2+} and SbO$^+$ or HSbO$_2$ as the reactive species, the redox reaction could take place by one or more of four paths. The hydrogen-ion dependence, which could throw light on this aspect, is somewhat complicated and inconclusive. However it does rule out the possibility of a reaction between the ions Tl^{3+} and SbO$^+$. The overall entropy change for the reaction is about the same as the normal value of -12 cal K^{-1} mol^{-1} for a bimolecular process, and hence highly charged transition states formed from the ions Tl^{3+} and SbO$^+$ and TlOH^{2+} and SbO$^+$ are less probable. Two reaction paths, TlOH^{2+} + HSbO$_2$ and Tl^{3+} + HSbO$_2$, remain with rate constants k_3 and k_3' respectively, giving the rate law (3). The observed rate constant k is

$$\frac{-\mathrm{d}[\mathrm{Sb^{III}}]}{\mathrm{d}t} = \frac{[\mathrm{Tl^{III}}][\mathrm{Sb^{III}}]}{(K_1 + [\mathrm{H^+}])}\left(\frac{k_3K_1K_2}{[\mathrm{H^+}]} + k_3'K_2\right) \quad (3)$$

thus given by (4).

$$k = \frac{(k_3K_1K_2/[\mathrm{H^+}]) + k_3'K_2}{(K_1 + [\mathrm{H^+}])} \quad (4)$$

Plots of $k(K_1 + [\mathrm{H^+}])$ against $1/[\mathrm{H^+}]$ gave straight lines with intercepts (Figure 2) in accordance with equation (4). From the gradients, values of k_3K_2 were found to be 2·66, 1·70, and 1·33 s^{-1} at 60, 55, and 50 °C respectively. Similarly from the intercepts, corresponding values of $k_3'K_2$ were found to be 0·35, 0·30, and 0·25 s^{-1} respectively. The heat of hydrolysis for reaction (2) is not known and hence k_3 and k_3' cannot be calculated, but the enthalpy appears to have a negative value because the difference in k_3K_2 or $k_3'K_2$ values at different temperatures is small. If free energies of formation [36] for the species SbO$^+$, HSbO$_2$, and H$_2$O are any guide, this enthalpy change would be small and negative. The quantity k_3/k_3' indicates that the contribution from the first path (TlOH^{2+} + HSbO$_2$) is *ca.* 85%. If, therefore, the overall energy effects have any significance, they refer to this major step.

Furthermore if the reaction path TlOH^{2+} + SbO$^+$ is assumed instead of that of Tl^{3+} + HSbO$_2$ for the minor contribution to the rate law, $k_3'K_2$ will be replaced by $k_3''K_1$ in (3), where k_3'' is the rate constant for the corresponding path. However, values of k_3'' calculated from the intercept in this way were found to vary irregularly at the three temperatures and hence the reaction path between the ions TlOH^{2+} and SbO$^+$ is again excluded.

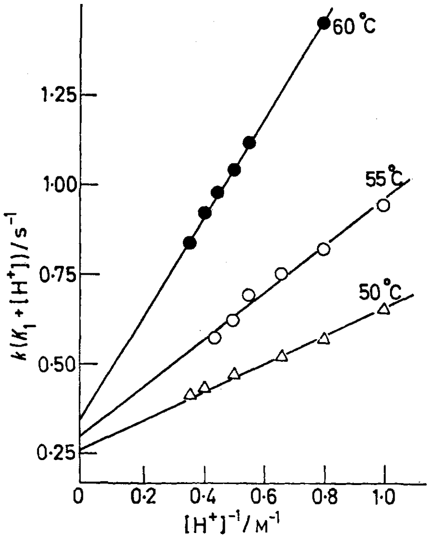

FIGURE 2 Plots of $k(K_1 + [\mathrm{H^+}])$ against $1/[\mathrm{H^+}]$ for the Tl^{III}–Sb^{III} reaction: $[\mathrm{Tl^{III}}] = [\mathrm{Sb^{III}}] = 0{\cdot}002\mathrm{M}$; $I = 3\mathrm{M}$; (●), 60; (○), 55; (△), 50 °C

A comparison of the rate constant (1·48 s^{-1} at 35 °C) for the corresponding oxidation of As^{III} by Tl^{III} (ref. 12) shows that the rate of oxidation of Sb^{III} ion is slower in spite of its lower energy of activation (E_a for As^{III} = 21·5 kcal mol^{-1}). The much larger entropy change (+10·0 cal K^{-1} mol^{-1}) for the former reaction more than compensates the high energy of activation.

[2/580 *Received, 13th March*, 1972]

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