Kinetics and Mechanism of Electron-transfer Reactions of Aqueous and Co-ordinated Thallium(III). Part IX.† Stoicheiometry and Kinetics of Reduction of Hexa-aquathallium(III) by Hydroxylamine

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The stoicheiometry of the reaction between Tl^{III} and NH_3OH^+ depends on the relative concentrations of the reactants, and measurements under different conditions have indicated that the products may be formed by transfer of two, four, and six electrons in stages from hydroxylamine to produce N^I, HNO_2, or NO_3^-, respectively. In the presence of excess of NH_3OH^+, the stoicheiometry of the reaction is as in (i) with the corresponding rate law

$$Tl^{III} + NH_2OH^+ \longrightarrow Tl^I + N^I + 3H^+ \qquad (i)$$

$-d[Tl^{III}]/dt = k_A[Tl^{III}][NH_2OH^+]$; a mechanism is proposed which relates the observed effect of acidity to the entity $k_A = kK_h/([H^+] + K_h)$, where k is the rate constant for reaction of $[Tl(OH)]^{2+}(aq)$ with NH_3OH^+ and K_h is the acid-dissociation constant of $Tl^{3+}(aq)$. These parameters are 154 ± 8 l mol^{-1} s^{-1} and 0·078 ± 0·008 respectively at 25 °C and ionic strength 1M. The energy and entropy of activation for the rate-determining step were found to be 10·0 ± 1·0 kcal mol^{-1} and −17 ± 4 cal K^{-1} mol^{-1} respecitvely; ΔH and ΔS associated with K_h were found to be 16·6 ± 3·3 kcal mol^{-1} and 51 ± 14 cal K^{-1} mol^{-1} respectively. Addition of Tl^I, oxygen, and sulphate or nitrate ions has no observable effect on the rate, but chloride ions strongly inhibit the reaction, which is also inhibited by an increase in ionic strength. Comparison of the observed enthalpy of activation with those for other oxidations by Tl^{III} and the observaticn of chloride inhibition suggest that the reaction proceeds *via* an intermediate complex.

OXIDATION of hydroxylamine has been carried out with a large number of oxidants, but kinetic studies with metal-ion oxidants appear to be few. Recently one-equivalent oxidants, *e.g.* Ag^I,[1] Ag^{II},[2] Mn^{III},[3] and Ce^{IV},[4] have been employed for this purpose. In most cases the nature of the products depends on the type of oxidant, the acidity of the medium, and the relative concentrations of the oxidant and reductant, and free radicals are reported to be formed. The present oxidation study with Tl^{III} is of special interest. Thallium(III) is a two-equivalent oxidant which is known to undergo reduction either in two successive one-electron steps as in the oxidation of Fe^{II} (ref. 5) and V^{III} (ref. 6) or in single two-electron steps as in the case of U^{IV},[7] Hg_2^{2+},[8] As^{III},[9] Sb^{III},[10] phosphite,[11] and hypophosphite.[12] The oxidation of hydroxylamine by Tl^{III} appears to occur in a single two-electron step *via* a straightforward bimolecular process.

EXPERIMENTAL

The stock solution of thallium(III) perchlorate was prepared by dissolving thallium(III) oxide (B.D.H., AnalaR) in 60% perchloric acid (Riedal, AnalaR) and standardized by an iodometric method.[13] Hydroxylamine solutions were prepared from hydroxylamine sulphate (Riedel, AnalaR) and standardized by the bromate method.[14] Sulphate ions were without any effect on the rate. Lithium perchlorate solution was prepared by neutralizing 60% perchloric acid with lithium carbonate (E. Merck) to pH 6·8. All other chemicals were either B.D.H. AnalaR or Merck G.R. quality. All solutions were prepared in twice-distilled water, the second distillation being from potassium tetraoxomanganate(VII) solution.

The kinetic experiments were carried out in a temperature-controlled (±0·1 °C) water-bath. The rate of reaction was followed by measuring thallium(III) colorimetrically.[15] Aliquot portions (5 cm^3) were withdrawn from the reaction mixture after suitable intervals and added to a mixture of 2 cm^3 of 0·05M-NaCl or 2·5M-HCl (when the perchloric acid concentration of the reaction mixture was low) and 10% urea (1 cm^3).‡ After *ca.* 10 min, 2% KI (2 cm^3) was added and the liberated iodine was determined on a Spectronic 20 colorimeter at 380 nm. The reference solution was a mixture of KI, NaCl or HCl, urea, and $HClO_4$ of the same concentrations as employed in the iodometric determination. Sodium chloride was employed to quench the reaction and urea was used to decompose the traces of nitrite which are formed, particularly in the later part of the reaction. Concentrations of the reactants were low and there was no possibility of precipitation of Tl^I (ref. 9) which could otherwise interfere with the colorimetric measurements. Duplicate rate measurements were reproducible to ±6%.

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† Part VIII is ref. 29.

‡ 1M = 1 mol dm^{-3}.

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A few kinetic runs were made with the product of reaction initially present in the reaction mixture. Equimolar quantities of Tl^{III} and NH_3OH^+ were allowed to react completely. The time for completion of reaction with concentrations of the order of 1×10^{-5}M was *ca.* 1 h, and for concentrations of the order of 1×10^{-3}M was *ca.* 2 min. More Tl^{III} was then added and the kinetics followed by determining Tl^{III} iodometrically after treatment with urea as in the colorimetric measurements. Such reactions are later referred to as 'further reaction with the products.'

RESULTS AND DISCUSSION

Stoicheiometry.—Thallium(III) perchlorate and hydroxylamine (sulphate) of different concentrations in suitable perchloric acid solutions were mixed and kept for *ca.* 8—10 h. Excess of Tl^{III} was determined iodometrically[13] after decomposing the nitrite, if any, by urea, and excess of hydroxylamine was determined by direct titration[16] with iodine–potassium iodide solution in the presence of MgO. In fact Tl^{I} interfered with this method of determination of hydroxylamine and the results were 10—15% low. However, hydroxylamine could be determined, even in the presence of Tl^{I}, in an empirical way by the following method. Solutions of hydroxylamine in the concentration range expected for that remaining in the reaction mixtures were standardized[16] in the presence of Tl^{I} (of the concentration expected to be formed in the reaction mixtures, assuming 1 : 1 stoicheiometry). Other methods[17] of determining hydroxylamine were not suitable.

When $[Tl^{III}]_0$ was greater than $3[NH_3OH^+]_0$, 2·9 mol Tl^{III} were consumed by each mole of hydroxylamine. A detailed study under different conditions proved helpful in understanding the nature of the products. When excess of Tl^{III} was determined after 1 or 2 h, 2 mol Tl^{III} per mole of hydroxylamine were consumed, suggesting formation of nitrite by a four-electron change. This was confirmed by estimation of the nitrite by Ce^{IV}.[18] The amount of Tl^{III} consumed increased with time. However, the rate of decrease of $[Tl^{III}]$ was slower if a greater excess of Tl^{III} was utilized. This is in agreement with our results with nitrite.[19] A stoicheiometry of $[Tl^{III}]/[NH_3OH^+] = 2{\cdot}9$ was obtained either after keeping the reaction mixtures for a sufficiently long time, sometimes more than a week, or by heating at 70—80 °C for *ca.* 20 min. Although Higginson *et al.*[20] have reported slow decomposition of Tl^{III} at 60—80 °C, we did not observe any detectable decomposition of Tl^{III} within 15—20 min as also reported by Sagi and Ramanna[21] and Gupta and Gupta.[11]

To some of the reaction mixtures, urea was initially added to decompose the nitrite formed and in all such cases 2 mol Tl^{III} were consumed by each mole of hydroxylamine. No further increase in the consumption of Tl^{III} was noted even after several months. Thus in the presence of urea the stoicheiometry is given by (1). In the absence of urea, nitrite is further oxidized

$$2Tl^{III} + NH_3OH^+ + H_2O \longrightarrow 2Tl^{I} + HNO_2 + 5H^+ \quad (1)$$

to nitrate, but exactly 3 mol Tl^{III} are not consumed because some of the nitrite undergoes decomposition.

When excess of hydroxylamine was present, 1 mol Tl^{III} was consumed per mole of hydroxylamine suggesting formation of hyponitrous acid as in (2). Many

$$Tl^{III} + NH_3OH^+ \longrightarrow Tl^{I} + \tfrac{1}{2}H_2N_2O_2 + 3H^+ \quad (2)$$

workers[1,22-24] have reported that oxidation of hydroxylamine occurs *via* intermediate formation of HNO. This is said to dimerize yielding hyponitrous acid which can exist in *trans-* and *cis*-forms.[24] The *trans*-form is considered to be quite stable[25] but the *cis*-form decomposes to nitrogen oxide. However, in the present investigation, no precipitate of silver(I) hyponitrite was obtained on addition of silver(I) nitrate to the reaction mixtures. Similarly an attempt to extract[24] the aqueous solution with diethyl ether or benzene, and to re-extract the ether or benzene solution with sodium hydroxide solution, failed to yield any positive results. In the absence of any positive test, it is difficult to say what is the exact form of nitrogen(I) in the reaction mixtures, but there is no doubt that the product is fairly stable and decomposes slowly. This was confirmed by the fact that when 1 mol Tl^{III} and 1 mol NH_3OH^+ were allowed to react completely [1 mol nitrogen(I) product expected] and then another mole of Tl^{III} was added, 70—90% of the latter was consumed and nitrite was formed. The consumption of Tl^{III} was not 100% because the hyponitrous acid itself undergoes decomposition.

In conclusion the stoicheiometry and products of the reaction depend on the relative concentrations of Tl^{III} and hydroxylamine. Varying stoicheiometry was also noted in oxidations by Mn^{III},[3] peroxonitrite,[26] and Ce^{IV}.[4] Although variable stoicheiometry has not been reported in the oxidation of Ag^{II},[2] by implication it appears that the stoicheiometry of the Ag^{II}–NH_3OH^+ reaction may vary under conditions other than those specified. The results of the stoicheiometric measurements of the present investigation are shown in Table 1.

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Kinetic experiments were carried out in the presence of excess of hydroxylamine.

TABLE 1

Stoicheiometry of the Tl^{III}–NH_3OH^+ reaction at 25 °C

$10^3[Tl^{III}]$/M	$10^3[NH_3OH^+]$/M	$[Tl^{III}] : [NH_3OH^+]$
12	2·4	2·85
12	4·0	2·9
12	3·0	2·85
6	2·0	2·9
8	2·0	2·9
10	2·0	2·9
12	3·0	2·0 *
6	2·0	2·0 *
10	4·0	1·98 *
4·0	20	1·0
4·0	40	0·98
4·0	8·0	1·0
6·0	48	0·97

* In the presence of urea.

Kinetic Orders.—The order of reaction with respect to $[Tl^{III}]$ and $[NH_3OH^+]$ (when present in excess) was found to be one in each case from plots of log (initial rate) against concentration. Thus the kinetic results were in accord with equation (3). The apparent

$$-d[Tl^{III}]/dt = k_A[Tl^{III}][NH_3OH^+] \qquad (3)$$

second-order rate constants, k_A, were calculated from equation (3) and also from the gradient of straight-line plots of $\log [Tl^{III}]_t/[NH_3OH^+]_t$ against time. Second-order rate constants were also calculated from linear pseudo-first-order plots of $\log [Tl^{III}]_t$ against time. 70—80% Completion of reaction, with 8 or 9 measurements, was followed in each case. At least six points were on the straight lines of the above plots. An average value of k_A from 34 experiments was found to be 10·4 ± 0·2 l mol^{-1} s^{-1} over the concentration ranges $[Tl^{III}] = 2 \times 10^{-5}$—$12 \times 10^{-5}$ and $[NH_3OH^+] = 1 \times 10^{-4}$—$15 \times 10^{-4}$M at $[HClO_4] = 1{\cdot}0$M, $I = 1{\cdot}0$M, and 25 °C.

TABLE 3

Effect of chloride ions and ionic strength on the Tl^{III}–NH_3OH^+ reaction at 25 °C

$[Tl^{III}] = 4 \times 10^{-3}$, $[NH_3OH^+] = 8 \times 10^{-2}$, $[HClO_4] = 0{\cdot}5$, and $I = 0{\cdot}5$M (kinetics followed volumetrically by iodometric determination of Tl^{III})

$[Cl^-]$/M	0	5×10^{-3}	8×10^{-3}	2×10^{-2}	1×10^{-1}
k_A/l mol^{-1} s^{-1}	Very fast	$(7 \pm 0{\cdot}5) \times 10^{-3}$	$(3 \pm 0{\cdot}2) \times 10^{-3}$	$(1{\cdot}6 \pm 0{\cdot}1) \times 10^{-5}$	Very slow

$[Tl^{III}] = 4 \times 10^{-5}$, $[NH_3OH^+] = 5 \times 10^{-4}$, and $[HClO_4] = 1{\cdot}0$M

$[LiClO_4]$/M	0	0·4	0·8	1·2	1·6	2·0
I/M	1·0	1·4	1·8	2·2	2·6	3·0
k_A/l mol^{-1} s^{-1}	11·4 ± 0·8	6·9 ± 0·5	2·4 ± 0·1	0·72 ± 0·06	0·25 ± 0·02	0·12 ± 0·01

Effect of Hydrogen Ion.—The effect of varying the hydrogen-ion concentration was noted at three temperatures by varying the concentration of perchloric acid at constant ionic strength adjusted with lithium perchlorate. The rate decreased on increasing the concentration of perchloric acid (Table 2).

TABLE 2

Effect of hydrogen ion on the Tl^{III}–NH_3OH^+ reaction at different temperatures: $[Tl^{III}] = 6 \times 10^{-5}$; $[NH_3OH^+] = 3 \times 10^{-4}$; $I = 1{\cdot}0$M

$[H^+]$/M θ_c/°C	k_A/ l mol^{-1} s^{-1} 0·1	 0·2	 0·3	 0·4	 0·6	 0·8	 1·0
25	65	43	32	25	17	13·5	10·5
20	44	28	19	14	9·7	7·4	6·0
16		13	9·7	7·5	4·9	3·7	3·1
12		7·9	5·3	4·6	3·1	2·2	1·8
8		4·4		2·4	1·6	1·2	0·96

Effect of Chloride Ions.—The effect of chloride ion in Tl^{III} oxidations has been variously reported. It catalyses oxidations of Fe^{II},[5] phosphite,[11] hypophosphite,[12,27] and Sb^{III},[28] and inhibits oxidations of As^{III} (ref. 29) and formic acid.[30] In the present investigation too the rate of reaction considerably decreased in the presence of chloride ions and was very slow when the $Cl^- : Tl^{III}$ ratio was greater than 3 : 1 (Table 3). This decrease in the rate is ascribed to complexing[31] of Tl^{III} by chloride ion.

Effect of Ionic Strength.—Lithium perchlorate was employed for investigating the effect of ionic strength. The rate of reaction decreased with increasing ionic strength (Table 3). When sodium perchlorate was used instead of lithium perchlorate, the decrease in the rate was larger for the same concentration of salt and reaction ceased in the presence of 2·5M-$NaClO_4$. This may be attributed to trace chloride impurities present in the sample of sodium perchlorate. Chloride ions are known to form strong complexes[31] with Tl^{III} and, since the concentration of Tl^{III} employed in the present investigation was low, the small amount of chloride present as impurity in sodium perchlorate is sufficient for complexing. In other investigations where large

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concentrations (greater than 0·001M) of Tl^{III} were employed, the difference in behaviour of lithium and sodium perchlorates was either nil or small.

Effect of Thallium(I) *and Oxygen*.—Reactions were carried out in the presence of 0·001—0·01M thallium(I) nitrate, but there was no change in the rate of reaction. Similarly the change (decrease) in rate was not more than 5% when oxygen was continuously bubbled through the reaction mixture.

Further Reaction with the Product.—If hyponitrous acid is considered to be the product of oxidation of hydroxylamine, further reaction on addition of Tl^{III} should occur in the form of oxidation of hyponitrous acid by Tl^{III} in the presence of Tl^{I}. Since the concentration of hyponitrous acid was not known exactly, the results were only qualitative; the accuracy was not better than 20%. With equimolar quantities of the reactants (Tl^{III} and NH_3OH^+) the amount of nitrite formed was not more than 2—3% when the concentrations of the reactants were of the order of 1×10^{-3}M. When Tl^{III} was added after a longer period than that required for completion of the reaction, some of the hyponitrous acid decomposed in this period and 'further reaction' was slower. The orders of reaction with respect to [Tl^{III}] and [$H_2N_2O_2$] were approximately one. The apparent second-order rate constant at 25 °C and [$HClO_4$] = 0·36M was found to be 14 ± 2 l mol^{-1} s^{-1} which is about half that for the Tl^{III}–NH_3OH^+ reaction under identical conditions.

Mechanism.—The stoicheiometric results have revealed that nitrite or nitrate is obtained as a product when the concentration of Tl^{III} is greater than that of NH_3OH^+. Although in the presence of excess of NH_3OH^+ hyponitrous acid is formed by a two-electron change, the possibility of formation of traces of nitrite also exists. With Tl^{III}, NH_3OH^+, $H_2N_2O_2$, and HNO_2 in the system, subsequent reactions (4)—(8) probably

$$\mathrm{Tl^{III}} + H_2N_2O_2 \longrightarrow \qquad (4)$$

$$NH_3OH^+ + H_2N_2O_2 \longrightarrow \qquad (5)$$

$$NH_3OH^+ + HNO_2 \longrightarrow \qquad (6)$$

$$\mathrm{Tl^{III}} + HNO_2 \longrightarrow \qquad (7)$$

$$H_2N_2O_2 + HNO_2 \longrightarrow \qquad (8)$$

occur. Reaction (7) is quite slow[19] compared to that between Tl^{III} and NH_3OH^+, particularly when traces of HNO_2 are present. So far as reaction (5) is concerned, nothing has been reported about it, but it is likely to be insignificant since in the presence of excess of NH_3OH^+ the stoicheiometry [Tl^{III}] : [NH_3OH^+] is 1 : 1. Since $H_2N_2O_2$ and HNO_2 are formed in consecutive steps, their concentrations will not be large. Moreover, the reaction between them is slow, the second-order rate constant[32] at 0·08M-[H^+] and 25 °C being 0·48—0·45 l mol^{-1} s^{-1}. Hence reaction (8) also may be ignored. For reaction (6), the second-order rate constant is[24] *ca.* $2{\cdot}4 \times 10^{-2}$ l mol^{-1} s^{-1} at 0 °C and 0·1M-[H^+]. With 14·7 kcal mol^{-1} as the energy of activation,* the second-order rate constant was calculated to be 0·234 l mol^{-1} s^{-1} at 25 °C, and hence it is much less than the corresponding value of 65·4 l mol^{-1} s^{-1} for the present reaction. Finally reaction (4) may also be ignored in comparison to the main reaction because (*a*) the first-order and second-order plots gave straight lines up to three half-lives, and (*b*) the second-order rate constant for reaction (4) at the corresponding [H^+] is smaller as mentioned earlier and the concentration of $H_2N_2O_2$ is much less in comparison to that of hydroxylamine. Thus in the presence of excess of NH_3OH^+, the only reaction to be considered for treatment of the rate data is that between Tl^{III} and NH_3OH^+.

At the perchloric acid concentrations employed in the present investigation, hydroxylamine is present as NH_3OH^+ since the acid dissociation constant[33] of the latter is only $1{\cdot}09 \times 10^{-6}$ mol l^{-1}. The neutral-substrate path, therefore, is not expected to contribute. In most of the previous studies involving Tl^{III}, the hydrolysed species [Tl(OH)]$^{2+}$ has been considered as the reactive species, *e.g.*, in the oxidations of Hg_2^{2+},[8] U^{IV},[34] and formic acid.[30] The nature of the acid dependence of the present reaction shows that [Tl(OH)]$^{2+}$ is far more reactive than Tl^{3+}. The mechanism in equations (9)—(11) leads to rate law (12). Plots of

$$\mathrm{Tl^{3+}} + H_2O \overset{K_h}{\rightleftharpoons} [\mathrm{Tl(OH)}]^{2+} + H^+ \qquad (9)$$

$$[\mathrm{Tl(OH)}]^{2+} + NH_3OH^+ \xrightarrow{k} \mathrm{Tl^+} + \tfrac{1}{2}H_2N_2O_2 + 2H^+ + H_2O \qquad (10)$$

$$H_2N_2O_2\ (\textit{trans}) \longrightarrow H_2N_2O_2\ (\textit{cis}) \longrightarrow N_2O \qquad (11)$$

(1/rate) against [H^+] yielded straight lines, in agreement with equation (12). From the gradient and

$$-\mathrm{d}[\mathrm{Tl^{III}}]/\mathrm{d}t = \{kK_h/([H^+] + K_h)\}[\mathrm{Tl^{III}}][NH_3OH^+] \qquad (12)$$

intercept K_h and k were found to be 0·078 ± 0·01 mol l^{-1} and 154 ± 8 l mol^{-1} s^{-1} at 25 °C respectively. The most widely accepted value of K_h based on e.m.f. measurements[35] is 0·073 mol l^{-1} at I = 3·0M and 25 °C; Rogers and Waind[36] reported a value of 0·086 mol l^{-1} at I = 1·5M and 25 °C. Thus the value of K_h found in the present investigation is in fair agreement with the reported values. Similarly, values of K_h found at 20, 16, 12, and 8 °C were 0·052 ± 0·01, 0·034 ± 0·005, 0·025 ± 0·005, and 0·015 ± 0·003 mol l^{-1} re-

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* 1 cal = 4·184 J.

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spectively and those of k were 123 ± 7, 92 ± 6, 70 ± 10, and 56 ± 8 l mol^{-1} s^{-1} respectively. The energy and entropy of activation for step (10) were found to be $10{\cdot}0 \pm 1{\cdot}00$ kcal mol^{-1} and -17 ± 4 cal K^{-1} mol^{-1} respectively. ΔH and ΔS values associated with K_h were $16{\cdot}6 \pm 3{\cdot}3$ kcal mol^{-1} and 51 ± 14 cal K^{-1} mol^{-1} respectively; recently reported[37] values are 21 ± 6 kcal mol^{-1} and 70 ± 20 cal K^{-1} mol^{-1} respectively.

Although complex formation between the reactants is not indicated by the kinetics results, such a possibility exists in view of the ligand properties of hydroxylamine[38] and the tendency of Tl^{III} to act as a co-ordinating centre. There is kinetic and spectrophotometric evidence for such behaviour[11,12] of Tl^{III}. Hence k in step (10) may also include the formation constant of such a complex. Thus if weak complexing between $[Tl(OH)]^{2+}$ and NH_3OH^+ is assumed with K as the formation constant and k' the rate constant for the redox step, rate law (13) is obtained.

$$-d[Tl^{III}]/dt = k'KK_h[Tl^{III}][NH_3OH^+]/([H^+] + K_h + KK_h[NH_3OH^+]) \quad (13)$$

Since K is small, $KK_h[NH_3OH^+] \ll ([H^+] + K_h)$ and rate law (13) reduces to (12) with $k = k'K$. The inhibition by chloride ions in the present reaction further supports the concept of weak complexing. It has been suggested[27] that all oxidations by Tl^{III} which are inhibited by chloride ions proceed through an intermediate complex formed between Tl^{III} and the substrate. The low energy of activation for the $[Tl(OH)]^{2+}$–NH_3OH^+ reaction also strongly suggests that the reaction proceeds *via* intermediate-complex formation. The overall energy effect was found to be 26 kcal mol^{-1} (calc. 26·6 kcal mol^{-1}), similar to those observed in other oxidations.[11,30,39] Thus the scheme for the present reaction probably includes a hydrolytic equilibrium of Tl^{3+} and a complex-formation equilibrium involving $[Tl(OH)]^{2+}$ and/or Tl^{3+}.

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