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Aqueous Chemistry of Thallium(II). Part II.[1] Kinetics of Reaction of Thallium(II) with Manganese(II), Iron(II), and Cobalt(III) Ions

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Thallium(II) ions generated by flash photolysis of thallium(III) solutions oxidise manganese(II) and iron(II) and reduce cobalt(III). Rate constants for the reactions are: ($Tl^{2+} + Mn^{2+} \longrightarrow Tl^{+} + Mn^{3+}$) $(1·9 \pm 0·2) \times 10^{4}$ (0·5M-acid, $I = 0·75$M, and 22 ± 3 °C); ($Tl^{2+} + Fe^{2+} \longrightarrow Tl^{+} + Fe^{3+}$) $(2·6 \pm 0·1) \times 10^{6}$ (0·25M-acid, $I = 0·30$M, and 25 °C); $\Delta H^{\ddagger} = 4·8 \pm 2$ kJ mol^{-1}; and ($Tl^{2+} + Co^{3+} \longrightarrow Tl^{3+} + Co^{2+}$) $(9·5 \pm 0·5) \times 10^{6}$ l mol^{-1} s^{-1} (0·5M-acid, $I = 0·55$M, and 22 ± 3 °C). The reactions are apparently outer sphere in type, and comparison of the standard free energies of reaction and the activation free energies for these and other one-electron-transfer reactions involving thallium(II) with the same parameters for two-electron transfers of thallium(III) shows that the latter have activation free energies which are some 25 kJ mol^{-1} larger than those for one-electron-transfer reactions with the same standard free-energy change, reflecting the increased organisation needed in the transition state for the transfer of two electrons.

THE factors governing the relative rates of one- and two-electron-transfer reactions of metal-ion oxidants or reductants which can partake in both processes have not been extensively investigated. Both one- and two-electron-transfer paths have been identified in the reaction between vanadium(II) and mercury(II) and standard free energies of reaction and rate constants are known for both paths.[2] Comparison of one- and two-electron-transfer processes is simplified if no change in the nature of the ligands co-ordinated to the metal centre accompanies the change in oxidation state. Oxidation-reduction reactions of thallium(III) and thallium(I) are particularly suitable for studies of this kind and the kinetics of a large number of one- and two-equivalent reactions have been studied,[3] but data for the intermediate oxidation state, thallium(II), are lacking. Reactions of thallium(II) have frequently been inferred from kinetic evidence, but may be studied directly using pulse radiolysis[4] or flash photolysis[1,5] to generate the intermediate oxidation state. In Part I of this series[1] we reported standard reduction potentials of the Tl^{III}–Tl^{II} and Tl^{II}–Tl^{I} couples, which were obtained from measurement of rate constants for the reactions of Tl^{II} with Fe^{III} and Co^{II}. The relation between standard free-energy changes and rates of one-electron-transfer reactions of the three oxidation states of thallium may therefore be compared with that for two-electron-transfer reactions of thallium(I) and thallium(III).

Oxidation of Fe^{2+} by Tl^{2+} was proposed as the rapid second stage in the oxidation of Fe^{2+} by Tl^{3+} and the ratio of the rate constants for the reactions of Tl^{2+} with Fe^{3+} and Fe^{2+} was determined.[6] Measurement of the rate of the reaction between Tl^{2+} and Fe^{2+} can therefore lead to a second estimate of the reduction potential of the Tl^{III}–Tl^{II} couple for comparison with that obtained previously.[1] The reaction between Tl^{2+} and Co^{3+} was proposed as the second stage in the oxidation of Tl^{+} by Co^{3+}.[7] Data for a number of one- and two-electron-transfer reactions involving the three oxidation states of thallium indicate that the free energy of activation is always much larger for the two-electron than for the one-electron process, for the same standard free-energy change.

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[1] Part I, B. Falcinella, P. D. Felgate, and G. S. Laurence, *J.C.S. Dalton*, 1974, 1367.

[2] A. G. Sykes and M. Green, *J. Chem. Soc.* (*A*), 1970, 3221; 1971, 3067.

[3] A. G. Sykes, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 153.

[4] B. Cercek, M. Ebert, and A. J. Swallow, *J. Chem. Soc.* (*A*), 1966, 612.

[5] C. E. Burchill and W. H. Wolodarsky, *Canad. J. Chem.*, 1970, **48**, 2955.

[6] K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 1953, 3044.

[7] K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 1956, 343.

EXPERIMENTAL

Solutions of Tl^{III} were prepared and analysed as previously described.[1] Solutions of Mn^{II} were prepared from the perchlorate salt (Fluka) and were standardised by titration with $KMnO_4$. Solutions of Fe^{II} were prepared from the perchlorate salt (G. F. Smith). The Fe^{III} content of stock Fe^{II} solutions was reduced to less than 0·001% by reduction, either electrolytically or with zinc amalgam. The Fe^{II} solutions were reduced, stored, and used under an atmosphere of nitrogen, and were standardised by titration with $KMnO_4$. Blank experiments showed that there was no observable reaction between Tl^{2+} and Zn^{2+} in solutions containing zinc(II) perchlorate (0·1M).* This concentration of Zn^{2+} ions was very much higher than that in the Fe^{II} solutions which had been reduced with zinc amalgam.

Solutions of Co^{III} were prepared from solutions of cobalt(II) perchlorate (Fluka) by electrolytic oxidation in 1M-perchloric acid at *ca.* 5 °C. Because of the reaction of Co^{3+} with water, reaction mixtures containing Co^{III} were made up from a Co^{III} stock solution which was continuously electrolysed. The concentration of Co^{III} in the stock solution was determined immediately before use. Cobalt(III) concentrations were determined spectrophotometrically at 605 nm (ε 36·2 ± 0·2 l mol^{-1} cm^{-1} in agreement with the range of values in the literature [8]). The Co^{II} concentrations of the solutions before electrolytic oxidation were determined by electrodeposition, and the concentration of Co^{II} in the solutions of Co^{III} after oxidation was calculated by difference. Reaction solutions containing Co^{3+} were always flashed within 5 min of measurement of the Co^{III} concentration, and in most cases the half-life of Co^{3+} in these solutions was an hour or more. The Co^{III} concentrations in the reactant solutions were probably correct within 3—4%. The Co^{III} solutions always contained Co^{II} at about ten times the Co^{III} concentration.

All solutions were prepared in water distilled from alkaline potassium permanganate and acidified potassium dichromate. The acid concentrations and ionic strengths of the solutions were adjusted with perchloric acid (AnalaR) and sodium perchlorate (Fluka).

The flash-photolysis apparatus and general experimental procedure have been described.[1,9] Experiments involving Mn^{2+} and Co^{3+} were carried out in aerated solutions as we found that oxygen had no effect on the rate of disproportionation of Tl^{2+}. Experiments with Fe^{2+} were carried out in deoxygenated solutions under an atmosphere of nitrogen. The reactions were followed by monitoring the absorbance of the Tl^{2+} ions produced by the flash. The maximum absorbance of Tl^{2+} is at 260 nm or less, but the Tl^{2+} concentration was more conveniently measured at 303 nm where the signal-to-noise ratio was higher and interference due to absorption by the Mn^{3+}, Fe^{3+}, and Co^{3+} ions was reduced. At 303 nm the absorption coefficient of Tl^{2+} was $2{\cdot}4 \times 10^3$ l mol^{-1} cm^{-1}. At least three oscilloscope traces of transmittance against time were analysed for each set of experimental conditions.

Reaction (1) (M = Mn or Fe) or (2) (M = Co) competed with disproportionation (3). Reactions (1) and (2) were pseudo-first order because the concentrations of the metal ions were always very much greater than the micromolar concentrations of Tl^{2+} produced by the flash. The rate of disappearance of Tl^{2+} after the flash was therefore mixed

$$Tl^{2+} + M^{II} \xrightarrow{k'} Tl^{+} + M^{III} \qquad (1)$$

$$Tl^{2+} + M^{III} \xrightarrow{k'} Tl^{3+} + M^{II} \qquad (2)$$

$$Tl^{2+} + Tl^{2+} \xrightarrow{k''} Tl^{+} + Tl^{3+} \qquad (3)$$

first and second order [equation (4)]. Pseudo-first-order rate constants k' were calculated by a numerical integration

$$-d[Tl^{2+}]/dt = k'[M][Tl^{2+}] + k''[Tl^{2+}]^2 \qquad (4)$$

procedure from the dependence of the Tl^{2+} concentration on time using the value of k'' for the same temperature and ionic strength.[1]

Production of Tl^{2+} *Ions*.—The Tl^{2+} ions were produced by flash photolysis of solutions of Tl^{III}. At the acid concentrations used in these experiments, most of the light from the flash was absorbed by the hydrolysed Tl^{III} species, $[Tl(OH)]^{2+}$. Photolysis of $[Tl(OH)]^{2+}$ [reaction (5)] gives Tl^{2+} ions and OH radicals. In solutions which contained

$$[Tl(OH)]^{2+} \xrightarrow{h\nu} Tl^{2+} + OH \qquad (5)$$

Mn^{2+} or Fe^{2+} in addition to Tl^{III} only a negligible fraction of the light from the flash lamp was absorbed by these ions. The OH radicals produced by reaction (5) were efficiently scavenged in these solutions, half-times for reactions of the OH radicals with the Mn^{2+} or Fe^{2+} ions being much smaller than those for reactions of the Tl^{2+} ions. Production of Mn^{3+} or Fe^{3+} [reaction (6), M = Mn or Fe] had an effect on the absorption against time curves

$$M^{II} + OH \longrightarrow M^{III} + OH^{-} \qquad (6)$$

because the absorbance due to the Mn^{3+} or Fe^{3+} ions when the reactions were complete was not that produced by reaction (1) alone. The effect was small and allowance was made for it in analysing the data. Removal of OH radicals prevented interference from the reaction between Tl^{2+} ions and OH radicals and the change in concentration of Mn^{2+} and Fe^{2+} was negligible.

The yield of Tl^{II} was decreased in solutions which contained Co^{3+} ions because of the absorption of light from the flash by Co^{3+} and $[Co(OH)]^{2+}$ ions and the higher acid concentration. The acid concentration was raised from 0·25 to 0·5M to reduce the rate of reaction between Co^{3+} and water, but the concentration of $[Tl(OH)]^{2+}$ was lowered and the yield of Tl^{2+} reduced. Experiments in which solutions containing Co^{III} (10^{-3}M) and acid (0·5M) but no Tl^{III} were flashed showed that Co^{3+} and $[Co(OH)]^{2+}$ were photolysed by light from the flash lamp. The photolysis of Co^{3+} and $[Co(OH)]^{2+}$ ions does not appear to have been reported previously but must be analogous to photolysis of Fe^{III} or Tl^{III} solutions. Absorption of light in the ligand-to-metal charge-transfer band of the hydrolysed ion $[Co(OH)]^{2+}$ will produce Co^{2+} ions and OH radicals

$$[Co(OH)]^{2+} \xrightarrow{h\nu} Co^{2+} + OH \qquad (7)$$

[reaction (7)]. In solutions which contained only Co^{III}, absorbance at 303 nm decreased during the flash and then recovered with a half-life of *ca.* 5 μs. The recovery of the original absorbance was probably due to reaction (6)

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* 1M = 1 mol dm^{-3}.

[8] G. Davies and B. Warnquist, *Co-ordination Chem. Rev.*, 1970, **5**, 349.

[9] A. T. Thoronton and G. S. Laurence, *J.C.S. Dalton*, 1973, 804.

(M = Co), which has a rate constant of 5×10^7 l mol^{-1} s^{-1} (ref. 10) and a half-life of a few microseconds in solutions containing *ca.* 5×10^{-3}M-Co^{2+}. Because this reaction was so much faster than (2) under these conditions, the decay of the Tl^{2+} ions was unaffected by photolysis of Co^{III} and OH radicals were adequately scavenged by the Co^{2+} ions.

RESULTS

Reaction of Tl^{2+} *with* Mn^{2+}.—The rate of disappearance of Tl^{2+} after the flash was increased because of reaction (1) (M = Mn) when Mn^{2+} ions (10^{-1}M) were added to the Tl^{III} solution. The transient absorbance of the Tl^{2+} ions decayed to zero within 5—10 ms after the flash but a small increase in absorbance remained in the 270—400 nm region. This absorbance was *ca.* 3% of that due to the initial Tl^{2+} concentration and was probably due to Mn^{III} produced by reactions (1) and (6) (M = Mn). In 0·5M-acid Mn^{3+} ions are appreciably hydrolysed and both Mn^{3+} and [Mn(OH)]$^{2+}$ contribute to the absorbance in this region of the spectrum. We observed a similar absorbance due to Mn^{III} species following oxidation of Mn^{2+} ions by OH radicals and halogen radical anions.[11] This absorbance was always so much smaller than that of Tl^{2+} that no correction was applied to the kinetic data to allow for simultaneous growth of the Mn^{III} and decay of the Tl^{II} absorbances, but a correction was made to allow for the change in the effective 100% transmittance level due to reaction (6).

The rate of reaction (1) was studied in solutions which contained Tl^{III} (10^{-3}M), H$^+$ (0·5M), and Mn^{2+} ions (5×10^{-3}—10^{-1}M). The ionic strength varied from 0·75 to 0·80 mol l^{-1}. The rate of decay of the Tl^{2+} absorbance was always mixed first and second order [equation (4)] because even at the highest Mn^{II} concentrations the rate of reaction (1) was not large enough to allow the contribution of (3) to the decay of Tl^{2+} to be neglected. The second-order rate constant for reaction (1) (M = Mn), k', was calculated from the gradient of a plot of the pseudo-first-order rate constants against the manganese(II) concentration (Figure 1). At room temperature (22 ± 3 °C) in an ionic strength of 0·75 mol l^{-1} and an acid concentration of 0·50M, k' was $(1·9 \pm 0·2) \times 10^4$ l mol^{-1} s^{-1}.

Reaction of Tl^{2+} *with* Fe^{2+}.—The addition of Fe^{2+} ions (10^{-2}M) to solutions of Tl^{III} increased the rate of disappearance of Tl^{2+} produced by the flash. After the decay of the absorbance due to Tl^{2+} there remained a small residual absorbance in the 270—350 nm region. We attribute this to Fe^{III} produced by reactions (1) and (6) (M = Fe) and at 303 nm it was *ca.* 2% of the initial Tl^{2+} absorbance. No correction was made for the time dependence of the absorption due to Fe^{III} produced by reaction (1). Reaction (6) (M^{II} = Fe^{2+}) has a rate constant of $2·3 \times 10^8$ l mol^{-1} s^{-1} (ref. 12) and the OH radicals were effectively scavenged in times much shorter than the mean life-times of the Tl^{2+} ions. Thallium(III) reacts with Fe^{2+} [reverse of reaction (2) followed by reaction (1)] and the rate constant for the former rate-determining step is $4·6 \times 10^{-2}$ l mol^{-1} s^{-1}.[6] At the highest Fe^{2+} concentrations (10^{-2}M) the rate of removal of Tl^{III} and of production of Fe^{III} by the reverse of reaction (2) (M = Fe) was significant (the half-time of the thermal reaction was *ca.* 25 min) and the reaction mixtures were therefore flashed within 1 or 2 min of mixing of the Tl^{III} and Fe^{II} stock solutions. The Fe^{III} produced by the thermal reaction can react with Tl^{2+} with a rate constant comparable with that of reaction (1) [1] and it was important to flash the solutions while the concentration of Fe^{III} was small enough to be neglected. The reverse of reaction (2) was unimportant during the time of observation of (1) (M = Fe).

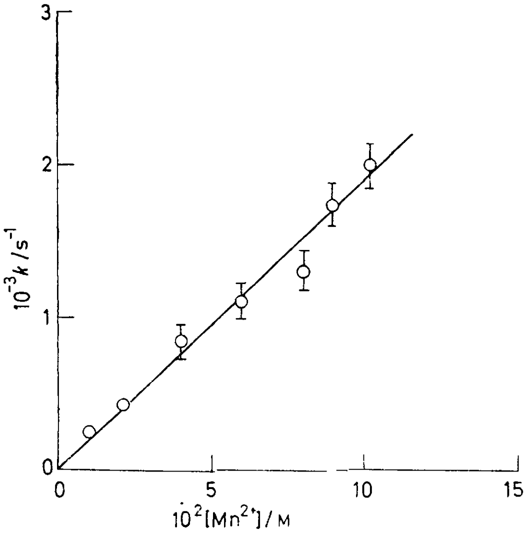

FIGURE 1 Dependence of the pseudo-first-order rate constant for the reaction of Mn^{2+} and Tl^{2+} on the Mn^{II} concentration at room temperature (22 ± 3 °C). The solutions contained 10^{-3}M-Tl^{III} and 0·5M-H$^+$, and I = 0·75M

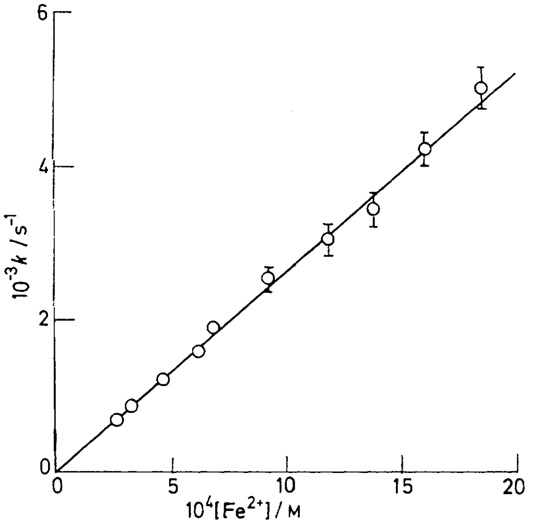

FIGURE 2 Dependence of the pseudo-first-order rate constant for the reaction of Fe^{2+} and Tl^{2+} on the Fe^{II} concentration at 25 °C. The solutions contained 10^{-3}M-Tl^{III} and 0·25 M-H$^+$, and I = 0·3M

The rate of reaction (1) was studied in solutions which contained Tl^{III} (10^{-3}M), H$^+$ (0·25M), and Fe^{2+} ions (2×10^{-4}—10^{-2}M). The ionic strength was 0·30 mol l^{-1}. The rate of decay of Tl^{2+} was always mixed first and second order [equation (4)]. Pseudo-first-order rate constants for reaction (1) were calculated for each Fe^{II} concentration and the second-order rate constant, k', was calculated from the gradient of a plot of pseudo-first-order rate constants

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[10] A. T. Thornton and G. S. Laurence, unpublished work.

[11] G. S. Laurence and A. T. Thornton, *J.C.S. Dalton*, 1973, 1637.

[12] G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J.C.S. Faraday I*, 1972, **68**, 2053.

against the iron(II) concentration (Figure 2). The second-order rate constant was $(2\cdot6 \pm 0\cdot1) \times 10^6$ l mol^{-1} s^{-1} at 25 °C in an ionic strength of 0·30 mol l^{-1} and an acid concentration of 0·25M. The rate constant was determined at several temperatures between 15 and 40 °C. At temperatures other than 25 °C the rate constant was determined by measuring the pseudo-first-order rate constant at a single Fe^{II} concentration ($2\cdot0 \times 10^{-3}$M). At this concentration the rate of reaction (1) was approximately twice the initial rate of (3). The pseudo-first-order rate constant for reaction (1) was calculated at each temperature using the appropriate value of k'' [1] and the second-order rate constant obtained by dividing the pseudo-first-order rate constant by the Fe^{II} concentration. The rate constant k' was almost independent of temperature between 15 and 40 °C (Table 1). The activation energy for reaction (1) (M = Fe) obtained from an Arrhenius plot of this data was 4·8 ± 2 kJ mol^{-1}.

TABLE 1

Rate constants for reactions of Tl^{2+} with Mn^{2+}, Fe^{2+}, and Co^{3+}

Reaction	θ_c/°C	k/l mol^{-1} s^{-1}
$Tl^{2+} + Mn^{2+} \longrightarrow Tl^{+} + Mn^{3+}$	22 ± 3	$(1\cdot9 \pm 0\cdot2) \times 10^4$ [a]
$Tl^{2+} + Fe^{2+} \longrightarrow Tl^{+} + Fe^{3+}$	14·7	$(2\cdot42 \pm 0\cdot1) \times 10^6$ [b]
	18·3	$(2\cdot50 \pm 0\cdot1) \times 10^6$
	20·7	$(2\cdot53 \pm 0\cdot1) \times 10^6$
	24·8	$(2\cdot60 \pm 0\cdot1) \times 10^6$
	29·0	$(2\cdot70 \pm 0\cdot1) \times 10^6$
	33·9	$(2\cdot73 \pm 0\cdot1) \times 10^6$
	36·0	$(2\cdot81 \pm 0\cdot1) \times 10^6$
	39·6	$(2\cdot91 \pm 0\cdot1) \times 10^6$
$Tl^{2+} + Co^{3+} \longrightarrow Tl^{3+} + Co^{2+}$	22 ± 3	$(9\cdot5 \pm 0\cdot5) \times 10^6$ [c]

[a] 0·5M-Acid, I = 0·75M. [b] 0·25M-Acid, I = 0·30M. [c] 0·5M-Acid, I = 0·55M.

Reaction of Tl^{2+} *with* Co^{3+}.—In the presence of Co^{3+} ions (10^{-3}M) the rate of disappearance of Tl^{2+} ions was increased. Because of the method of preparation, Co^{III} solutions always contained a large excess of Co^{2+} ions. We have shown [1] that Co^{2+} reacts with Tl^{2+} [reaction (1)] with a rate constant of $6\cdot2 \times 10^3$ l mol^{-1} s^{-1}, but the increase in the rate of removal of Tl^{2+} was not due to this reaction. The concentration of Co^{II} in the Co^{III} solutions was never more than about ten times the Co^{III} concentration and the rate constant for reaction of Co^{3+} with Tl^{2+}, reaction (2) (M = Co), is over three orders of magnitude greater than that for reaction (1), so that even for a Co^{II} concentration one hundred times greater than that of Co^{III} no more than 10% of the Tl^{2+} will react with the Co^{2+} rather than with the Co^{3+}. The Co^{2+} scavenged the OH radicals [reaction (6) (M = Co)] and, as reaction (2) was complete within a few milliseconds, the reaction of Co^{3+} with water did not interfere with the rate measurements.

The rate of reaction (2) (M = Co) was studied in solutions which contained Tl^{III} (10^{-3}M), H^+ (0·50M), and Co^{3+} ions (10^{-4}—10^{-3}M) in the presence of Co^{2+} ions (10^{-3}—10^{2}M). The ionic strength was 0·50—0·56 mol l^{-1} and the acid concentration was liable to vary from run to run by *ca.* 5% because of uncertainties in the acid concentration of the Co^{III} stock solution due to the electrolysis. Competition between the pseudo-first-order reaction of Tl^{2+} with Co^{3+} and second-order disproportionation of the Tl^{2+} ions was treated in the same way as for the other reactions of Tl^{2+} with metal ions. The second-order rate constant for reaction (2) (M = Co), k', was calculated from the gradient of a plot of the pseudo-first-order rate constants for the reaction against the cobalt(III) concentration (Figure 3). At room temperature (22 ± 3 °C) in an ionic strength of 0·55 mol l^{-1} and an acid concentration of 0·50M, k' was $(9\cdot5 \pm 0\cdot5) \times 10^6$ l mol^{-1} s^{-1}.

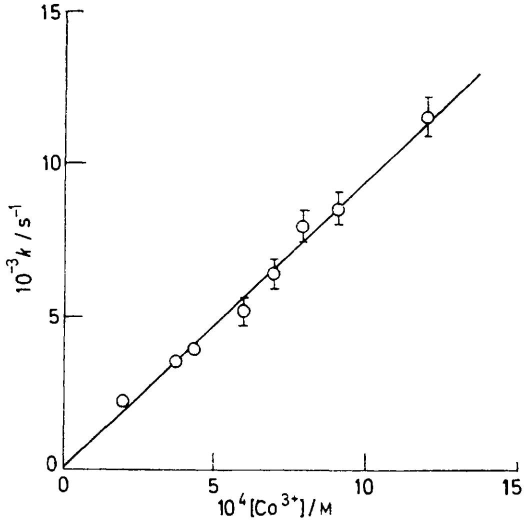

FIGURE 3 Dependence of the pseudo-first-order rate constant for the reaction of Co^{3+} and Tl^{2+} on the Co^{III} concentration at room temperature (22 ± 3 °C). The solutions contained 10^{-3}M-Tl^{III}, 0·5M-H^+, and Co^{II} at *ca.* 10 times the Co^{III} concentrations, and I = 0·55M

DISCUSSION

Manganese(III) does not react with Tl^+ ions even at 80 °C but on prolonged heating MnO_2 is formed and catalyses the reaction, which is also catalysed by Cl^- ions.[13] The probable explanation of the very slow rate of the uncatalysed reaction is the unfavourable standard free-energy change. The standard reduction potential of Mn^{3+}(aq) is 1·56 V, and, although that of the Tl^{III}–Tl^{I} couple is +1·25 V, the standard reduction potential of the Tl^{II}–Tl^{I} couple is +2·2 V [1] so that for the one-electron transfer [reverse of reaction (1) (M = Mn)] $\Delta G^{\ominus}$ is +62 kJ mol^{-1}. The rate constant for reaction (1) is $1\cdot9 \times 10^4$ l mol^{-1} s^{-1} so that the rate constant for the reverse of (1) will be *ca.* $2\cdot5 \times 10^{-7}$ l mol^{-1} s^{-1} at 25 °C. The mechanism of the chloride-ion catalysed reaction between Mn^{3+} and Tl^+ is complex and the formation of Cl_2^- radical anions by reaction (8) is the rate-determining step. The reaction is retarded by Mn^{2+} ions, and the retardation was attributed by Rosseinsky and Hill [13] to the reverse of reaction (8), but as the ratio of the concentration of Mn^{II} to that of Mn^{III} was always

$$[MnCl]^{2+} + Cl^- \longrightarrow Mn^{2+} + Cl_2^- \qquad (8)$$

10 : 1 or greater in their experiments the retardation may also have been due to reaction (1) between Mn^{2+} and Tl^{2+} ions produced from the one-electron oxidation of Tl^+ by the Cl_2^- radical ions.

We have no direct evidence of the mechanism of the reaction between Tl^{2+} and Mn^{2+} ions. The rate of substitution and of water exchange on Mn^{2+}(aq) ions

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[13] D. R. Rosseinsky and R. J. Hill, *J.C.S. Dalton*, 1972, 715.

is of the order of 10^7 l mol^{-1} s^{-1}.[14] The rate of ligand exchange on Tl^{3+} ions is greater than 10^8 l mol^{-1} s^{-1} (ref. 15) and for non-transition metal ions the rate of substitution on a bivalent ion is normally greater than that on a trivalent ion of about the same size. The rate of substitution on Tl^{2+} ions is therefore likely to be faster than 10^4 l mol^{-1} s^{-1}, and reaction (1) could be inner sphere, the Tl^{2+} and Mn^{2+} ions sharing a common water molecule in the inner-sphere complex. If this is the case, the rate must be controlled not by the rate of substitution but by that of electron transfer. For the oxidation of Mn^{2+}(aq) by the radical ion Cl_2^- the standard free-energy change is almost the same as that for the reaction (1) and the reaction is of this inner-sphere electron-transfer-controlled type.[11] But an outer-sphere mechanism for the electron transfer is equally compatible with the experimental facts, and electron transfer by an outer-sphere mechanism at large internuclear distances will be favoured by the $6s^1$ electron configuration for all the reactions of Tl^{2+}.

Reaction between Tl^{2+} and Fe^{2+} [reaction (1) (M = Fe)] was proposed as the fast second step in the oxidation of Fe^{2+} by Tl^{3+}, the first, rate-determining, step being the reverse of reaction (2) (M = Fe).[6] The reaction was retarded by Fe^{3+} ions because of reaction (2) and Ashurst and Higginson [6] measured the ratio of the rate constants for reactions (1) and (2). The ratio was inversely dependent on the acid concentration and at 25 °C in an ionic strength of 3·0 mol l^{-1} was 23·6 : 1 in 0·668M-acid and 16·2 : 1 in 0·40M-acid. Our measurements of the rate constant for (1) were made in solutions of lower ionic strength (0·30 mol l^{-1}) and acidity (0·25M) but we can estimate the rate constant for (2) approximately from the two sets of data. The ratio, extrapolated from the data of Ashurst and Higginson, is *ca.* 10 in 0·25M-acid, so that using the rate constant for (1) found in the present work, that for (2) must be *ca.* $2{\cdot}6 \times 10^5$ l mol^{-1} s^{-1}. From this value and the value of the rate constant for the reverse of reaction (2) obtained by Ashurst and Higginson [6] in 0·40M-acid at an ionic strength of 3·0 mol l^{-1}, the approximate value of the equilibrium constant for the reverse of reaction (2) is $1{\cdot}8 \times 10^{-7}$. This gives a value of +0·37 V for the standard reduction potential of the Tl^{III}–Tl^{II} couple. The values of the rate constant and reduction potential calculated in this way can be compared with the values obtained by us from direct measurement of the rate of reaction (2), which were $1{\cdot}1 \times 10^6$ l mol^{-1} s^{-1} and $E^\ominus$ +0·33 V.[1] The two sets of values are in reasonable agreement in view of the different ionic strengths and acidities used in the experiments of Ashurst and Higginson and the present work.

The apparent activation energy of reaction (1) (M = Fe), 4·8 kJ mol^{-1}, is very low. In water at 25 °C the rate constant for diffusion-controlled encounters between two bivalent positive ions with an encounter distance of 5 Å is *ca.* 3×10^8 l mol^{-1} s^{-1} at zero ionic strength and will be larger than this at an ionic strength of 0·3 mol l^{-1}. The activation energy for diffusion-controlled encounters would be expected to be *ca.* 12 kJ mol^{-1}. Very low activation energies were also observed for oxidations of Fe^{2+}(aq) ions by $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) and $[IrCl_6]^{2-}$ (3·3 and 8 kJ mol^{-1} respectively for reactions with rate constants of $3{\cdot}7 \times 10^4$ and $3{\cdot}2 \times 10^6$ l mol^{-1} s^{-1}).[16] The rate constants and activation parameters for the oxidation of Fe^{2+} by Tl^{2+} and $[IrCl_6]^{2-}$ are almost identical (Table 2) despite the difference in $\Delta G^\ominus$ of 141 kJ mol^{-1} and the difference in the charge associated with the transition state. The charge difference would make $\Delta S^\ddagger$ more negative for the Fe^{2+}–Tl^{2+} reaction than for the Fe^{2+}–$[IrCl_6]^{2-}$ reaction. Rate constants for the two reactions are very close to the rate of substitution on Fe^{2+}(aq) (the rate constant for water exchange is $3{\cdot}2 \times 10^6$ s^{-1}),[17] but the activation energy for water exchange is 35 kJ mol^{-1} and an activation energy of 4·8 kJ mol^{-1} cannot be reconciled with a simple inner-sphere substitution-controlled electron-transfer mechanism. Even for a highly labile Tl^{2+}(aq) ion, the activation energy appears

TABLE 2

Rate constants, free energies of activation, and standard free-energy changes for Co^{III} oxidations and Fe^{II} reductions

Co^{3+} Reactions Reductant	*k* (25 °C)/ l mol^{-1} s^{-1}	$\Delta G^\ddagger$/ kJ mol^{-1}	$\Delta G^\ominus$/ kJ mol^{-1}	Ref.
Tl^+	$3{\cdot}2 \times 10^{-3}$	88·3	35·7	7
Co^{2+}	3·3	70·9	0	*a*
Mn^{2+}	$1{\cdot}3 \times 10^{2}$	61·7	−32·8	*b*
$[Fe(5\text{-}NO_2phen)_3]^{2+}$	$1{\cdot}5 \times 10^{3}$	55·6	−58·2	*c*
Hydroquinone	$2{\cdot}2 \times 10^{3}$	54·6	−70·8	*d*
$[Fe(phen)_3]^{2+}$	$1{\cdot}4 \times 10^{4}$	50·0	−76·7	*c*
I^-	8×10^{3}	51·4	−82·5 [e]	*d*
Fe^{2+}	$2{\cdot}5 \times 10^{2}$	60·1	−104·8	*b*
Tl^{2+}	$9{\cdot}5 \times 10^{6}$	33·6	−149	This work
V^{2+}	$8{\cdot}8 \times 10^{5}$	39·6	−200	21
Cr^{2+}	$1{\cdot}3 \times 10^{4}$	50·2	−218	21
Fe^{2+} Reactions Oxidant				
Tl^{3+}	$4{\cdot}6 \times 10^{-2}$	81·6	44·5	6
Fe^{3+}	4·0	70·4	0	*f*
$[Os(bipy)_3]^{3+}$	$1{\cdot}4 \times 10^{3}$	55·7	−5·8	16
$[Fe(phen)_3]^{3+}$	$3{\cdot}2 \times 10^{4}$	47·9	−28·1	16
$[IrCl_6]^{2-}$	$3{\cdot}2 \times 10^{6}$	36·3	−28·1	16
$[Ru(bipy)_3]^{3+}$	$7{\cdot}2 \times 10^{5}$	40·1	−48·5	16
$[Ag(phen)_2]^{2+}$	$1{\cdot}7 \times 10^{6}$	37·9	−64·0	16
Mn^{3+}	$1{\cdot}7 \times 10^{4}$	49·5	−71·6	*g*
Tl^{2+}	$2{\cdot}6 \times 10^{6}$	36·9	−140	This work
Cl_2^-	$1{\cdot}0 \times 10^{7}$ [h]	33·5	−147	9
OH	$2{\cdot}3 \times 10^{8}$	25·6	−204	12

[a] H. S. Habib and J. P. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 1668. [b] G. Davies, *Inorg. Chem.*, 1971, **10**, 1155. [c] R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, 1964, **3**, 1091. [d] G. Davies and K. O. Watkins, *J. Phys. Chem.*, 1970, **74**, 3388. [e] $\Delta G^\ominus$ Calculated using the $E^\ominus$ value given in A. T. Thornton and G. S. Laurence, *J.C.S. Dalton*, 1973, 1632 for the oxidation of I^- to I_2^-. [f] S. Fukishima and W. L. Reynolds, *Talanta*, 1964, **11**, 283. [g] H. Diebler and N. Sutin, *J. Phys. Chem.*, 1964, **68**, 174. [h] This rate constant is for outer-sphere oxidation of Fe^{2+} by Cl_2^-.

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[14] R. G. Hayes and R. J. Myers, *J. Chem. Phys.*, 1964, **40**, 877.

[15] S. F. Lincoln, personal communication.

[16] B. M. Gordon and N. Sutin, *J. Amer. Chem. Soc.*, 1961, **83**, 70; B. M. Gordon, L. L. Williams, and N. Sutin, *ibid.*, p. 2061.

[17] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 807.

too low to permit an inner-sphere mechanism of replacement in the co-ordination sphere of Tl^{2+}. Like the reaction with Mn^{2+}, reaction (1) (M = Fe) is probably outer sphere.

The oxidation of Tl^{+} ions by Co^{3+} ions takes place in two one-electron transfer stages. The rate-determining first stage is the reverse of reaction (1) (M = Co), which is followed by (2) (M = Co).[7] The reaction is retarded by Co^{2+}, due to reaction (1), but the effect is much smaller than in the retardation of oxidation of Fe^{2+} by Tl^{3+}. Qualitative observations by Ashurst and Higginson [7] on the effect of Co^{2+} suggest that the ratio of rate constants of reactions (2) and (1) (M = Co) is greater than $10^{2}:1$. We previously measured the rate constant for (1) (M = Co) [1] as $6{\cdot}2 \times 10^{3}$ l mol^{-1} s^{-1} so that the ratio is $1{\cdot}5 \times 10^{3}:1$. The rate constant for reaction (2) (M = Co) is one of the highest known for an oxidation by Co^{3+}(aq) (Table 2) and is very much higher than the substitution rate for Co^{3+}(aq).[18] Like the other reactions of Tl^{2+}, reaction (2) (M = Co) is probably outer sphere.

The reactions of Tl^{2+} with Fe^{2+} and Co^{3+} can be compared with other outer-sphere oxidations of Fe^{2+} and reductions of Co^{3+} in terms of the $\Delta G^{\ominus}$ and $\Delta G^{\ddagger}$ values for the reactions. The data are presented in Table 2, and in the form of a plot of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ in Figure 4. The data cover a wide range of $\Delta G^{\ominus}$ (*ca.* 250 kJ mol^{-1}) and application of the Marcus theory [19,20] of the relation between $\Delta G^{\ddagger}$ for oxidation-reduction reactions with outer-sphere mechanisms, $\Delta G^{\ddagger}$ values for the electron-exchange reactions ($\Delta G_{11}^{\ddagger}$ and $\Delta G_{22}^{\ddagger}$), and the standard free energy of the reaction, $\Delta G^{\ominus}$, can only be qualitative over such a wide range of $\Delta G^{\ominus}$. The relevant expression is (9),[19] where w^{r} and w^{p} are terms for the work required

$$\Delta G^{\ddagger} = w^{r} + \lambda[1 + (4\Delta G_{r}^{\ominus\prime}/\lambda)]^{2}/4 \qquad (9)$$

to bring the reactants or products together in the transition state, $\Delta G_{r}^{\ominus\prime} = \Delta G^{\ominus} + w^{p} - w^{r}$, and $\lambda/4$ is the 'intrinsic' contribution to the energy barrier for electron transfer and is the average of the reorganisational energy barriers for the electron-exchange reactions of the two reactants. Equation (9) can be rearranged in terms of the free energies of activation for the two exchange reactions, $\Delta G_{11}^{\ddagger}$ and $\Delta G_{22}^{\ddagger}$, and the work terms for the exchange reactions, w_{11} and w_{22}, to give equation (10). For cases where $|\Delta G_{r}^{\ominus\prime}/4\Delta G_{0}^{\ddagger}| < 1$, the gradient of equation (10) will be given by (11),[20]

$$\Delta G^{\ddagger} = w^{r} + [(\Delta G_{11}^{\ddagger} - w_{11} + \Delta G_{22}^{\ddagger} - w_{22})/2] + (\Delta G_{r}^{\ominus\prime}/2) + (\Delta G_{r}^{\ominus\prime})^{2}/8(\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger}) \qquad (10)$$

where $\Delta G_{0}^{\ddagger}$ is the value of $\Delta G^{\ddagger}$ for $\Delta G^{\ominus}$ equal to zero. The expressions do not lead to a linear relation between $\Delta G^{\ddagger}$ and $\Delta G^{\ominus}$, except for a small range of $\Delta G^{\ominus}$ close to zero, where the gradient of a plot of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ should have a value of 0·5.

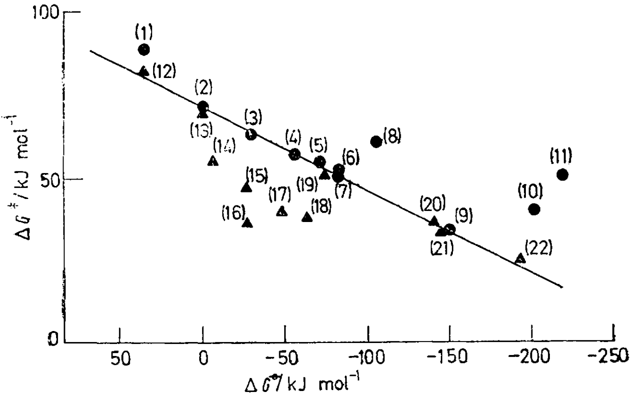

FIGURE 4 Plot of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ at 25 °C for the Co^{3+} oxidations (●) and Fe^{2+} reductions (▲) given in Table 2. For the Co^{3+} reactions the reductants are: (1), Tl^{+}; (2), Co^{2+}; (3), Mn^{2+}; (4), $[Fe(5\text{-}NO_{2}phen)_{3}]^{2+}$; (5), hydroquinone; (6), I^{-}; (7), $[Fe(phen)_{2}]^{2+}$; (8), Fe^{2+}; (9), Tl^{2+}; (10), V^{2+}; and (11), Cr^{2+}. For the Fe^{2+} reactions the oxidants are: (12), Tl^{3+}; (13), Fe^{3+}; (14), $[Os(bipy)_{3}]^{3+}$; (15), $[Fe(phen)_{3}]^{3+}$; (16), $[IrCl_{6}]^{2-}$; (17), $[Ru(bipy)_{3}]^{2+}$; (18), $[Ag(phen)_{2}]^{2+}$; (19), Mn^{3+}; (20), Tl^{2+}; (21), Cl_{2}^{-} (outer-sphere reaction); and (22), OH. The straight line has a gradient of 0·25

$$\text{Gradient} = [1 + (\Delta G_{r}^{\ominus\prime}/4\Delta G^{\ddagger}_{0})]/2 \qquad (11)$$

In a previous comparison [21] of $\Delta G^{\ddagger}$ and $\Delta G^{\ominus}$ for a wide range of reductions of Co^{3+}, the change in the gradient of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ expected from equation (11) (at very large values of $-\Delta G^{\ominus}$ the gradient will change sign, so that $\Delta G^{\ddagger}$ increases with further increases in $-\Delta G^{\ominus}$) appeared to be shown by data for reductions of Co^{3+} by V^{2+} and Cr^{2+}. However $\Delta G^{\ddagger}$ for the reduction of Co^{3+} by Tl^{2+} (Figure 4) is less than the $\Delta G^{\ddagger}$ values for the reactions of Co^{3+} with V^{2+} and Cr^{2+} even though $-\Delta G^{\ominus}$ for reaction (2) is 50 kJ mol^{-1} or more less than values for the V^{2+} and Cr^{2+} reactions. Despite the expectations of equations (10) and (11), data for the reductions of Co^{3+} fall (in all but three cases) on a straight line of gradient 0·25 (Figure 4). Some reductions of Co^{3+} by substituted phen complexes of Fe^{2+} were omitted from Figure 4 for the sake of clarity, but lay on the line of gradient 0·25 in the region between the points for the hydroquinone and $[Fe(phen)_{3}]^{2+}$ oxidations, and were included in a previous compilation.[21] The $\Delta G^{\ominus}$ values for Tl^{I}, Tl^{II}, and Tl^{III} one-electron transfer reactions may be in error by up to 10 kJ mol^{-1} because of the uncertainty in the $E^{\ominus}$ values,[1] but the overall correlation is not changed significantly by errors of this size. In the region of $\Delta G^{\ominus}$ close to zero (between the Co^{2+}–Co^{3+} exchange reaction and the Mn^{2+}–Co^{3+} reaction, for which the range of $\Delta G^{\ominus}$ is only 30 kJ mol^{-1}) where equation (11) should apply,[20] the line has a gradient of 0·25 (although for positive $\Delta G^{\ominus}$ between the Tl^{+}–Co^{3+} reaction and the exchange reaction the gradient is almost exactly the 0·5 expected). For the wide range of substrates, although $\Delta G_{11}^{\ddagger}$ is constant for the single oxidant Co^{3+}, the changes in $\Delta G_{22}^{\ddagger}$ are large and in some cases unknown. The difficulty of calculating the work terms and of knowing the exchange rates for species such as hydroquinone and Tl^{2+} limit the application of equation (10). The smaller de-

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[18] A. McAuley, M. N. Malik, and J. Hill, *J. Chem. Soc.* (*A*), 1970, 2461.

[19] R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 679.

[20] R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891.

[21] M. R. Hyde, R. Davies, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1838.

pendence of $\Delta G^{\ddagger}$ on $\Delta G^{\ominus}$ for the reactions of Co^{3+} with Fe^{2+}, V^{2+}, and Cr^{2+} may reflect not only the changes in $\Delta G_{22}^{\ddagger}$ but also the greater dependence of these reactions on intrinsic rather than thermodynamic factors.

The oxidations of Fe^{2+} included in Table 2 and Figure 4 resemble the reduction of Co^{3+}. Electron-exchange rates for Co^{2+}–Co^{3+} and Fe^{2+}–Fe^{3+} are very similar and the range of $\Delta G^{\ominus}$ for which a gradient of 0·5 would be expected for the plot of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ will be the same. In fact for reactions of Fe^{2+} covering a range of 250 kJ mol^{-1} in $\Delta G^{\ominus}$, a linear plot with a gradient of 0·25 was again observed (Figure 4). The lines of gradient 0·25 for oxidations of Fe^{2+} and reductions of Co^{3+} are identical, no doubt because $\Delta G^{\ddagger}$ is the same for the two exchange reactions. The oxidation of Fe^{2+} by Co^{3+} is outside the relation for the Fe^{2+} reactions as it is for the Co^{3+} reactions, and a group of rapid oxidations of Fe^{2+} by complex ions such as $[Fe(phen)_3]^{3+}$ and $[IrCl_6]^{2-}$ fall well below the line of gradient 0·25. For these reactions the dependence of $\Delta G^{\ddagger}$ on $\Delta G^{\ominus}$ is small $\{[IrCl_6]^{2-}$ and $[Ag(phen)_2]^{2+}$ react with Fe^{2+} with almost the same rate constant, but the $\Delta G^{\ominus}$ values differ by 32 kJ mol^{-1}, and the $[IrCl_6]^{2-}$ and $[Fe(phen)_3]^{3+}$ reactions have the same $\Delta G^{\ominus}$ but differ in rate by a factor of $10^2\}$.[16] The reactions have low activation energies and the main influence on the rates are the differences in $\Delta S^{\ddagger}$ arising from differences in the charges of the reactants. The exchange rates are also very different from those of many of the other oxidants in Figure 4. Figure 4 does not indicate that the $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ plot for oxidations of Fe^{2+} changes significantly in gradient before diffusion-controlled rates are reached and indicates the difficulty in estimating the effects of the two parameters in equation (10) which are substrate dependent: the work terms and the barrier represented by $\Delta G^{\ddagger}$ for the electron-exchange reactions.

TABLE 3

Rate constants, free energies of activation, and standard free-energy changes for thallium oxidation-reduction reactions

Reaction	k(25 °C)/l mol^{-1} s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}	$\Delta G^{\ominus}$/kJ mol^{-1}	Reference
Two-electron transfers				
$Tl^+ + Tl^{3+} \longrightarrow Tl^+ + Tl^{3+}$	7×10^{-5}	97·9	0	*a*
$Tl^{3+} + Hg^0 \longrightarrow Tl^+ + Hg^{2+}$	7.5×10^{-3} [b]	86·1	−69·7	*c*
$Tl^{3+} + U^{IV} \longrightarrow Tl^+ + U^{VI}$	2.1×10^{-2}	83·6	−100·2	23
$Tl^{3+} + V^{2+} \longrightarrow Tl^+ + V^{IV}$	7×10^{1} [d]	63·7	−222·6	24
One-electron transfers				
$Tl^{3+} + V^{IV} \longrightarrow Tl^{2+} + V^{V}$	1.1×10^{-2} [e]	84·8	66·8	*f*
$Tl^+ + Ce^{IV} \longrightarrow Tl^{2+} + Ce^{3+}$	3.4×10^{-4} [g]	94·1	61·7	*h*
$Tl^{3+} + Fe^{2+} \longrightarrow Tl^{2+} + Fe^{3+}$	4.6×10^{-2}	81·5	44·5	6
$Tl^+ + Co^{3+} \longrightarrow Tl^{2+} + Co^{2+}$	3.2×10^{-3}	88·2	35·8	7
$Tl^{3+} + V^{3+} \longrightarrow Tl^{2+} + V^{IV}$	3.1×10^{3}	53·8	3·8	*i*
$Tl^+ + Tl^{2+} \longrightarrow Tl^+ + Tl^{2+}$	*ca.* 5×10^{4}	46·6	0	25
$Tl^{2+} + Tl^{3+} \longrightarrow Tl^{2+} + Tl^{3+}$	*ca.* 10^{5}	44·9	0	25
$Tl^{2+} + Co^{2+} \longrightarrow Tl^+ + Co^{3+}$	6.2×10^{3}	52·1	−35·7	1
$Tl^{2+} + Fe^{3+} \longrightarrow Tl^{3+} + Fe^{2+}$	1.1×10^{6}	39·1	−44·5	1
$Tl^{2+} + Mn^{2+} \longrightarrow Tl^+ + Mn^{3+}$	1.9×10^{4}	49·1	−65·1	This work
$Tl^{2+} + Fe^{2+} \longrightarrow Tl^+ + Fe^{3+}$	2.6×10^{6}	37·0	−140·3	This work
$Tl^{2+} + Co^{3+} \longrightarrow Tl^{3+} + Co^{2+}$	9.5×10^{6}	33·6	−149·1	This work
$Tl^{2+} + Tl^{2+} \longrightarrow Tl^+ + Tl^{3+}$	5.5×10^{8}	23·5	−184·8	1

[a] S. W. Gilks and G. M. Waind, *Discuss. Faraday Soc.*, 1960, **29**, 102; E. Roig and R. W. Dodson, *J. Phys. Chem.*, 1961, **65**, 2175. [b] Calculated from the authors' data using the value for the equilibrium constant for the disproportionation $Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg$ given by F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, London, 2nd edn., 1966, p. 613, of 6×10^{-3} l mol^{-1}. [c] A. M. Armstrong, J. Halpern, and W. C. E. Higginson, *J. Phys. Chem.*, 1956, **60**, 1661; A. M. Armstrong and J. Halpern, *Canad. J. Chem.*, 1957, **35**, 1022. [d] 0 °C. [e] 80 °C. [f] W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, 1960, **29**, 49; A. G. Sykes, *J. Chem. Soc.*, 1961, 5549. [g] 54 °C. [h] J. W. Gryder and M. Dorfman, *J. Amer. Chem. Soc.*, 1961, **83**, 1254. [i] N. Daugherty, *J. Amer. Chem. Soc.*, 1965, **87**, 5026.

Standard free energies of reaction can now be calculated [1] from $E^{\ominus}$ values for the Tl^{III}–Tl^{II} and Tl^{II}–Tl^{I} couples and the dependence of the one-electron transfer reactions of Tl^+ and Tl^{3+} on $\Delta G^{\ominus}$ can be examined for the first time. Data for reactions of Tl^+, Tl^{2+}, and Tl^{3+} are presented in Table 3 and as a plot of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ in Figure 5. Reactions for which the mechanism is uncertain, such as the oxidation of Tl^+ by Ag^{2+} which may take place through the intervention of NO_3 radicals,[22] have been omitted. The data again cover a wide range of $\Delta G^{\ominus}$ and reveal a very obvious difference between one- and two-electron transfers of the thallium oxidation states. For a particular $\Delta G^{\ominus}$, the two-electron-transfer reactions have $\Delta G^{\ddagger}$ values higher than those for one-electron transfer reactions by 25—30 kJ mol^{-1}. This difference applies over the whole range of $\Delta G^{\ominus}$ from the Tl^+–Tl^{3+} exchange reaction ($\Delta G^{\ominus}$ 0) * to the Tl^{3+}–V^{2+} reaction [23] ($\Delta G^{\ominus}$ −220 kJ mol^{-1}). For a two-electron transfer the necessary adjustments of the co-ordination environments of the reactants will be more severe than for one-electron transfers as environmental differences (solvation, *etc.*) between reactants and products are larger. Unfortunately the data for thallium oxidation-reduction reactions are not extensive enough to permit separate evaluation of the contribution of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to the values of $\Delta G^{\ddagger}$ for the one- and two-electron transfers. The two-electron transfers show only a

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* That the thermal-exchange reaction must definitely be classed as a two-electron-transfer reaction was established in the first paper of this series.[1]

[22] R. W. Dundon and J. W. Gryder, *Inorg. Chem.*, 1966, **5**, 986.

[23] A. C. Harkness and J. Halpern, *J. Amer. Chem. Soc.*, 1959, **81**, 3526; J. D. Wear, *J. Chem. Soc.*, 1965, 5596.

small variation in $\Delta G^{\ddagger}$ for large changes in $\Delta G^{\ominus}$ and intrinsic effects predominate over thermodynamic. The oxidation of U^{IV} by Tl^{3+} is slower than might be expected[23] (Figure 5) perhaps because of increased demands for reorganisation of the co-ordination sphere in going from $[UO]^{2+}$ to $[UO_2]^{+}$, but similar restrictions are not apparent for the oxidation of V^{2+} to $[VO]^{2+}$.[24] The data included in Table 3 and Figure 5 are subject to many uncertainties in some cases (*e.g.* some of the $\Delta G^{\ddagger}$ values are for measurements at 80 °C) and, while these cannot change the conclusion that two-electron transfers have more stringent $\Delta G^{\ddagger}$ requirements than one-electron transfers, some scatter is expected in Figure 5.

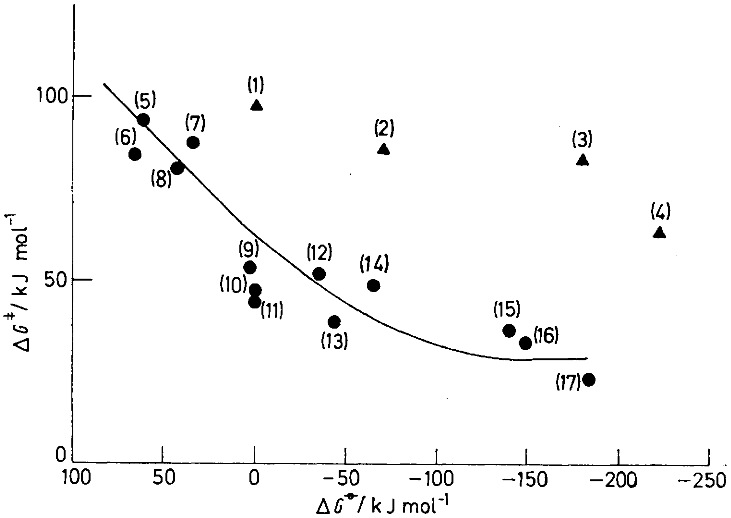

FIGURE 5 Plot of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ for the oxidation and reduction reactions of thallium given in Table 3: (▲), two-electron transfers; (●), one-electron transfers. The reactants are: (1), Tl^{+}–Tl^{3+}; (2), Tl^{3+}–Hg^{0}; (3), Tl^{3+}–U^{IV}; (4), Tl^{3+}–V^{2+}; (5), Tl^{+}–Ce^{IV}; (6), Tl^{3+}–V^{IV}; (7), Tl^{+}–Co^{3+}; (8), Tl^{3+}–Fe^{2+}; (9), Tl^{3+}–V^{3+}; (10), Tl^{+}–Tl^{2+}; (11), Tl^{2+}–Tl^{3+}; (12), Tl^{2+}–Co^{2+}; (13), Tl^{2+}–Fe^{3+}; (14), Tl^{2+}–Mn^{2+}; (15), Tl^{2+}–Fe^{2+}; (16), Tl^{2+}–Co^{3+}; and (17), Tl^{2+}–Tl^{2+}

One-electron transfers involving thallium species show the expected decrease in $\Delta G^{\ddagger}$ with increasing $-\Delta G^{\ominus}$, but this general trend cannot be directly related to equations (10) and (11). The appropriate exchange reactions are different for the oxidation of Tl^{+} and the reduction of Tl^{3+}. Rates of the Tl^{+}–Tl^{2+} and Tl^{2+}–Tl^{3+} electron exchanges were estimated to be *ca.* 10^5 l mol^{-1} s^{-1} by Stranks and Yandell[25] and these estimates are included in Figure 5. Their measurements indicated that the Tl^{+}–Tl^{2+} exchange was the slower by a factor of two, but Warnquist and Dodson[26] estimate from their results that the rate of the Tl^{+}–Tl^{2+} exchange is the larger of the two. The Fe^{2+}–Tl^{3+} and Fe^{3+}–Tl^{2+} reactions involve the Tl^{2+}–Tl^{3+} pair, and lie on a line of gradient 0·5 (Figure 5) which is below the line of the same gradient for the Co^{3+}–Tl^{+} and Co^{2+}–Tl^{2+} reactions which involve the Tl^{+}–Tl^{2+} pair. As $\Delta G^{\ddagger}$ is the same for the Fe^{2+}–Fe^{3+} and Co^{2+}–Co^{3+} exchange reactions, this may indicate that the Tl^{+}–Tl^{2+} exchange reaction is slower than that of Tl^{2+}–Tl^{3+}, as suggested by Stranks and Yandell. No more than general trends can be established in Figure 5, but the gradient in the region of $\Delta G^{\ominus} = 0$ is *ca.* 0·5 and falls until the diffusion-controlled region is reached at about the disproportionation reaction of Tl^{2+}.

Oxidations of the tris(1,10-phenanthroline) and tris(2,2′-bipyridyl) complexes of ruthenium(II)[27] and osmium(II)[28] by Tl^{3+} have been omitted from Figure 5 because for these reactions $\Delta G^{\ddagger}$ is apparently smaller than $\Delta G^{\ominus}$. The oxidation of the $[Fe(phen)_3]^{2+}$ complex by Tl^{3+} (ref. 29) has been shown to involve ligand decomposition,[28] but in the case of the ruthenium(II) and osmium(II) complexes the dipositive complex could be recovered unchanged after the reaction, by reduction of the trivalent complex formed by the oxidation. The ligands do not therefore undergo permanent change during the oxidation reaction in these cases. Ligands like phen and bipy can participate in electron-transfer reactions of the Ru^{II} and Ru^{III} complexes by forming co-ordinated radical intermediates[30] and excited states,[31] and the oxidations of the ruthenium and osmium complexes may involve formation of such intermediate species followed by intermolecular electron transfer from the metal to the ligand. The oxidation of $[Ru(bipy)_3]^{2+}$ by Tl^{3+} is photosensitive and involves the ^{3}CT state of $[Ru(bipy)_3]^{2+}$. The ^{3}CT state reacts with Tl^{3+} with a rate constant[32] of 2×10^8 l mol^{-1} s^{-1}, very much faster than the rate of the thermal reaction,

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[24] F. B. Baker, W. D. Brewer, and T. W. Newton, *Inorg. Chem.*, 1966, **5**, 1294.

[25] D. R. Stranks and J. K. Yandell, *J. Phys. Chem.*, 1969, **73**, 840.

[26] B. Warnquist and R. W. Dodson, *Inorg. Chem.*, 1971, **10**, 2624.

[27] J. D. Miller and R. H. Prince, *J. Chem. Soc.* (*A*), 1966, 1048.

[28] D. H. Irvine, *J. Chem. Soc.*, 1957, 1841.

[29] P. George and D. H. Irvine, *J. Chem. Soc.*, 1954, 587.

[30] J. H. Baxendale and M. Fiti, *J.C.S. Dalton*, 1972, 1995.

[31] J. E. Martin, E. J. Hart, A. W. Adamson, H. Gafney, and J. Halpern, *J. Amer. Chem. Soc.*, 1972, **94**, 9238.

[32] G. S. Laurence and V. Balzani, *Inorg. Chem.*, in the press.

0·19 l mol^{-1} s^{-1}. This suggests that participation of charge-transfer intermediates in the oxidations of these complexes may provide the easiest path for electron transfer and account for the inconsistency in $\Delta G^{\ddagger}$ and $\Delta G^{\ominus}$.

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