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

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Thallium(III) perchlorate and hydrazine react in aqueous perchloric acid as in equation (i). The kinetic results conform to rate law (ii), where $k_2 = 8.4 \pm 0.3$ dm^3 mol^{-1} s^{-1} at 8 °C. The energy and entropy of activation associated with k_2 are 138 ± 6 kJ mol^{-1} and 259 ± 25 J K^{-1} mol^{-1} respectively. The rate of reaction is independent of ionic strength, but chloride ion strongly inhibits the reaction.

$$2\mathrm{Tl}^{\mathrm{III}} + \mathrm{N_2H_5}^+ \longrightarrow 2\mathrm{Tl}^{\mathrm{I}} + \mathrm{N_2} + 5\mathrm{H}^+ \tag{i}$$

$$-\tfrac{1}{2}\mathrm{d}[\mathrm{Tl}^{\mathrm{III}}]/\mathrm{d}t = k_2[\mathrm{Tl}^{\mathrm{III}}][\mathrm{N_2H_5}^+][\mathrm{H}^+]^{-1} \tag{ii}$$

THE present paper reports a further study of oxidation by thallium(III) and was made in order to determine whether an intermediate complex is formed or not. Complex formation of hydrazine with metal ions is well known [1] and this is also a possibility here. However, it is sometimes difficult to obtain kinetic evidence of complex formation in view of the highly reactive nature of the complex, as found in the oxidation by cerium(IV).[2]

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† Part XI is ref. 18.

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Oxidation of hydrazine by Tl^{III} has been reported by Higginson *et al.*[3] Aqueous Tl^{III} quickly oxidizes[4] hydrazine to nitrogen at room temperature. Kinetics studies have been made in the presence of the complexing ions sulphate,[3] chloride,[5] and acetate.[6] The present paper reports the results of a study in aqueous perchlorate media.

EXPERIMENTAL

The stock solution of thallium(III) perchlorate was prepared by dissolving thallium(III) oxide (B.D.H. AnalaR) in 60% perchloric acid (Riedel, AnalaR) and standardized iodometrically. Hydrazine solutions were prepared from hydrazine hydrate (B.D.H., AnalaR) and standardized using standard iodate solution[7,8] immediately before use. Lithium perchlorate solution was prepared by neutralizing 60% perchloric acid with lithium carbonate (E. Merck) to pH 6.8. All solutions were prepared in twice-distilled water, the second distillation being from potassium permanganate.

Kinetic Procedure.—The experiments were made in stoppered glass vessels in a temperature-controlled (±0.1 °C) water-bath. The reaction was initiated by adding thallium(III) perchlorate solution to the reaction mixture containing hydrazine perchlorate, perchloric acid, *etc.*, both solutions being equilibrated at 8 °C unless otherwise stated. The rate of reaction was followed by determining the thallium(III) concentration colorimetrically.[9] Aliquot portions (5 cm³) were withdrawn from the reaction mixture and added to NaCl (3 cm³, 1 mol dm⁻³) to arrest the reaction. Potassium iodide (2 cm³, 2%) was then added and the liberated iodine was immediately determined on a Spectronic 20 colorimeter at 380 nm. The reference solution was a mixture of NaCl, KI, and $HClO_4$ of the same concentrations as in the reaction mixture. With the concentrations employed in this investigation there was no possibility of a precipitate of TlI, as also stated earlier[10] for the oxidation of arsenic(III). In most cases, duplicate rate measurements were reproducible to 6%.

RESULTS

Stoicheiometry.—Thallium(III) perchlorate and hydrazine of different concentrations were mixed and kept for *ca.* 48 h. Excess of Tl^{III} was determined[7] as stated earlier. Excess of hydrazine was determined by allowing it to react with iodine in the presence of $Na[HCO_3]$ and back titrating excess of iodine with sodium thiosulphate. 1.98 ± 0.01 Moles of Tl^{III} were found to react with 1 mole of hydrazine. A similar stoicheiometry was reported earlier.[11]

Kinetic Orders.—The orders with respect to the concentrations of Tl^{III} and hydrazine were *ca.* 1 from log–log plots of the rate and concentration. Apparent rate constants, k_A, were calculated from equation (1) at constant hydrogen-ion concentration; k_A was also calculated from pseudo-first-order plots of log $[Tl^{III}]_t$ against time when hydrazine was in excess, from conventional plots of $\log([Tl^{III}]_t/[N_2H_5^+]_t)$ against time, and from plots of $(1/[Tl^{III}])$ against time when the reactants were present in stoicheiometric concentrations. The pseudo-first- and second-order rate constants are given in the Table.

$$-\tfrac{1}{2}d[Tl^{III}]/dt = k_A[Tl^{III}][N_2H_5^+] \qquad (1)$$

$$= k'[Tl^{III}] \text{ (when excess of hydrazine was present)} \qquad (2)$$

Pseudo-first- (k') and second-order (k_A) rate constants for the Tl^{III}–$N_2H_5^+$ reaction at 8 °C and $[HClO_4]$ = 1.0 mol dm⁻³, I = 1.0 mol dm⁻³, and 380 nm

$10^5[Tl^{III}]$ / mol dm⁻³	$10^5[N_2H_5^+]$ / mol dm⁻³	k' / s⁻¹	k_A / dm³ mol⁻¹ s⁻¹
4.0	5.0		8.7
4.0	10.0		8.0
4.0	20.0	1.71	9.0
4.0	30.0	2.53	8.7
4.0	40.0	3.45	8.8
4.0	50.0	4.30	8.8
4.0	60.0	4.97	8.4
4.0	80.0	6.34	8.0
4.0	100.0	8.00	8.1
5.0	5.0		8.0
5.0	10.0		8.4
5.0	20.0		8.3
5.0	40.0	3.48	9.0
5.0	60.0	5.23	8.9
5.0	80.0	6.87	8.7
5.0	100.0	8.25	8.4
2.0	30.0	2.62	8.9
3.0	30.0	2.51	8.6
4.0	30.0	2.62	9.0
6.0	30.0	2.62	8.2
8.0	30.0		8.2
9.0	30.0		8.0
10.0	30.0		8.1
2.0	50.0	3.94	8.0
4.0	50.0	3.90	8.0
6.0	50.0	3.90	8.1
8.0	50.0	4.07	8.5
10.0	50.0	3.84	8.1
4.0	2.0		8.5
6.0	3.0		7.8
8.0	4.0		8.0
10.0	5.0		7.9
			Av. 8.4 ± 0.3

Effect of Chloride Ion.—A systematic study of the effect of chloride was made in view of the catalytic activity of this ion in the oxidations of hypophosphite,[12] phosphite,[13] Sb^{III},[14] and Fe^{II},[15] and its inhibiting role in the oxidations of As^{III},[16] formic acid,[17] and hydroxylamine.[18] A sharp decrease in the rate was observed with increasing chloride-ion concentration (lower curve in Figure 1). In all these cases and also in the ionic-strength investigations, the rate

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constants were calculated from the initial rates. Since a number of chloride complexes [19] of different reactivities are formed in the presence of chloride, only 5—10% reaction was considered for calculating the initial rates so that the ratio of chloride to Tl^{III} does not change significantly.

Effect of Ionic Strength and Chloride-ion Impurity.—There was a small effect (10% increase in the rate) of the ionic strength on the rate of the present reaction when the measurements were made with barium nitrate (0.02—0.1 mol dm^{-3}) and with the other reactants having concentrations as in the Table. Larger concentrations of barium nitrate could not be employed because nitric acid is formed in the system, which is likely to oxidise KI used in the kinetic procedure. It was difficult to obtain a salt for the ionic-strength investigations which was free from trace amounts of chloride and other complications. In other systems the ionic strength has little or no effect. For example, in the oxidation [20] of Sb^{III} by Tl^{III} no effect was observed, there was only a 15% increase in the rate of oxidation [21] of H_3PO_2 by Tl^{III} on increasing the ionic strength from 0.34 to 5.34 mol dm^{-3}, and in the oxidation [22] of Hg_2^{2+} the effect of sodium perchlorate was ascribed to perchlorate complexing of Hg_2^{2+} rather than to any ionic-strength effect.

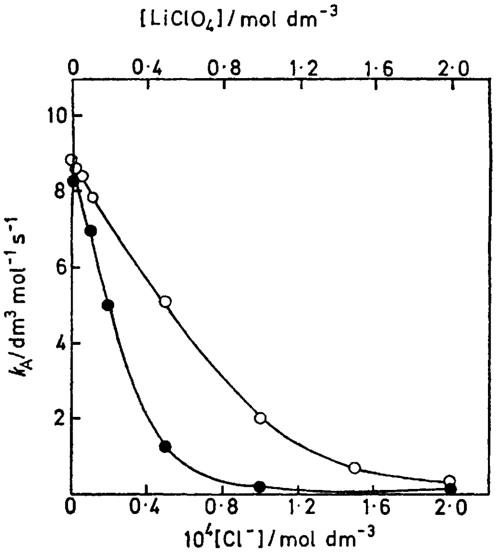

FIGURE 1 Effect of NaCl (●) and Li[ClO$_4$] (○) on the Tl^{III}–$N_2H_5^+$ reaction at 8 °C, $[Tl^{III}] = 5 \times 10^{-5}$ mol dm^{-3}, $[N_2H_5^+] = 8 \times 10^{-4}$ mol dm^{-3}, and $[HClO_4] = 1.0$ mol dm^{-3}

Ionic-strength effects are generally investigated with sodium or lithium perchlorates. The former was not employed in order to avoid medium effects [23] and chloride-ion impurity.[23a,24] Ionic-strength effects were therefore also studied by employing lithium perchlorate in the concentration range 0.02—2.0 mol dm^{-3}. The rate of reaction decreased significantly. This appears to be due to the trace amounts of chloride present in the lithium perchlorate, sufficient to complex the small concentrations of Tl^{III} employed. The two curves in Figure 1 would overlap if 1.0 mol dm^{-3} Li[ClO$_4$] were equivalent to 4×10^{-5} mol dm^{-3} NaCl. Thus it can be concluded that the decrease in the rate on addition of Li[ClO$_4$] is due to the chloride present (0.0022%) in it. No such effect was encountered in the oxidation [21] of hypophosphite because the concentrations of Tl^{III} employed were large. Similar behaviour was observed in the oxidation of hydroxylamine.[18] When the perchloric acid concentration was varied at a large constant concentration of Li[ClO$_4$] so that effects due to ionic strength and/or chloride impurity are constant, an inverse hydrogen-ion dependence was obtained as shown in Figure 2.

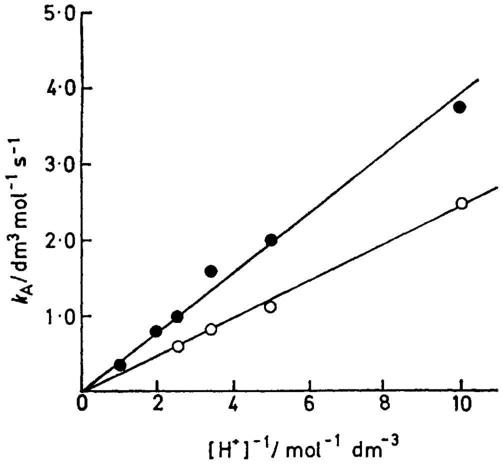

FIGURE 2 Effect of $HClO_4$ on the Tl^{III}–$N_2H_5^+$ reaction at 8 °C, $[Tl^{III}] = 4 \times 10^{-5}$ mol dm^{-3}, $[N_2H_5^+] = 3 \times 10^{-4}$ mol dm^{-3} and $[LiClO_4] = 2.5$ (○) and 2.0 mol dm^{-3} (●)

Effect of Hydrogen Ion.—The effect of the hydrogen-ion concentration was studied in the range 0.1—1.0 mol dm^{-3} without adjusting the ionic strength (ionic strength solely determined by $HClO_4$) since there is no effect of the latter (solid line in Figure 3). Thus the reaction has an inverse

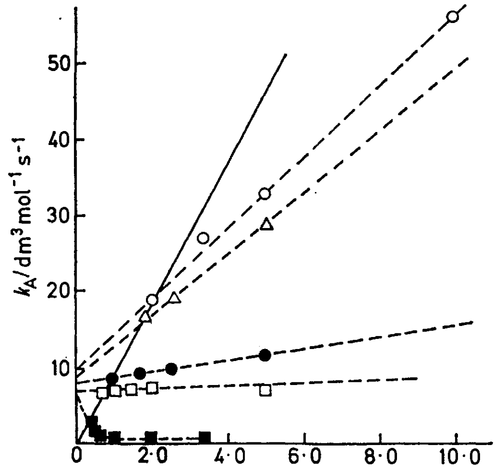

FIGURE 3 Plots of k_A at different [H$^+$] for the Tl^{III}–$N_2H_5^+$ reaction at 8 °C, $[Tl^{III}] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[N_2H_5^+] = 3 \times 10^{-4}$ mol dm^{-3}, and $I = 0.5$ (○), 0.6 (△), 1.0 (●), 1.5 (□), and 2.5 mol dm^{-3} (■)

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hydrogen-ion dependence. When the effect was studied at constant ionic strengths adjusted with lithium perchlorate (as is generally done), however, and plots of rate constant against $[H^+]^{-1}$ were made, broken lines were obtained as shown in Figure 3. This variation in the rate of reaction with the change in ionic strength at the same $[H^+]$ can again be ascribed to the chloride-ion impurity in the samples of lithium perchlorate. Thus the linear relation obtained in the presence of lithium perchlorate employed to adjust the ionic strength is fortuitous. A similar situation was noticed in the oxidation[25] of thiols by neptunium(VI) and the refs. mentioned therein. The small positive intercept was assigned to the substitution of hydrogen by lithium ions in the ionic medium. However, this factor does not appear to be important in the present reaction.

Energy and Entropy of Activation.—The reaction was studied at four different temperatures. Rate constants, k_2, at $[H^+] = 1.0$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, and 5, 8, 10, and 12 °C were 4.6, 8.4, 13.2, and 19.5 dm^3 mol^{-1} s^{-1} respectively. The Arrhenius energy and entropy of activation associated with k_2 were 138 ± 6 kJ mol^{-1} and 259 ± 25 J K^{-1} mol^{-1} respectively.

DISCUSSION

The reaction of Tl^{III} with hydrazine shows significant acid dependence. In the oxidations of Hg_2^{2+},[22,26] U^{IV},[27] formic acid,[17] hydroxylamine,[18] and tris(2,2′-bipyridyl)osmium(II)[28] the species $[Tl(OH)]^{2+}$ has been considered to be reactive. However, in the present investigation the acid dependence can be explained by assuming both Tl^{3+} and $[Tl(OH)]^{2+}$ as reactive species. Hydrazine exists in the protonated form, $N_2H_5^+$, in the acid solutions since the acid dissociation constant[29] for $N_2H_5^+$ is 1.2×10^{-8} mol dm^{-3} at 25 °C. Both forms of hydrazine could be reactive. Protonated hydrazine has been considered to be reactive in other oxidations.[2,30]

The oxidation of hydrazine by different oxidants has been reported[4] to take place by two paths depending on whether the oxidant is a one- or two-electron agent. Since nitrogen is a product of the oxidation of hydrazine by Tl^{III}, it appears that thallium(III) is acting as a two-electron oxidant as in most of its oxidation reactions and as discussed by Higginson *et al.*[3] Also, intermediate species have been reported by Huang and Spence[31] in the oxidation of hydrazine by Mo^{VI} and by Beck and Durham[32] in the oxidation by Cr^{VI}. Based on these facts, the stoicheiometry, the orders with respect to $[Tl^{III}]$ and $[N_2H_5^+]$, and the hydrogen-ion dependence, the following mechanism is suggested.

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

$$[Tl(OH)]^{2+} + N_2H_5^+ \xrightarrow{k} Tl^+ + N_2H_2 + 2H^+ + H_2O \tag{4}$$

$$Tl^{III} + N_2H_2 \xrightarrow{\text{fast}} Tl^I + N_2 + 2H^+ \tag{5}$$

The above mechanism leads to the rate law (6).

$$-\tfrac{1}{2}d[Tl^{III}]/dt = kK_h[Tl^{III}][N_2H_5^+]/([H^+] + K_h) \tag{6}$$

Biedermann[33] found a value of 0.073 mol dm^{-3} for K_h at $I = 3.0$ mol dm^{-3} and 25 °C, whereas Rogers and Waind[34] reported the value 0.086 mol dm^{-3} at $I = 1.5$ mol dm^{-3} and 25 °C. Using 69.4 kJ mol^{-1} as the enthalpy[35] of hydrolysis of Tl^{3+}, K_h was estimated to be 0.015 mol dm^{-3} at 8 °C. Since the concentration of perchloric acid used in most experiments was 1.0 mol dm^{-3}, K_h could be neglected in the denominator of equation (6) and the simplified rate law (7) or (8) is obtained. The equation is of the same form as (1) if

$$-\tfrac{1}{2}d[Tl^{III}]/dt = kK_h\,[Tl^{III}][N_2H_5^+][H^+]^{-1} \tag{7}$$

$$= k_2[Tl^{III}][N_2H_5^+][H^+]^{-1} \tag{8}$$

$kK_h/[H^+] = k_A$. From the gradient of the solid line in Figure 1, k_2 was estimated to be 8.9 dm^3 mol^{-1} s^{-1} which is similar to the value reported in the Table.

Alternatively the rate law (11) where $kK = k_A$ can be obtained by assuming that only Tl^{3+} is present in significant amounts and is reactive, and that reaction occurs *via* an intermediate complex formed between Tl^{3+} and $N_2H_5^+$ with release of a proton and subsequent decomposition of the complex. No kinetic evidence for complex formation between Tl^{3+} and $N_2H_5^+$ was obtained. However, the possibility of formation of a weak complex does exist. The rate of reaction is very slow in the presence of chloride[5] and acetate[6] ions which form strong covalent complexes with Tl^{3+}. Obviously the co-ordination sites on Tl^{3+} are blocked by these ions and the formation of the intermediate complex (if it is a prerequisite for the activated complex) is inhibited. This is further supported by the fact that the rate in the presence of sulphate ions is faster than in these two cases (chloride and acetate), presumably because sulphate ions form weak complexes[36] or only ion pairs. In perchlorate media the reaction is so fast that spectrophotometric evidence for complex formation cannot be provided even with low concentrations of the reactants.

$$Tl^{3+} + N_2H_5^+ \overset{K}{\rightleftharpoons} [Tl{\cdot}N_2H_4]^{3+} + H^+ \tag{9}$$

$$[Tl{\cdot}N_2H_4]^{3+} \xrightarrow{k} Tl^I + N_2H_2 + 2H^+ \tag{10}$$

$$-\tfrac{1}{2}d[Tl^{III}]/dt = kK[Tl^{III}][N_2H_5^+][H^+]^{-1} \tag{11}$$

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The results of hydrogen-ion dependence show that either there is no such complex formation, or if there is, it involves release of a proton.

$$N_2H_5^+ \overset{K_d}{\rightleftharpoons} N_2H_4 + H^+ \qquad (12)$$

$$Tl^{3+} + N_2H_4 \xrightarrow{k} Tl^+ + N_2H_2 + 2H^+ \qquad (13)$$

$$-\tfrac{1}{2}d[Tl^{III}]/dt = kK_d[N_2H_5^+][Tl^{3+}][H^+]^{-1}$$
$$= k_A[N_2H_5^+][Tl^{III}][H^+]^{-1} \qquad (14)$$

A third mechanism consistent with the observed rate law involves the reaction between Tl^{3+} and N_2H_4 and release of a proton, as in equations (12) and (13).

Here $[Tl^{3+}] = [Tl^{III}]$ since it has already been mentioned that $[H^+] \gg K_h$ in equation (6). The fact that the rate of reaction is almost independent of ionic strength strongly supports a reaction between Tl^{3+} and N_2H_4 in preference to that between $[Tl(OH)]^{2+}$ and $N_2H_5^+$.

[5/808 *Received, 29th April,* 1975]