Kinetics and Mechanism of the Reduction of Thallium(III) by Arsenic(III) in Perchloric Acid Solution

By **P. D. Sharma** and **Y. K. Gupta,*** Department of Chemistry, University of Rajasthan, Jaipur, India

Thallium(III) and Arsenic(III) react in aqueous perchloric acid solution to give $\mathrm{Tl^{I}}$ and $\mathrm{As^{V}}$. The kinetics were followed by determining $\mathrm{Tl^{III}}$ iodometrically under critical conditions. The empirical rate law is:

$$\frac{-\mathrm{d}[\mathrm{Tl^{III}}]}{\mathrm{d}t} = \frac{k_3'[\mathrm{Tl^{III}}][\mathrm{As^{III}}]}{[\mathrm{H^+}]} \qquad \text{(a)}$$

k_3' was found to be 88·5 ± 5·7 min^{-1} at 35 ± 0·1 °C. The energy and entropy of activation were found to be 21·5 ± 1 kcal and −15·5 ± 3 cal mol^{-1} deg^{-1} respectively. The reactive species are $\mathrm{TlOH^{2+}}$ and $\mathrm{HAsO_2}$. The rate decreases with increasing ionic strength and with decreasing dielectric constant. Chloride ions strongly inhibit the reaction.

A NUMBER of inorganic substrates undergoing two-electron-change oxidation have been studied in this laboratory and so far no kinetic evidence for two successive one-electron-change steps for $\mathrm{Tl^{III}}$ has been obtained as in the oxidation of $\mathrm{Fe^{II}}$.[1] $\mathrm{As^{III}}$ also undergoes two-electron-change, but no evidence for $\mathrm{As^{IV}}$ or $\mathrm{Tl^{II}}$ was obtained. The oxidation–reduction seems to be accomplished in a single step as in the case of hypophosphite,[2] phosphite,[3] $\mathrm{U^{IV}}$,[4] $\mathrm{Hg_2^{2+}}$,[5,6] *etc.* A special feature of oxidation by hypophosphite and phosphite is that they form complexes with $\mathrm{Tl^{III}}$ and that the rate of hypophosphite oxidation depends on the water activity.[7]

EXPERIMENTAL

The stock solution of thallic perchlorate was prepared by dissolving thallic oxide (B.D.H. AnalaR) in perchloric acid (Riedel) and standardized iodometrically.[8] The end-point was marked by the change from dirty blue to the clear yellow colour of the precipitate of thallous iodide. The stock solution of arsenious acid was prepared by dissolving $\mathrm{As_2O_3}$ (May and Baker) in water by boiling and standardized by the bromate [9] or the permanganate [10] method. All other chemicals were either B.D.H. AnalaR or Merck G.R. quality.

Lithium perchlorate was prepared by neutralizing perchloric acid (60% AnalaR Riedel; no detectable chloride) with lithium carbonate (B.D.H. Laboratory grade) to pH 6·8. The kinetic experiments were made in a thermostatted water bath at 35° ± 0·1° unless stated otherwise. The details have been described earlier.[2] All solutions were prepared in doubly distilled water, the second distillation being from permanganate solution.

The kinetics were followed by determining $\mathrm{Tl^{III}}$ colorimetrically.[11] 2% KI (2 ml) and 5·0M HCl (5 ml) were mixed just before the addition of reaction mixture (5 ml). The liberated iodine was estimated with a Spectronic 20 colorimeter at 440 and 450 mμ. Reference solution was a mixture of KI, HCl, and $\mathrm{HClO_4}$ of the same concentrations as for the iodometric estimation of $\mathrm{Tl^{III}}$. In most cases duplicate rate measurements were reproducible to ±5%.

The present redox reaction is one of the difficult systems

---

[1] W. C. E. Higginson and K. G. Ashurst, *J. Chem. Soc.*, 1953, 3044; C. E. Johnson, *J. Amer. Chem. Soc.*, 1952, **74**, 959; O. L. Forcheimer and R. P. Epple, *J. Amer. Chem. Soc.*, 1952, **74**, 5772.

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

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

[4] A. C. Harkness and J. Halpern, *J. Amer. Chem. Soc.*, 1959, **81**, 3526.

[5] A. M. Armstrong, J. Halpern, and W. C. E. Higginson, *J. Phys. Chem.*, 1956, **60**, 1661.

[6] A. M. Armstrong and J. Halpern, *Canad. J. Chem.*, 1957, **35**, 1020.

[7] K. S. Gupta and Y. K. Gupta, *Indian J. Chem.*, 1970, **8**, 1001.

[8] I. M. Kolthoff and R. Belcher, 'Volumetric Analysis,' Interscience, New York, 1957, vol. 3, p. 370; H. G. S. Senger and Y. K. Gupta, *J. Indian Chem. Soc.*, 1966, **43**, 223.

[9] I. M. Kolthoff, R. Belcher, U. A. Stenger, and G. Matsuyama, 'Volumetric Analysis,' Interscience, New York, 1957, vol. 3 p. 44.

[10] G. F. Smith and R. L. May, *Ind. Eng. Chem., Analyt.*, 1941, **13**, 460.

[11] D. Betteridge and J. H. Yoe, *Analyt. Chim. Acta*, 1962, **27**, 1.

for kinetic study because the determination of any reactant or product in the presence of other species is not free of interference. The addition of KI for the liberation of iodine results in the precipitation of TlI which interferes with colorimetric determination, but the tolerable limit of the concentration of $\mathrm{Tl^{III}}$ was found to be 0·001M. $\mathrm{As^{V}}$ (a reaction product) also liberates [12] iodine from acidified KI but the reaction could be checked in low acid medium. On the other hand $\mathrm{As^{III}}$ reacts [13] with the iodine and the reaction can be checked only in a highly acid medium. The suitable acid medium for the determination was found to be *ca.* 2·5—5M HCl and the permissible limit of the concentration of $\mathrm{As^{V}}$ was found to be 5×10^{-4}M. Hence the extent of reaction to be kinetically followed in a particular run was determined by this limit.

RESULTS

Stoicheiometry.—Thallic perchlorate and arsenious acid of different concentrations were mixed and kept for *ca.* 48 h. Excess of $\mathrm{Tl^{III}}$ was determined iodometrically [8] and when excess $\mathrm{As^{III}}$ was used, $\mathrm{As^{V}}$ was determined iodometrically.

Order with Respect to Thallium(III) *and Arsenious Acid.*—The order from initial rates was found to be one with respect to each. The rate constants were calculated from equation (a), and also by a plot of log $[\mathrm{Tl^{III}}]$ *vs.* time in experiments with an excess of $[\mathrm{As^{III}}]$. The pseudo-first-order rate constants obtained from the slope of the straight line in the latter case, were divided by the average excess concentration of $\mathrm{As^{III}}$ in order to calculate the second-order rate constants. The pseudo-first-order and second-order rate constants with different reactant-concentrations are given in Table 1. The other second-order rate constants were obtained by the conventional plots of log $[\mathrm{Tl^{III}}]_t/[\mathrm{As^{III}}]_t$ *vs.* time. The reason for slightly smaller derived second-order rate constants (obtained from the pseudo-first-order rate constants) is not clear.

Effect of Hydrogen-ion.—This was studied by varying the concentration (0·5—2·5M) of perchloric acid at constant ionic strength adjusted by lithium perchlorate. Sodium perchlorate was not employed in order to avoid medium effects [14,15] due to changes in activity coefficients. The rate decreases on increasing the hydrogen-ion concentration and plots of k *vs.* $1/[\mathrm{H^+}]$ at five different ionic strengths yielded straight lines passing through the origin. These plots also show that the rate decreases on increasing the ionic strength at a fixed hydrogen-ion concentration. The results seem to obey the equation [16] (1) suggesting a reaction between

$$\log k = \log k_0 + (b_0 + b_A - b^{\ddagger})\mu \qquad (1)$$

an ion and an uncharged molecule.

Solvent-effect was studied by varying the dielectric constant by addition of ethyl alcohol. The rate decreases as dielectric constant falls. The results are shown in Table 2. A plot of log k *vs.* $1/D$ yields a straight line.

Chloride-ion Effect.—The role of chloride ion in oxidations by $\mathrm{Tl^{III}}$ has been variously reported. It catalyzes the oxidations of hypophosphite,[17] phosphite,[17] and $\mathrm{Fe^{II}}$,[18] but inhibits the oxidations of formic acid [19] and hydrazine.[20] In the present case too, it considerably decreases the rate. The rates in the presence of various chloride-ion concentrations are given in Table 3. It appears that chloro-complexes

TABLE 1

Pseudo-first-order (k') and second-order rate constants (k) for the reaction at 35° between $\mathrm{Tl^{III}}$ and $\mathrm{As^{III}}$ with $\mu = 2·5$M

$[\mathrm{HClO_4}] = 2·5$M. Expts. 1—24 at 440 mμ; Expts. 25—34 at 450 mμ and Expts. 35—37 at 390 mμ.

Expt. No.	$10^4[\mathrm{Tl^{III}}]$/M	$10^4[\mathrm{As^{III}}]$/M	$10^2k'$/ min^{-1}	k/l mol^{-1} min^{-1}
1	5·20	3·00		35·4
2	5·20	4·00		36·4
3	5·20	6·00		35·6
4	5·20	7·00		34·0
5	5·20	8·00		35·3
6	5·20	9·00		34·5
7	3·00	3·00		35·4
8	4·00	4·00		38·0
9	6·00	6·00		38·0
10	7·00	7·00		35·0
11	8·00	8·00		37·0
12	5·10	50·0	15·7	32·9
13	5·10	60·0	18·5	32·0
14	5·10	70·0	21·8	32·4
15	5·10	80·0	24·9	32·0
16	5·10	90·0	26·5	31·5
17	4·10	40·0	12·6	33·1
18	4·10	60·0	17·9	32·3
19	4·10	70·0	21·9	32·3
20	4·10	80·0	25·3	32·4
21	1·00	5·00		39·1
22	2·00	5·00		34·5
23	3·10	5·00		32·7
24	4·10	5·00		37·7
25	3·10	5·00		32·7
26	4·10	5·00		36·8
27	6·10	5·00		29·1
28	8·10	5·00		39·1
29	9·10	5·00		39·1
30	3·00	3·00		39·0
31	4·00	4·00		36·5
32	6·00	6·00		37·5
33	7·00	7·00		38·8
34	8·00	8·00		38·8
35	0·60	0·50		39·1
36	0·70	0·50		39·1
37	0·80	0·50		34·5
				35·4 ± 2·3

TABLE 2

Rate constants in mixtures of water and ethanol

$[\mathrm{Tl^{III}}] = 5·1 \times 10^{-4}$M; $[\mathrm{As^{III}}] = 1·0 \times 10^{-3}$M; $[\mathrm{HClO_4}] = 1·0$M; $\mu = 1·0$M; $t = 35$ °C; wavelength = 440 mμ.

% Ethanol	0	10	15	20	25	30	35
k/l mol^{-1} min^{-1}	240	165	150	136	118	103	94

TABLE 3

Rate constants in the presence of chloride ions

$[\mathrm{Tl^{III}}] = 5·1 \times 10^{-4}$M; $[\mathrm{As^{III}}] = 1 \times 10^{-3}$M; $[\mathrm{HClO_4}] = 0·5$M; at $\mu = 0·5$M; $t = 35$ °C and wavelength = 440 mμ.

$10^4[\mathrm{Cl^-}]$/M	1·0	3·0	5·0	7·0	9·0	10·0	30
$10^6(-\mathrm{d}(\mathrm{Tl^{III}}]/\mathrm{d}t)$ mol min^{-1}	144	57·5	28·8	13·2	10·7	6·58	3·29

$10^4[\mathrm{Cl^-}]$/M	50	70	90	100
$10^6(-\mathrm{d}[\mathrm{Tl^{III}}]/\mathrm{d}t$ mol min^{-1}	2·47	1·64	1·07	0·049

---

[12] L. Rosenthaler, *Z. analyt. Chem.*, 1906, **45**, 596.

[13] I. M. Kolthoff, *Pharm. Weekblad*, 1919, **56**, 1322.

[14] F. Roig and R. W. Dodson, *J. Phys. Chem.*, 1961, **65**, 2175.

[15] D. Huchital and H. Taube, *J. Amer. Chem. Soc.*, 1965, **87**, 5371.

[16] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1961, p. 152.

[17] K. S. Gupta and Y. K. Gupta, unpublished work.

[18] F. R. Duke and B. Bornong, *J. Phys. Chem.*, 1956, **60**, 1015.

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

[20] B. M. Thakuria and Y. K. Gupta, unpublished work.

of Tl^{III} are less reactive. A detailed study is under investigation. Sulphate and nitrate were without any effect on the rate of the reaction.

Energy and Entropy of Activation.—The reaction was studied at four different temperatures. The rate constants ($HClO_4 = 2{\cdot}0$M) at 35, 45, and 50 °C were found to be 50, 89, 146, and 258 l mol^{-1} min^{-1} respectively. The energy and entropy of activation were found to be $21{\cdot}5 \pm 1$ kcal mol^{-1} and $-15{\cdot}5 \pm 3$ cal deg^{-1} mol^{-1} respectively.

DISCUSSION

The orders in Tl^{III} and As^{III}, and inverse hydrogen-ion dependence suggest the following mechanism for the reaction:

$$Tl^{3+} + H_2O \overset{K_h}{\rightleftharpoons} TlOH^{2+} + H^+ \qquad (2)$$

$$TlOH^{2+} + HAsO_2 + H_2O \xrightarrow{k_3} Tl^{I} + H_2AsO_4 + H^+ \qquad (3)$$

Since no cationic chemistry of As^{III} is known,[21] the hydrogen-ion dependence is not related to As^{III}. The reactive species of As^{III} is likely to be H_3AsO_3 or $HAsO_2$ in the perchloric acid medium employed in the present investigation. The reactive Tl^{III} species is $TlOH^{2+}$ as has been suggested in many other oxidations, *e.g.*, those of U^{IV},[22] trisbipyridylosmium(II),[23] Hg_2^{2+},[6] formic acid,[19] *etc.* The slow step (3) is also in accordance with the effect of ionic strength. The entropy change of $-15{\cdot}5$ cal mol^{-1} deg^{-1} is not much different than the normal value for a bimolecular reaction.[24] This suggests an activated complex with charge not different from those of the reactants. A large entropy change is expected if both the reacting species are charged.[25]

The results of solvent-effect are inconclusive with respect to step (3). Theoretical considerations [26] would suggest a reaction between two similarly charged ions and since thallic ion or its hydrolyzed form is positively charged, the reactive form of As^{III} should also be positively charged. Such a species is not reported as mentioned earlier. Even if one assumes its existence, the rate would have a positive hydrogen-ion dependence. This is not found. If one assumed a reaction between an ion and an uncharged molecule, the rate would increase with decreasing dielectric constant, irrespective of the nature of charge on the reactant. This anomaly can, in part, probably be explained by the fact that the ionic radii of the reactants and the activated complex vary from solvent to solvent, but this could be well due to a change in the nature of the reactive Tl^{III} species. The latter may form a complex with ethyl alcohol.

The rate law (4) can be deduced in the following way from equations (2) and (3)

$$-d[Tl^{III}]/dt = k_3[TlOH^{2+}][HAsO_2] = \frac{k_3K_h[Tl^{III}][HAsO_2]}{[H^+] + K_h} \qquad (4)$$

There is some uncertainty and controversy concerning the magnitude of K_h. The most widely accepted value based on the e.m.f. measurements of Biedermann [27] is 0·073 at $\mu = 3$M and 25 °C. K_h was estimated to be *ca.* 0·11 using an enthalpy of hydrolysis of 11·0 kcal/mol. Most known heats of hydrolysis of metal ions are of this order.[28,29] In most of the experiments hydrogen-ion concentration was *ca.* 2·5M and hence K_h could be neglected in comparison with $[H^+]$. The rate law (5) then follows.

$$\frac{-d[Tl^{III}]}{dt} = k_3'[Tl^{III}][As^{III}]/[H^+] \qquad (5)$$

This may be transformed into (6) and (7) at constant $[H^+]$ and excess of $[As^{III}]$.

$$-d[Tl^{III}]/dt = k[Tl^{III}][As^{III}] \qquad (6)$$

$$= k'[Tl^{III}] \qquad (7)$$

Another mechanism which could explain the hydrogen-ion dependence is the following leading to the rate law (10).

$$Tl^{3+} + H_3AsO_3 \overset{K_8}{\rightleftharpoons} [TlAsO_3H_2]^{2+} + H^+ \qquad (8)$$

$$[TlAsO_3H_2]^{2+} + H_2O \xrightarrow{k_9} Tl^{I} + H_3AsO_4 + H^+ \qquad (9)$$

$$\frac{-d[Tl^{III}]}{dt} = \frac{k_9K_8[Tl^{III}][As^{III}]}{[H^+]} \qquad (10)$$

The rate law is of the same form as (5). It may be stated that no kinetic evidence for the complex formation between Tl^{3+} and H_3AsO_3 was obtained, nor has such a complex been reported elsewhere. However, the possibility of a weak complex does exist. The hydrogen-ion dependence can be explained also by assuming Tl^{3+} and $H_2AsO_3^-$ as the reactive species but since the ionization constant of H_3AsO_3 is very small, the rate would become diffusion controlled and hence such a possibility is excluded.

There appears to be no firm kinetic evidence for the manner of reduction of Tl^{III} in most of its redox reactions, whether it occurs in one step or in two steps. Even Schaffer's principle [30] of equivalent change in oxidations of As^{III}, U^{IV}, *etc.*, which undergo two-electron-change, is not proved. Catalysis by Cu^{II} found by Jones and Amis [31] in the oxidation of U^{IV} in water–methanol mixtures, has been explained on the basis of the existence of Tl^{II} and U^{V}. Ordinarily in aqueous solutions no

---

[21] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley Eastern, New Delhi, 1969, 2nd edn., p. 509.

[22] J. O. Wear, *J. Chem. Soc.*, 1965, 5596.

[23] D. H. Irwin, *J. Chem. Soc.*, 1957, 1841.

[24] K. J. Laidler, 'Reaction Kinetics,' Pergamon Press, London, 1966, vol. 1, p. 87.

[25] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1961, p. 143.

[26] E. S. Amis, 'Solvent Effects on Reaction Rates and Mechanism,' Academic Press, New York, 1966, p. 28, 33.

[27] G. Biedermann, *Arkiv Kemi*, 1964, **6**(**5**), 527.

[28] R. H. Betts, *Canad. J. Chem.*, 1955, **33**, 1775.

[29] K. A. Kraus and F. Nelson, *J. Amer. Chem. Soc.*, 1955, **77**, 3721.

[30] P. A. Schaffer, *J. Amer. Chem. Soc.*, 1933, **55**, 2196.

[31] F. A. Jones and E. S. Amis, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1045.

catalysis by Cu^{II} is observed. These and other results can be best explained by the cage effect. Reactive intermediate species such as, Tl^{II}, U^{V}, or As^{IV} would react within their solvent cage as soon as they are formed. However, in some cases they can diffuse out to react with other species such as Cu^{II} in the oxidation[31] of U^{IV}. It is perhaps due to the weak hydrogen bonding of the alcohol in the latter case that the weak solvent cage cannot hold the reactive intermediates. It is, therefore, obvious that the redox reactions probably occur in steps of one-electron change, but obtaining kinetic evidence for this would depend on the cage effect.

[1/295 *Received, March* 16*th*, 1971]