Aqueous Chemistry of Thallium(II). Part I. Kinetics of Reaction of Thallium(II) with Cobalt(II) and Iron(III) Ions and Oxidation–Reduction Potentials of Thallium(II)

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Reactions of Tl^{2+} ions [generated by flash photolysis of thallium(III) solutions] with cobalt(II) and iron(III) have been studied. For the reaction $Tl^{2+} + Co^{2+} \rightleftharpoons Tl^{+} + Co^{3+}$ the forward rate constant is $(6\cdot2 \pm 0\cdot5) \times 10^{3}$ l mol^{-1} s^{-1} (25 °C, [H$^+$] = 0·25, I = 0·75M) and the equilibrium constant calculated from this rate constant and that of the reverse reaction is $2\cdot0 \times 10^{6}$. The forward rate constant for the reaction $Tl^{2+} + Fe^{3+} \rightleftharpoons Tl^{3+} + Fe^{2+}$ is $(1\cdot1 \pm 0\cdot15) \times 10^{6}$ l mol^{-1} s^{-1} (25 °C, [H$^+$] = 0·25, I = 0·30M) and the equilibrium constant calculated from this value and that of the reverse reaction is $2\cdot4 \times 10^{7}$. Standard reduction potentials for the reactions $Tl^{3+} + e^- \rightleftharpoons Tl^{2+}$ (E_1^0) and $Tl^{2+} + e^- \rightleftharpoons Tl^{+}$ (E_2^0) are $+0\cdot33 \pm 0\cdot05$ and $+2\cdot22 \pm 0\cdot05$ V respectively. The thermal electron-exchange reaction between thallium(I) and thallium(III) is discussed and a mechanism involving intermediate formation of Tl^{2+} ions is shown to be inconsistent with equilibrium and kinetic data. The disproportionation reaction $Tl^{2+} + Tl^{2+} \longrightarrow Tl^{+} + Tl^{3+}$ has a rate constant of $(5\cdot5 \pm 0\cdot5) \times 10^{8}$ l mol^{-1} s^{-1} (25 °C, [H$^+$] = 0·25, I = 0·25M) and is diffusion controlled with an activation energy of $7\cdot9 \pm 1\cdot5$ kJ mol^{-1}.

FOR oxidation-reduction reactions between metal ions in which two-equivalent change is possible there has been considerable discussion of the factors determining whether such changes take place in successive one-electron-transfer steps or by a single step in which two electrons are transferred; the latter process may be observationally indistinguishable from two consecutive but nearly simultaneous one-electron-transfer steps. The problem has been reviewed by Sutin [1] and by Sykes [2] but detailed understanding has been limited by the lack of kinetic and thermodynamic information for reactions of the frequently highly reactive intermediate oxidation states which participate in two-equivalent reactions proceeding by one-electron-transfer steps. This information is also required for the application of theoretical treatments of electron-transfer processes, such as that of Marcus.[3]

Oxidation-reduction reactions of thallium(I) and thallium(III) ions have been extensively studied. For reactions with a number of one-electron oxidants and reductants the intermediate oxidation state thallium(II) has been inferred from kinetic evidence.[4-8] The mechanism of the thermal electron-exchange reaction between thallium(I) and thallium(III) ions is still uncertain however.[2] The photochemically induced exchange involves thallium(II) species [9] but there is evidence that thermal exchange does not involve free, scavengeable, thallium(II).[10] Theoretical treatments of the exchange reaction and of other oxidation reduction reactions of thallium have been limited by the absence of thermodynamic data for processes involving thallium(II) ions. Estimates have been made of the standard reduction potentials for reactions (1) and (2) but these are to some extent dependent on the mechanism assumed for the exchange reaction.[11,12]

$$Tl^{3+} + e^- \rightleftharpoons Tl^{2+} \quad E_1^0 \tag{1}$$

$$Tl^{2+} + e^- \rightleftharpoons Tl^{+} \quad E_2^0 \tag{2}$$

Thallium(II) has been generated by pulse radiolysis [13] and flash photolysis [14] and these techniques make the aqueous chemistry of thallium(II) more accessible. Oxidation reduction reactions of thallium(II) with transition metal ions can be studied directly and reduction potentials for couples involving thallium(II) can be derived from kinetic data for sets of complementary oxidation-reduction reactions.

EXPERIMENTAL

Solutions of Tl^{III} ions were prepared by dissolving Tl_2O_3 (B.D.H.) in perchloric acid. The Tl^{III} concentrations were determined by titration with KIO_3 after reduction to Tl^{I}. Acid concentrations of Tl^{III} stock solutions were determined by titration with NaOH to pH 8. Solutions of Co^{II} ions were prepared from the perchlorate salt (Fluka) and were standardised by electrodeposition. Solutions of Fe^{III} ions in perchloric acid were prepared from the perchlorate salt (Fluka) after recrystallisation from $HClO_4$ and were standardised by titration with ethylenediaminetetra-acetic acid. Acid concentrations of Fe^{III} solutions were determined by titration with NaOH to pH 9. 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

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[11] N. Hush, *Trans. Faraday Soc.*, 1961, **57**, 557.

[12] W. C. E. Higginson, *Discuss. Faraday Soc.*, 1960, **29**, 135.

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

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

procedure have been described previously.[15] During the course of this work a second Bausch and Lomb high-intensity grating monochromator was added to the spectrophotometric optical train. The use of two monochromators greatly reduced the stray light at wavelengths below 270 nm and correspondingly improved the accuracy of the photometry at these wavelengths. With two monochromators the stray light was less than 0·05% at 260 nm. In kinetic experiments the change in concentration of Tl^{II} species with time was usually followed as the change in absorbance at 297 nm. The Xe–Hg monitoring lamp has a large output at this wavelength and the signal-to-noise ratio is correspondingly high. At least three oscilloscope traces were analysed for each set of experimental conditions. Preliminary experiments showed that oxygen had no effect on the rate of the disproportionation reaction of thallium(II) ion and most experiments were therefore carried out in aerated solutions.

RESULTS

Production of Thallium(II) *Ions*.—In preliminary experiments we attempted to oxidise Tl^+ ions to Tl^{II} by using Br_2^- radical ions or OH radicals as the oxidising agents. The potential of the Tl^{II}–Tl^{I} couple was estimated by Hush[11] to be +1·5 V and as the standard reduction potential of Br_2^- radical ions is +1·77 V[16] we expected that the radical anions would oxidise Tl^{I} to Tl^{II}, reaction (3). Flash photolysis of Br^- ions (10^{-2}M) at pH 1 produced *ca.* 5μMBr_2^- in the presence of Tl^+ (*ca.* 10^{-4}M). The concentration of Tl^+ ions in the solutions was limited to *ca.* 10^{-4}M because of the low solubility of TlBr. At this concentration of Tl^{I} the decay of the Br_2^- radical ions was second order, with the same rate constant as that found previously for the disproportionation [reaction (4)].[15] There was no evidence of

$$Br_2^- + Tl^+ \xrightarrow{k_3} Tl^{2+} + 2Br^- \qquad (3)$$

$$Br_2^- + Br_2^- \longrightarrow Br_3^- + Br^- \qquad (4)$$

reaction with Tl^+ ions and we estimate that k_3 has an upper limit of *ca.* 10^6 l mol^{-1} s^{-1}.

Hydroxyl radicals oxidise Tl^{I} to Tl^{II} [reaction (5)].[13] Flash photolysis of H_2O_2 solutions (10^{-3}M) produced 10μM concentrations of OH radicals [reaction (6)]. When solutions of H_2O_2 (10^{-3}M) and Tl^+ ions (10^{-3}M) were flashed

$$OH + Tl^+ \xrightarrow{k_5} Tl^{2+} + OH^- \qquad (5)$$

$$H_2O_2 \xrightarrow{h\nu} 2OH \qquad (6)$$

we observed a transient absorbance at 270 nm which decayed rapidly ($t_{\frac{1}{2}} < 20$ μs). This absorbance was due to the Tl^{II} ions which react with H_2O_2 [reaction (7)] with a rate constant k_7 of 3×10^7 l mol^{-1} s^{-1} (ref. 13) giving a

$$Tl^{2+} + H_2O_2 \xrightarrow{k_7} Tl^+ + H^+ + HO_2 \qquad (7)$$

half-life under our conditions of *ca.* 20 μs. The rapid reaction of Tl^{2+} ions with H_2O_2 prevented the use of this method of producing Tl^{II} in the study of reactions of Tl^{II} with substrates other than H_2O_2.

Tl^{II} Ions can be produced by photolysis of Tl^{III} solutions. At acid concentrations between 0·1 and 1·0M the principal Tl^{III} species in aqueous solution are the ions Tl^{3+} and $TlOH^{2+}$ and the major light-absorbing species at wavelengths longer than *ca.* 220 nm is the $TlOH^{2+}$ ion. The absorption is a ligand-to-metal charge-transfer process [reaction (8)] and the products of photolysis are Tl^{2+} ions and OH radicals. Burchill and Wolodarsky[14] observed

$$TlOH^{2+} \xrightarrow{h\nu} Tl^{2+} + OH \qquad (8)$$

Tl^{II} ions in flash-photolysed solutions of Tl^{III}. When solutions containing Tl^{III} ions (10^{-3}M) and acid (0·25M) were flash photolysed in our apparatus we observed large transient absorbances in the wavelength range from 250 to 320 nm, the region in which Tl^{II} is reported to absorb strongly.[13,14] When the solutions also contained Tl^+ ions (10^{-4}M) the absorbance produced by the flash was approximately doubled due to efficient scavenging of OH radicals by the added Tl^+ ions [reaction (5)]. The absorbance decayed with an initial half-life of *ca.* 0·5 ms and the spectrum of the transient is shown in Figure 1. At wavelengths near 260 nm the spectrum is similar to that measured by Cercek *et al.*[13] in acid solution, but does not show the absorbance which they observed near 360 nm in air-saturated solutions at pH 5·5 and in N_2O-saturated solutions at pH 6·5. Our spectrum also differs from that of Burchill and Wolodarsky.[14] In early experiments using only a single monochromator we obtained a spectrum with the same rapid asymmetric fall in absorbance below 260 nm as that of Burchill and Wolodarsky, but static measurements in our apparatus of the spectrum of the Br_3^- ion, which has a maximum absorbance at 267 nm, showed that the asymmetry was due to the very low intensity of the Xe–Hg lamp in the vicinity of the Hg resonance line at 253·7 nm and the correspondingly larger stray-light factor at these wavelengths. The spectrum in Figure 1 was recorded using two monochromators and a Xe lamp. It was unaltered by changing the acid concentration in the range from 0·1 to 1·0M. Hydrolysis of Tl^{3+} ions prevented measurements over a wider range of acid concentration and it was not

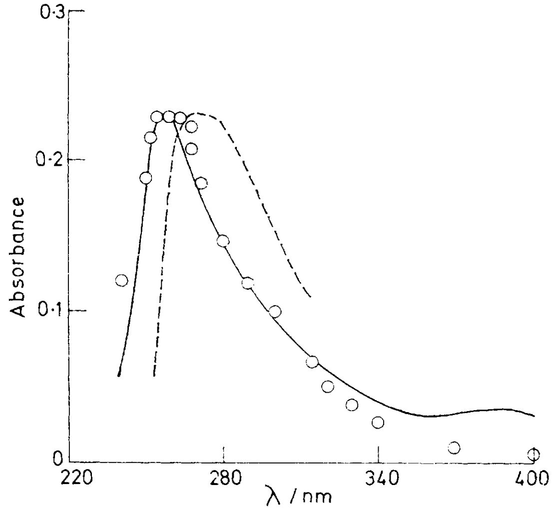

FIGURE 1 Spectrum of Tl^{II} ions produced by flash photolysis of 0·25M-H^+, 10^{-4}M-Tl^+, and 10^{-3}M-Tl^{3+} solutions: (○), 50 μs after the flash; (——), spectrum of Tl^{II} produced by pulse radiolysis of Tl^+ in aerated solutions at pH 2;[13] and (– – – –), spectrum of Tl^{II} produced by flash photolysis of Tl^{3+} solutions in 1·0M-acid[14]

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

[16] A. T. Thornton and G. S. Laurence, *J.C.S. Dalton*, 1973, 1632.

possible to establish the presence of hydrolysed forms of Tl^{II}, such as $TlOH^+$ ions, by direct observation.

Disproportionation of Thallium(II) *Ions*.—Tl^{II} Ions produced by pulse radiolysis and flash photolysis disproportionate to give Tl^I and Tl^{III} [reaction (9)]. In solutions containing Tl^{III} (10^{-3}M), acid (0·25M), and Tl^+ ions (10^{-3}M) the

$$Tl^{II} + Tl^{II} \longrightarrow Tl^{I} + Tl^{III} \qquad (9)$$

decay of the transient absorbance produced by the flash was good second order for at least two half-lives. The same second-order fit was obtained from experiments with aerated and deaerated solutions, indicating that Tl^{II} ions react only slowly with oxygen. The second-order rate constant, expressed as $2k_9/\varepsilon$ at 270 nm, was $(1{\cdot}0 \pm 0{\cdot}1) \times 10^5$ cm s^{-1} at 25 °C and ionic strength 0·25 mol l^{-1}. This value lies between the values obtained previously.[13,14] Absolute absorption coefficients of Tl^{II} ions could not be measured in our experiments and we have used the value of the absorption coefficient measured at 260 nm in pulse-radiolysis experiments [13] to calculate the second-order rate constant for reaction (9). Values from measurements at other wavelengths were calculated by using relative absorption coefficients obtained in our measurements of the spectrum. The rate constants obtained in this way from measurements at different wavelengths were self consistent and the average value of $2k_9$ at 25 °C and ionic strength 0·25 mol l^{-1} was $(5{\cdot}5 \pm 0{\cdot}5) \times 10^8$ l mol^{-1} s^{-1}.

The rate constant k_9 was independent of acid concentration over the range from 0·1 to 1·0M, but increased with increasing ionic strength over the same range (Table 1).

TABLE 1

Rate and equilibrium constants for reactions of Tl^{2+} ions

Reaction	$\frac{I}{\text{M}}$	$\frac{[H^+]}{\text{M}}$	$\frac{k\ (25\ °C)}{l\ mol^{-1}\ s^{-1}}$
(9) $2k_9$	0·25	0·10	$(5{\cdot}2 \pm 0{\cdot}5) \times 10^8$
	0·25	0·25	$(5{\cdot}5 \pm 0{\cdot}5) \times 10^8$
	0·50	0·25	$(9{\cdot}2 \pm 0{\cdot}9) \times 10^8$
	1·0	0·25	$(1{\cdot}3 \pm 0{\cdot}1) \times 10^9$
	1·0	0·50	$(1{\cdot}2 \pm 0{\cdot}1) \times 10^9$
	1·0	1·0	$(1{\cdot}3 \pm 0{\cdot}1) \times 10^9$
	1·0	1·0	$3{\cdot}3 \times 10^8$ [a]
	ca. 0	pH 6·5	$2{\cdot}8 \times 10^9$ [b]
(10) k_{10}	0·75	0·25	$(6{\cdot}2 \pm 0{\cdot}1) \times 10^3$
k_{-10} ($\equiv k_{13}$)	2·7	0·25	$3{\cdot}16 \times 10^{-3}$ [c]
K_{10} ($\equiv 1/K_{13}$) $2{\cdot}0 \times 10^6$			
(12) k_{12}	0·30	0·25	$(1{\cdot}1 \pm 0{\cdot}15) \times 10^6$
k_{-12} ($\equiv k_{15}$)	3·0	0·40	$4{\cdot}60 \times 10^{-2}$ [d]
K_{12} ($\equiv 1/K_{15}$) $7{\cdot}1 \times 10^7$			

[a] Ref. 14. [b] Ref. 13. [c] Ref. 5. [d] Ref. 4.

The rate constant was almost independent of temperature over the range from 15 to 45 °C; the apparent activation energy derived from an Arrhenius plot of the data is $7{\cdot}9 \pm 1{\cdot}5$ kJ mol^{-1}.

Reaction of Thallium(II) *Ions with* Co^{2+}.—In solutions of Tl^{III} (10^{-3}M) and acid (0·25M) containing Co^{2+} ions (0·02—0·2M) the decay of the absorbance due to Tl^{II} produced by the flash was faster than in solutions which did not contain Co^{2+}. In these solutions OH radicals produced by reaction (8) were scavenged by the Co^{2+} ions [16] and it was not necessary to add Tl^+ for this purpose. The decay of the absorbance was no longer second order because oxidation of Co^{2+} ions by Tl^{II} [reaction (10)] was competing with disproportionation reaction (9). The rate of disappearance of

$$Tl^{2+} + Co^{2+} \longrightarrow Tl^{+} + Co^{3+} \qquad (10)$$

Tl^{II} ions under these conditions was given by equation (11). Reaction (10) was pseudo-first order because the concentra-

$$-d[Tl^{II}]/dt = k_{10}[Co^{2+}][Tl^{II}] + 2k_9[Tl^{II}]^2 \qquad (11)$$

tion of Co^{2+} ions was always very much greater than that of Tl^{II} produced by the flash. The disappearance of the Tl^{II} ions was always a mixed first- and second-order process because, even at the highest Co^{II} concentrations, reaction (10) was not fast enough for (9) to be neglected. A numerical integration procedure [15] was used to calculate pseudo-first-order rate constants for reaction (10) from the experimental data, using the value for the disproportionation rate constant k_9 already determined. The second-order rate constant for reaction (10) was obtained from the gradient of a plot of the pseudo-first-order rate constants against the concentration of Co^{2+} ions (Figure 2). At 25 °C and ionic strength 0·75 mol l^{-1}, k_{10} was $(6{\cdot}2 \pm 0{\cdot}5) \times 10^3$ l mol^{-1} s^{-1}.

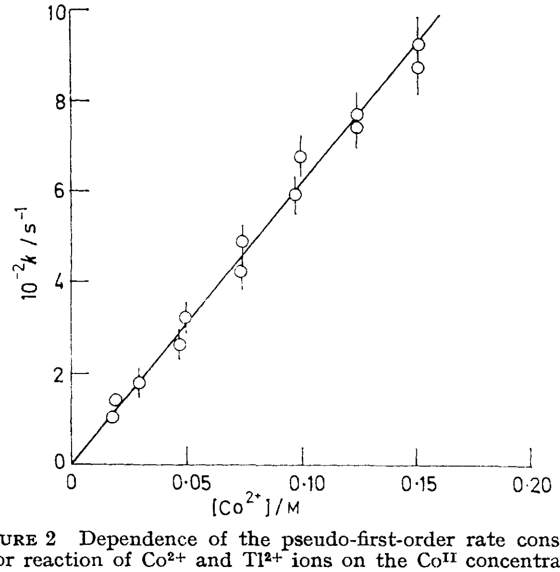

FIGURE 2 Dependence of the pseudo-first-order rate constant for reaction of Co^{2+} and Tl^{2+} ions on the Co^{II} concentration at 25 °C. The solutions contained 10^{-3}M-Tl^{3+} and 0·25M-H^+, and I = 0·75M

Reaction of Thallium(II) *Ions with* Fe^{3+}.—When solutions which contained both Tl^{III} and Fe^{III} ions were photolysed it was necessary to ensure that the major light-absorbing species was $TlOH^{2+}$ and that only a negligible fraction of the light from the flash lamp was absorbed by Fe^{III}. $FeOH^{2+}$ Ions have a ligand-to-metal charge-transfer absorption band at *ca.* 300 nm and could interfere with the absorption due to Tl^{III}. The concentration of $FeOH^{2+}$ ions was kept low by the use of relatively high (0·25M) acid and low ($<10^{-3}$M) Fe^{III} concentrations. Under these conditions, with Tl^+ ions (10^{-3}M) added to the solutions to scavenge OH radicals [produced by reaction (8) or by the equivalent reaction of $FeOH^{2+}$ ions] and produce further Tl^{II}, the yields of Tl^{II} were only slightly less than in experiments without added Fe^{III}.

Decay of the Tl^{II} absorbance was accelerated by the added Fe^{3+} ions, but absorbance against time curves were too complex for simple analysis. The initial increase in absorbance, due to Tl^{II} produced by the flash, decayed to a final value which was less than the initial absorbance before the flash because reaction between Tl^{II} and Fe^{3+} ions removed Fe^{III} which was also absorbing at the wavelengths of the measurements. The hydrolysis equilibrium between Fe^{3+} and $FeOH^{2+}$ ions was sufficiently rapid to be maintained during the course of reaction (12) and the absorbance did not change after the disappearance of Tl^{II}.

$$Tl^{2+} + Fe^{3+} \longrightarrow Tl^{3+} + Fe^{2+} \qquad (12)$$

The rate of disappearance of the Tl^{II} ions was dependent on the Fe^{III} concentration, but pseudo-first-order rate constants for reaction (12) could not be obtained by treating the competition between the disproportionation and reaction (12) in the same way as that between the disproportionation and (10). Numerical integration in the latter case is dependent on absolute determination, from experimental data for the variation of absorbance with time, of the concentration of the reactant consumed by the two simultaneous reaction paths. In the case of reaction (12) the experimental absorbance was dependent on the concentrations of both Tl^{II} and Fe^{III} ions and there was no simple relation between the absorbance and the concentration of Tl^{II}. Rate constants for reaction (12) were therefore obtained by calculating absorbance against time curves using as data absorption coefficients and initial concentrations of Tl^{II} and Fe^{III} ions, the measured disproportionation rate constant k_9, and trial values of the rate constant for reaction (12). The calculations were carried out on a CDC 6400 computer using a program which simulated coupled reactions by numerical integration.* Values of k_{12} were successively refined in this way to give the best fit to experimental absorbance against time curves. The results of the method are shown in Figure 3 and experimental curves could in general be reproduced with an accuracy of $\pm 5\%$ over three half-lives. For our experimental conditions the method was sufficiently sensitive to the value of k_{12} to give a precision of 10—15% to pseudo-first-order rate constants for reaction (12).

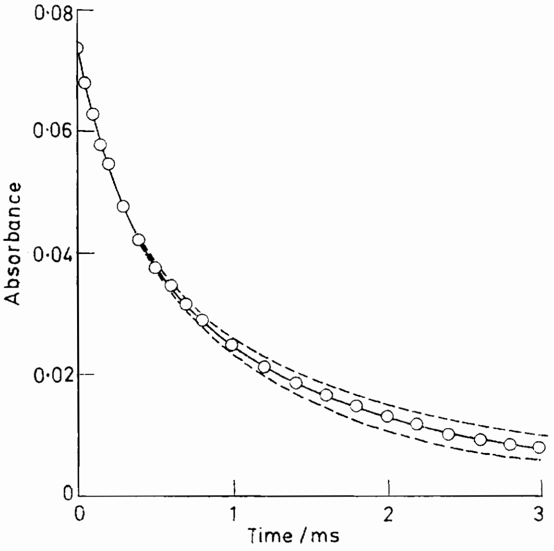

FIGURE 3 The reaction of Fe^{3+} and Tl^{2+} ions. An example of the fit of the computer synthesis of absorbances at various times to experimental data (○) for one run; (——) computed values for $k_9 = 5{\cdot}5 \times 10^8$ l mol^{-1} s^{-1} and for a pseudo-first-order rate constant for reaction (12) of $3{\cdot}2 \times 10^2$ s^{-1}; and (– – –), computed values for the same value of k_9 and for pseudo-first-order rate constants of $3{\cdot}8 \times 10^2$ (lower curve) and $2{\cdot}6 \times 10^2$ s^{-1} (upper curve). The solutions contained 2×10^{-3}M-Tl^{3+}, 10^{-3}M-Tl^{+}, and $2{\cdot}7 \times 10^{-4}$M-Fe^{3+} in 0·25M-acid

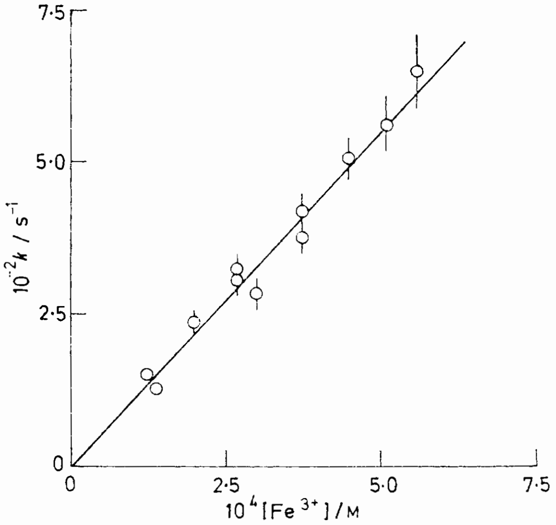

FIGURE 4 Dependence of the pseudo-first-order rate constant for the reaction of Fe^{3+} and Tl^{2+} ions on the Fe^{III} concentration at 25 °C. The solutions contained 10^{-3}M-Tl^{+}, 2×10^{-3}M-Tl^{3+}, and 0·25M-H^{+}, and $I = 0{\cdot}30$M

The second-order rate constant for reaction (12) was obtained from the gradient of a plot of the pseudo-first-order rate constants against the concentration of Fe^{3+} ions (Figure 4). At 25 °C and ionic strength 0·30 mol l^{-1}, k_{12} was $(1{\cdot}1 \pm 0{\cdot}15) \times 10^6$ l mol^{-1} s^{-1}.

DISCUSSION

The spectrum of Tl^{II} (Figure 1) was the same in both 0·1 and 1·0M acid and closely resembled that recorded by Cercek *et al.*[13] at pH 2 following pulse radiolysis of solutions of Tl^{+} ions in the absence of oxygen. At pH 6·5 in the presence of N_2O the peak at 260 nm was double the height of that recorded at pH 2 in the absence of N_2O and an additional peak with an absorption maximum at *ca.* 360 nm was found. The latter peak was not that at *ca.* 400 nm attributed by Cercek *et al.* to the Tl_2^{+} ion, and must also have been due to a Tl^{II} species produced by the OH radicals. The absorption at 360 nm is possibly due to a hydrolysed form of Tl^{II}, perhaps $TlOH^{+}$ ions. If the absorption at 260 nm is due to a charge-transfer band of Tl^{2+}_{aq} ions $TlOH^{+}$ would be expected to show a charge-transfer band at longer wavelengths. The spectrum of Tl^{II} could not be investigated by us over a wide range of acid concentration but the spectral difference between pH 1 and 6·5 is consistent with the assumption that Tl^{2+} ions undergo hydrolysis. The hydrolysis constant would be expected to be of the same magnitude as those of other bivalent metal ions of similar radius (the radius of the Tl^{2+} ion has been estimated to be 1·13 Å),[11] that is between 10^{-7} and 10^{-9} mol l^{-1}, and

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* The program is an extension of Program WR16 by K. H. Schmidt, Argonne Nat. Lab. Rep., ANL-7199 (TID-4500), Argonne, 1966.

from the spectral differences the value is probably at the higher end of this range.

The value of the disproportionation rate constant $2k_9$ (Table 1) lies between two previous values, whether expressed as $2k_9/\varepsilon$ or as the rate constant calculated using the absorption coefficient measured in pulse-radiolysis experiments. The value is higher than that of Burchill and Wolodarsky [14] possibly because of the different spectrum recorded by these authors. Our value of $2k_9$ is a factor of five smaller than that of Cercek *et al.*[13] and the difference is larger than the experimental errors. The ionic strength was considerably larger in the present work than in the pulse-radiolysis experiments, but the effect of increased ionic strength is to increase the rate constant not decrease it (Table 1). The reaction has a very low activation energy, 7·9 kJ mol^{-1}, and is certainly diffusion controlled. It has previously been suggested [14] that the reduction in the disproportionation rate in acid solution is due to different reaction rates for Tl^{2+} and $TlOH^+$ ions. The spectra suggest that hydrolysis of Tl^{2+} ions does occur in neutral solutions and, as the reaction is diffusion controlled, the main effect of hydrolysis will be to increase the encounter rate due to the lower charge product of the hydrolysed reactants.

Standard reduction potentials of reactive intermediate oxidation states such as Tl^{II} are valuable in assessing the probable participation of these oxidation states in reactions of stable oxidation states of the element, but are in general difficult to measure directly. For the two couples involving Tl^{II}, E_1^0 and E_2^0 [reactions (1) and (2)] have been estimated from theoretical calculations of the entropy of Tl^{2+} ions and by assuming that the mechanism of the electron-exchange reaction between Tl^I and Tl^{III} involves participation of Tl^{II} (ref. 11).

TABLE 2

Standard reduction potentials (in V) involving Tl^{2+} ions

$Tl^{3+} + e^- \rightleftharpoons Tl^{2+}$	0·31 ± 0·05
$Tl^{2+} + e^- \rightleftharpoons Tl^+$	2·22 ± 0·05
$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$	1·25 [a]

[a] Ref. 19.

Values of E_1^0 and E_2^0 can be obtained from measurements of the forward and reverse rate constants of suitable reactions. We chose to measure rate constants for reactions of Co^{2+} and Fe^{3+} ions with Tl^{2+} [reactions (10) and (12)], because for both reactions the reverse reactions had already been investigated and were known to involve production of Tl^{II}, the standard reduction potentials of $Co^{3+}{}_{aq}$ and $Fe^{3+}{}_{aq}$ ions are well defined, and the systems are kinetically uncomplicated.

The oxidation of Tl^+ by Co^{3+} ions [reactions (13) and (14)] was studied by Ashurst and Higginson [5] in the presence of Co^{2+}. At high ratios of the concentrations of Co^{2+} and Co^{3+} ions there was a reduction in the rate of oxidation of Tl^I which was interpreted as being due to competition between Co^{2+} and Co^{3+} for Tl^{2+} generated by

$$Tl^+ + Co^{3+} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} Tl^{2+} + Co^{2+} \tag{13}$$

$$Tl^{2+} + Co^{3+} \xrightarrow{k_{14}} Tl^{3+} + Co^{2+} \tag{14}$$

the first step, reaction (13). The second step, reaction (14), was assumed to be rapid * and, at the lowest initial Co^{2+} ion concentrations, the rate constant which they measured was the forward rate constant for reaction (13), k_{13}. At 25 °C and ionic strength 2·7 mol l^{-1} in 0·25M-perchloric acid, k_{13} was $3{\cdot}16 \times 10^{-3}$ l mol^{-1} s^{-1}. We measured the rate constant for the reaction between Co^{2+} and Tl^{2+} ions [reaction (10)]; k_{10} is equivalent to k_{-13} at the same acid concentration but at a lower ionic strength, 0·75 mol l^{-1}, but within limitations imposed by neglecting any effects due to the different media we can calculate K_{13}, the equilibrium constant for the reaction between Tl^+ and Co^{3+} ions, as the ratio $k_{13} : k_{10}$. At 25 °C K_{13} is $5{\cdot}1 \times 10^{-7}$. The standard reduction potential of $Co^{3+}{}_{aq}$ ions in 0·5M-perchloric acid is +1·85 V [18] which leads to a value of +2·22 ± 0·05 V for E_2^0, the standard reduction potential of Tl^{2+} ions. This calculation neglects environmental differences between the measurements of the two rate constants and the quoted error in E_2^0 includes an estimate of the error arising from this neglect. The value of E_2^0 is considerably higher than that of +1·5 V estimated by Hush,[11] but confirms a previous expectation that Tl^{II} would prove to be a powerful oxidising agent.[12]

The rate of reduction of Tl^{3+} by Fe^{2+} ions was found by Ashurst and Higginson [4] to be retarded by Fe^{3+} produced in the reaction and by added Fe^{3+}. This was the first direct evidence of participation of Tl^{II} in oxidation-reduction reactions of Tl^I and Tl^{III} ions. The two steps in the reaction [(15) and (16)] were less clearly differentiated than in the reaction of Tl^+ and Co^{3+} ions, and the

$$Tl^{3+} + Fe^{2+} \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} Tl^{2+} + Fe^{3+} \tag{15}$$

$$Tl^{2+} + Fe^{2+} \xrightarrow{k_{16}} Tl^+ + Fe^{3+} \tag{16}$$

rate constants k_{16} and k_{-15} (k_{-15} is equivalent to k_{12}) were of the same order of magnitude. The forward rate constant k_{15} was obtained from initial rate measurements and at 25 °C and ionic strength 3·0 mol l^{-1} was $4{\cdot}6 \times 10^{-2}$ l mol^{-1} s^{-1} in 0·4M-perchloric acid. The conditions under which we measured the rate constant for the reverse reaction, k_{12}, were lower in both ionic strength (0·30 mol l^{-1}) and acid concentration (0·25M) but once again, within limits imposed by the neglect of these differences, we can calculate the equilibrium

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* The assumption was correct. We have measured k_{14} and found it to be $9{\cdot}5 \times 10^6$ l mol^{-1} s^{-1}.[17]

[17] B. Falcinella and G. S. Laurence, *J.C.S. Dalton*, in the press.

[18] B. Warnquist, *Inorg. Chem.*, 1970, **9**, 682.

[19] W. M. Latimer, ' Oxidation Potentials,' 2nd edn., Prentice-Hall, New York, 1952.

constant for reaction (15), k_{15}, as the ratio $k_{15} : k_{12}$. At 25° C K_{15} is $4{\cdot}2 \times 10^{-8}$. From the standard reduction potential of Fe^{3+}_{aq} ions in acid solution, +0·77 V,[19] and the value of K_{15} we obtain a value of $+0{\cdot}33 \pm 0{\cdot}05$ V for E_1^0, the standard one-equivalent reduction potential of Tl^{3+} ions. The quoted error in the value of E_1^0 includes an estimate of errors arising from differences in acidity and ionic strengths of the solutions in which the kinetic measurements were made. The value of E_1^0 is very much lower than the estimate of +1·0 V made by Hush.[11]

Values which we have obtained for E_1^0 and E_2^0 are independent of the standard reduction potential for the Tl^{III}–Tl^{I} couple, which can therefore be used to check the reliability of these values. The standard potential of the Tl^{III}–Tl^{I} couple should be equal to one-half of the sum of the potentials E_1^0 and E_2^0. Calculated from our values of E_1^0 and E_2^0 the standard potential of the Tl^{III}–Tl^{I} couple is $+1{\cdot}28 \pm 0{\cdot}1$ V, in excellent agreement with the accepted value of +1·25 V.[19] The agreement suggests that the neglect of environmental effects introduces no very large errors in the values of E_1^0 and E_2^0 and confirms the correctness of these reduction potentials obtained from kinetic data for two independent reaction systems.†

The values of E_1^0 and E_2^0 are markedly different from earlier estimates and although Higginson [12] has suggested that E_2^0 should have a value in excess of +1·5 V the very high value which we have obtained is unexpected. The estimate of the reduction potentials by Hush [11] was dependent on the assumption that the electron-exchange reaction between Tl^+ and Tl^{3+} ions involves two successive one-electron-transfer steps, and this assumption is to some extent conditioned by values of the reduction potentials. The reduction potentials provide a more reliable base than was previously available for discussing oxidation-reduction chemistry of thallium. Tl^{2+}_{aq} ions are much stronger oxidising agents than Co^{3+}_{aq} and the reduction potential is close to that of Cu^{3+}_{aq}. The value of E_2^0 is so high that it is possible that in neutral solutions Tl^{2+} ions may exist in equilibrium with OH radicals, as do Cu^{3+}_{aq} ions.[20] Recently radical species produced by a one-electron-transfer process from Tl^{III} have been detected by e.s.r. spectroscopy in the reaction of thallium(III) trifluoroacetate with aromatic hydrocarbons,[21] and in aqueous solutions some organic oxidations by Tl^{III} may involve Tl^{II} or OH radicals equilibrated with Tl^{II}.

The failure to observe reaction between Tl^+ ions and Br_2^- radical ions is explained by the large value of E_2^0. For reaction (3) the standard free-energy change is +44 kJ mol^{-1} and the extent of reaction will be small even if the reaction rate is high enough for it to compete with disproportionation of the radical anions. The oxidation of Tl^+ ions by Br_2 has been investigated [22] and it was concluded that the reaction follows a two-equivalent-change path. This conclusion is supported by thermodynamic data, for ΔG^0 for the one-electron-transfer reaction (17) is +176 kJ mol^{-1}.

$$Tl^+ + Br_2 \longrightarrow Tl^{2+} + Br_2^- \tag{17}$$

The standard reduction potential of Tl^{2+} ions is so close to that of OH radicals that some limitation is placed on the mechanism of reaction (5). The standard reduction potential of the hydroxyl radical in basic solution is +2·0 V [19] and the equilibrium constant for reaction (5), K_5, is therefore $1{\cdot}8 \times 10^{-4}$. The rate constant for the reaction between OH radicals and Tl^+ ions is 8×10^9 l mol^{-1} s^{-1} (ref. 13) and the reaction cannot take place in a single step, for then the rate constant of the reverse reaction, k_{-5}, would have to exceed the diffusion-controlled limit by four orders of magnitude. The most reasonable mechanism consistent with both kinetic and equilibrium data is that in which the first step is production of $TlOH^{2+}$ ions, which will rapidly protonate in acid solution [reactions (18) and (19)]. For this mechanism the product of the equilibrium constants K_{18} and K_{19} is

$$Tl^+ + OH \underset{k_{-18}}{\overset{k_{18}}{\rightleftharpoons}} TlOH^+ \tag{18}$$

$$TlOH^+ + H^+ \rightleftharpoons Tl^{2+} + H_2O \tag{19}$$

$1{\cdot}8 \times 10^{10}$ l^2 mol^{-2}. If the rate constant k_5 applies to the forward path of reaction (18) there is no limitation on the rate constant for the reverse reaction, k_{-18}, if any reasonable value is assumed for K_{19} (a value of *ca.* 10^7 has been argued above). It has recently been shown that reaction between Fe^{2+} ions and OH radicals proceeds by an outer-sphere mechanism without intermediate formation of $FeOH^{2+}$ (ref. 23), but the standard free-energy change for this reaction imposes no limitation on the rate of the reverse reaction. In the oxidation of Cu^{2+} ions by OH radicals the favourable free-energy change for formation of Cu^{III} is also small in acid solution and a mechanism involving $CuOH^{2+}$ formation has been proposed.[20]

The mechanism of the electron-exchange reaction between Tl^{I} and Tl^{III} ions [24] has been the subject of much discussion and both a successive one-electron-transfer mechanism [reactions (20)—(22)] and a two-

$$Tl^{+*} + Tl^{3+} \underset{k_{-20}}{\overset{k_{20}}{\rightleftharpoons}} Tl^{2+*} + Tl^{2+} \tag{20}$$

$$Tl^{2+*} + Tl^+ \rightleftharpoons Tl^{+*} + Tl^{2+} \tag{21}$$

$$Tl^{2+*} + Tl^{3+} \rightleftharpoons Tl^{3+*} + Tl^{2+} \tag{22}$$

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† An independent measure of E_1^0 may be obtained from the rate constants k_{15} and k_{16} combined with the ratio $k_{16} : k_{-15}$ obtained by Ashurst and Higginson.[4] We have measured k_{16} (ref. 17) and from this data obtain a value of $+0{\cdot}37 \pm 0{\cdot}1$ V for E_1^0.

[20] D. Meyerstein, *Inorg. Chem.*, 1971, **10**, 638.

[21] I. H. Elson and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 5060.

[22] L. G. Carpenter, N. H. Ford-Smith, R. P. Bell, and R. W. Dodson, *Discuss. Faraday Soc.*, 1960, **29**, 92; N. H. Ford-Smith, N. Sutin, and R. W. Dodson, *ibid.*, p. 134.

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

[24] R. J. Prestwood and A. C. Wahl, *J. Amer. Chem. Soc.*, 1949, **71**, 3137; G. Harbottle and R. W. Dodson, *ibid.*, 1951, **73**, 2442.

electron-transfer mechanism [reaction (23)] have been proposed. The participation of $\mathrm{Tl^{II}}$ ions in the electron-exchange reaction is less easy to demonstrate than in reactions involving net chemical change. Sykes[10] observed that the rate of oxidation of $\mathrm{V^{IV}}$ by $\mathrm{Tl^{III}}$ was not changed by addition of $\mathrm{Tl^{+}}$ ions in conditions where

$$\mathrm{Tl^{+*} + Tl^{3+} \rightleftharpoons Tl^{+} + Tl^{3+*}} \qquad (23)$$

the rate of electron exchange between $\mathrm{Tl^{I}}$ and $\mathrm{Tl^{III}}$ was faster than the rate of oxidation of $\mathrm{V^{IV}}$. The oxidation is known to proceed through intermediate formation of $\mathrm{Tl^{2+}}$ ions[8] and he concluded that these were not produced by the electron-exchange reaction. The exchange rate is however increased if $\mathrm{Tl^{2+}}$ ions are produced photochemically[9] or chemically[25] in the exchange solutions. Stranks and Yandell[9] suggested that observation of the $\mathrm{Tl^{2+}}$ ions is not necessary for their participation in thermal electron exchange. The $\mathrm{Tl^{2+}}$ ions formed as a geminate pair in a solvent cage by reaction (20) are so reactive [the disproportionation, reaction (9), is diffusion controlled] that they do not escape from the solvent cage before undergoing a second electron transfer, which in half of the events results in exchange. In these circumstances $\mathrm{Tl^{2+}}$ ions will not be experimentally observable in the bulk of the solution and will not be scavenged by normal scavenging reactions.

The mechanism of the electron-exchange reaction can be discussed in greater detail using ΔG^0 for reaction (20) calculated from the standard reduction potentials $E_1{}^0$ and $E_2{}^0$; $\Delta G_{20}{}^\circ$ is $+185$ kJ mol^{-1}, equivalent to a value for the equilibrium constant K_{20} of 8×10^{-33}. The rate constant k_{-20} ($\equiv k_9$) is $5{\cdot}5 \times 10^8$ l mol^{-1} s^{-1} and therefore the forward rate constant, k_{20}, must be $4{\cdot}4 \times 10^{-24}$ l mol^{-1} s^{-1}. This rate constant is so much smaller than that for the electron-exchange reaction (k_{ex} is *ca.* 7×10^{-5} l mol^{-1} s^{-1} at 25 °C)[26] that free $\mathrm{Tl^{2+}}$ ions in the bulk of the solution, formed by reaction (20), cannot be involved in the electron-exchange reaction. In terms of free energy, $\Delta G_{20}{}^\circ$ is 87 kJ mol^{-1} more positive than the free energy of activation for the exchange reaction. The hypothesis that $\mathrm{Tl^{2+}}$ ions are formed as geminate pairs which do not escape from the solvent cage makes little difference to the conclusion that $\mathrm{Tl^{II}}$ does not take part in the thermal electron-exchange reaction. The reaction can be treated as three equilibrium steps [reactions (24—(26)], diffusion of $\mathrm{Tl^{+}}$ and $\mathrm{Tl^{3+}}$ ions into the solvent cage, electron transfer inside the cage, and

$$\mathrm{Tl^{+} + Tl^{3+} \rightleftharpoons (Tl^{+},Tl^{3+})_{cage}} \qquad (24)$$

$$\mathrm{(Tl^{+},Tl^{3+})_{cage}} \underset{k_{-25}}{\overset{k_{25}}{\rightleftharpoons}} \mathrm{(Tl^{2+},Tl^{2+})_{cage}} \qquad (25)$$

$$\mathrm{(Tl^{2+},Tl^{2+})_{cage} \rightleftharpoons Tl^{2+} + Tl^{2+}} \qquad (26)$$

diffusion of $\mathrm{Tl^{2+}}$ ions from the cage into the bulk solution. The overall equilibrium constant $K_{20} = K_{24}K_{25}K_{26}$. The constants K_{24} and $1/K_{26}$ are those for equilibrium formation of the pairs of ions $\mathrm{Tl^{+},Tl^{3+}}$ and $\mathrm{Tl^{2+},Tl^{2+}}$ in a solvent cage, from ions in the bulk solution, and the values may be estimated from a model for ion association. For the present argument it is sufficient to observe that the models[27] suggest that the difference between K_{24} and K_{26} is probably no more than two or three orders of magnitude. The constant K_{25} will therefore have a maximum value of *ca.* 10^{-29} and represent the ratio of the rates of electron transfer between a $\mathrm{Tl^{+}}$ and a $\mathrm{Tl^{3+}}$ ion and between two $\mathrm{Tl^{2+}}$ ions. The rate of electron transfer between two $\mathrm{Tl^{2+}}$ ions in the cage, k_{-25}, is not known from the rate of the disproportionation reaction as this is diffusion controlled, but the rate cannot be greater than rates of electronic transitions, *i.e. ca.* 10^{14} s^{-1}. Even this rate leads to a rate constant, k_{25}, for electron transfer between $\mathrm{Tl^{+}}$ and $\mathrm{Tl^{3+}}$ ions in the solvent cage of 10^{-15} s^{-1}, which is many orders of magnitude smaller than the thermal-exchange rate constant.

We conclude that the thermal-exchange reaction between $\mathrm{Tl^{I}}$ and $\mathrm{Tl^{III}}$ cannot take place by a mechanism which involves formation of $\mathrm{Tl^{II}}$ either as individualised ions in the bulk solution or as geminate pairs in a solvent cage. The mechanism of thermal exchange must be a two-equivalent one, with a transition state in which two electrons are transferred. This transition state is considerably lower in energy than the energy required to form a pair of $\mathrm{Tl^{2+}}$ ions from $\mathrm{Tl^{+}}$ and $\mathrm{Tl^{3+}}$ and the much lower $\Delta G^{\ddagger}$ for the two-equivalent process is in marked contrast to the reaction between $\mathrm{V^{II}}$ and $\mathrm{Hg^{II}}$ where, at 25 °C, $\Delta G^{\ddagger}$ is approximately the same for both one- and two-equivalent paths.[28]

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