Electron Transfer Reaction between Thallium(I) and Thallium(III) in the Presence of Cerium(IV) in Aqueous Solution

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The kinetics of the electron transfer reaction between Tl(I) and Tl(III) was investigated in the presence of Ce(IV) by use of a radioactive tracer ^{204}Tl. The apparent rate constant of the reaction, k_{app}, was dependent upon [H$^+$] and [Co(IV)] ($<0.6\times10^{-3}$ M) and can be expressed by

$$k_{\text{app}} = k_{\text{A}} + \frac{k_{\text{B}}}{[\text{H}^+]} + \left(k_{\text{C}} + \frac{k_{\text{D}}}{[\text{H}^+]}\right)[\text{Ce(IV)}].$$

k_{app} is gradually saturated to a limiting value according to [H$^+$] at higher [Ce(IV)]. The observed values are $k_{\text{A}}=4.70\text{ M}^{-1}\text{ h}^{-1}$, $k_{\text{B}}=2.13\text{ h}^{-1}$, $k_{\text{C}}=1.30\times10^3\text{ M}^{-2}\text{ h}^{-1}$, and $k_{\text{D}}=2.61\times10^3\text{ M}^{-1}\text{ h}^{-1}$ at 50 °C. Since Ce(IV) is a one-electron-oxidant, Tl(I) is oxidized by one-electron transfer to produce Tl(II) as an intermediate. However, in the absence of one-electron-oxidant or -reductant, two electrons are transferred from Tl(I) to Tl(III) not through double steps of one-electron transfer but predominantly through a single step of two-electron transfer.

The electron transfer reaction between thallium(I) and thallium(III) has been investigated on the effects of hydrogen ion,[1-6)] anions such as NO_3^-,[1)] Cl^-,[2,7-9)] CN^-,[10)] SO_4^{2-},[11,12)] Br^-,[13,14)] and N_3^-,[15)] organic acids such as acetic,[16,17)] succinic,[16,17)] and mono-, di-, and tri-chloroacetic acids,[18)] and various organic substances[19-21)] by using a radioactive isotope ^{204}Tl as a tracer. The investigations clarified the roles of the effective substances on the electron transfer reaction.

An important feature of this "thallous-thallic" redox reaction is that two electrons in total are transferred between them. The occurrence of thallium(II) has been proposed as a reaction intermediate on the basis of kinetic studies of the redox reaction between iron(II) and thallium(III)[22)] and between thallium(I) and cerium(IV)[23)] and on the irradiation of X-rays[24)] and ultraviolet rays[25)] upon the thallium(I)-thallium(III) system. Consequently, the electron transfer reaction between thallium(I) and thallium(III) in the absence of catalyst has been considered to proceed not *via* a single step of "two-electron transfer" but *via* two successive steps of "one-electron transfer" with thallium(II) as an intermediate.

Recently, the acceleration due to the addition of iron(II) to thallium(I)-thallium(III) system[26)] and of iron(III) to uranium(IV)-uranium(VI) system[27)] was reported, the latter being also an overall reaction with a two-electron transfer. We have investigated the thallium(I)-thallium(III) system in the presence of cerium(IV), and the functions of thallium(II) when it occurs.

Experimental

Materials. Thallium(I) perchlorate was prepared by dissolving thallium metal of 99.99% purity in warm perchloric acid, crystallized, washed by ethanol and dried. The crystal thus obtained was in anhydrous form.

Thallium(III) perchlorate was prepared by dissolving Tl_2O_3 in 4 M perchloric acid at 60—70 °C for many hours. Both thallium(I) and thallium(III) salts were confirmed to be free of chloride ion.

$\text{Ce}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$ and $\text{Ce}(\text{SO}_4)_2\cdot n\text{H}_2\text{O}$ were used in aqueous perchloric acid as salts of cerium(III) and cerium(IV) respectively. The sulfate ion concentration was regulated with sodium sulfate. As a radioactive tracer, ^{204}Tl obtained in the form of TlNO_3 was converted into TlClO_4 in perchloric acid. The ionic strength of the reaction solutions was adjusted with sodium perchlorate.

Pure water was made by treating tap water with ion-exchange resin, followed by distillation of the alkaline permanganate solution.

Analyses of Thallium Concentrations. Thallium(III) was determined by titration with disodium ethylenediaminetetraacetate (EDTA) by use of Xylenol Orange as an indicator at pH 4—5 and 50—55 °C. Thallium(I) was oxidized by bromine to thallium(III), most of the excess bromine being removed by heating and the rest completely removed by addition of a few drops of methanolic solution of phenol. Thallium(III) was then titrated in a similar way. A mixture of thallium(I) and (III) was titrated before and after the treatment with bromine, and the concentration of thallium (I) was determined from the difference.

Rate of Oxidation of Thallium(I) by Cerium(IV). Cerium(IV) was spectrophotometrically observed to exhibit an absorption peak at a wavelength of 320 nm, while no absorption was observed in thallium(I), (III), or cerium(III) at wavelengths greater than 300 nm in perchloric and sulfuric acid solution. Thus, the rate of oxidation of thallium(I) by cerium(IV) could be followed by virtue of the decrease in the absorbance of cerium(IV). The absorbance was measured with a Hitachi UV-VIS spectrophotometer Model 139. The oxidation rate could be also followed by measuring the increase in the radioactivity of thallium(III), when thallium(I) was labeled, by a method similar to that for the electron transfer reaction.

Rate of Electron Transfer Reaction Between Thallium(I) and Thallium(III). A reaction mixture containing TlClO_4, $\text{Tl(ClO}_4)_3$, $\text{Ce(SO}_4)_2$, HClO_4, Na_2SO_4, and NaClO_4 was set in a thermostat in advance. The reaction was initiated at the instant the radioactive thallium(I) was added to the solution. The concentration of sulfate ion, the ionic strength, and temperature of the reaction were always maintained at $[\text{SO}_4^{2-}]=0.02$ M, $\mu=3$ M, and 50 °C, respectively.

An aliquot of the reaction solution was taken out into a quenching solution at appropriate time intervals. The quenching solution contained EDTA and was cooled in ice-water beforehand. Ten minutes after removal of an aliquot of the reaction solution, sodium chromate was added as a precipitating reagent for thallium(I), and the pH value was adjusted to about 4—5 with ammonia and ammonium acetate solution. Fifteen minutes later, the solution was filtered, thallium(III) being separated from thallium(I) into the filtrate. A small portion of the filtrate was gently evaporated in a stainless-steel dish with irradiation by an infrared lamp and the β-radioactivity due to thallium(III) was counted with an Aloka G-M scaler Model TDC-102.

In earlier works on thallium(I)-thallium(III) systems, cyanide ion was usually used as a masking reagent for thallium(III). However, since cyanide ion is highly poisonous, EDTA was adopted in its place. The rate of masking of thallium(III) by EDTA is slower than that by cyanide ion, and EDTA has a masking action even toward thallium(I) in an alkaline medium. Thus, EDTA sometimes induced a zero-time exchange as much as 30—40%, which could be attributed to the accelerated exchange on the interface at the moment of precipitation, whenever EDTA was added at the same time as chromate ion and ammonia. In spite of these disadvantages of EDTA, the procedure described above was found to be accurate enough.

Results and Discussion

Oxidation of Thallium(I) by Cerium (IV). The standard redox potentials of Tl^{3+}/Tl^{+} and Ce^{4+}/Ce^{3+} are 1.28 V[28] and 1.74 V[29] at 25 °C, respectively. Thus, the reaction $Tl^{+}+2Ce^{4+}\rightleftarrows Tl^{3+}+2Ce^{3+}$ occurs almost completely towards right with an equilibrium constant $\log K=15.6$. But the rate of the reaction is very small as observed photometrically at a wavelength of 360 nm (Fig. 1). In practice, the autoreduction of cerium(IV) takes place even in the absence of thallium(I) in the air, besides the reduction by thallium(I). Consequently, the values of [Ce(IV)] at time t employed in the figure are the observed ones corrected for the autoreduction.

If the reaction proceeds *via* the following two successive paths by stepwise reductions,

$$\mathrm{Tl(I)} + \mathrm{Ce(IV)} \rightleftarrows \mathrm{Tl(II)} + \mathrm{Ce(III)} \quad (k_1,\ k_{-1}) \tag{1}$$

$$\mathrm{Tl(II)} + \mathrm{Ce(IV)} \rightarrow \mathrm{Tl(III)} + \mathrm{Ce(III)} \quad (k_2) \tag{2}$$

Tl(II) is produced as an intermediate species. By the method of steady state applied to Tl(II), the following rate equation is obtained, when $[\mathrm{Tl(I)}]_0$ is much greater than $[\mathrm{Ce(IV)}]_0$.

$$\ln\frac{[\mathrm{Ce(IV)}]}{[\mathrm{Ce(IV)}]_0} - \frac{k_{-1}}{k_2-k_{-1}}\left(\frac{[\mathrm{Ce(IV)}]_0}{[\mathrm{Ce(IV)}]}-1\right) = \frac{-2k_1k_2[\mathrm{Tl(I)}]}{k_2-k_{-1}}t \tag{3}$$

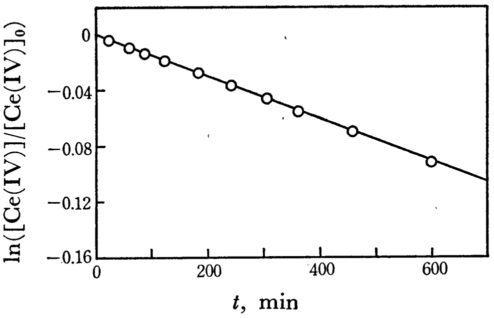

Fig. 1. Rate of oxidation of Tl(I) by Ce(IV) at $[H^+]=1.0$ M, $[SO_4^{2-}]=0.02$ M, $\mu=3$ M, and 50 °C, observed at 360 nm.
$[\mathrm{Tl(I)}]_0=0.03$ M, $[\mathrm{Ce(IV)}]_0=0.001$ M

Since k_{-1} is supposed to be negligibly small as compared with k_2, Eq. 3 may be simplified as follows.

$$\ln\frac{[\mathrm{Ce(IV)}]}{[\mathrm{Ce(IV)}]_0} = -2k_1[\mathrm{Tl(I)}]t \tag{4}$$

This is satisfied in Fig. 1, where the plot of $\ln([\mathrm{Ce(IV)}]/[\mathrm{Ce(IV)}]_0)$ against t shows a straight line, from the slope of which $k_1=0.17\ \mathrm{M^{-1}\,h^{-1}}$ is obtained at 50 °C.

If k_{-1} were much greater than k_2, Eq. 3 would become the following equation, whose linear relationship does not hold in this case.

$$\ln\frac{[\mathrm{Ce(IV)}]}{[\mathrm{Ce(IV)}]_0} + \frac{[\mathrm{Ce(IV)}]_0}{[\mathrm{Ce(IV)}]} - 1 = \frac{2k_1k_2[\mathrm{Tl(I)}]}{k_{-1}}t \tag{5}$$

Electron Transfer Reaction Between Thallium(I) and Thallium(III). When $\log(x_\infty - x)$ was plotted against t, straight lines were always obtained irrespective of the presence or absence of cerium(IV), x and x_∞ being the specific radioactivities of thallium(III) in the reaction solution at time t and at time of equilibrium, respectively. Two typical plots in the absence and presence of cerium(IV) are shown in Fig. 2.

Since the reaction was very slow and it was too troublesome to determine x_∞ by observation for every kinetic run, x_∞ was estimated by calculation on the basis of statistical distribution of radioactivity between thallium(I) and thallium(III) at equilibrium as $x=x_t\cdot[\mathrm{Tl(III)}]/([\mathrm{Tl(I)}]+[\mathrm{Tl(III)}])$, where x_t is the total radioactivity of ^{204}Tl.

Thus, the apparent rate constant k_{app} of the electron transfer reaction is given from McKay's relation,[30] since the reaction is of the first order with respect to both [Tl(I)] and [Tl(III)], Rate$=k_{app}[\mathrm{Tl(I)}][\mathrm{Tl(III)}]$.

$$k_{app} = \frac{0.693}{([\mathrm{Tl(I)}]+[\mathrm{Tl(III)}])t_{1/2}} \tag{6}$$

Here $t_{1/2}$ is the half-life period of the reaction, which is easily obtained from the slope of the straight line in Fig. 2.

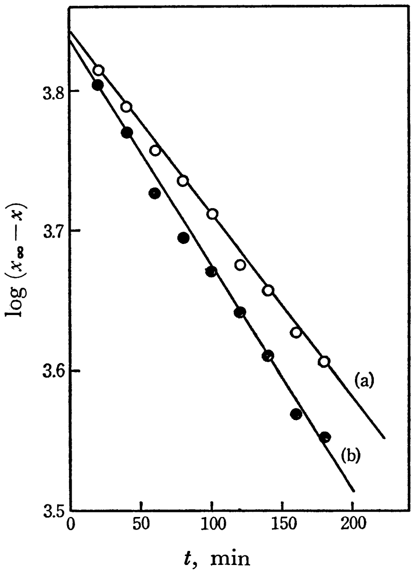

Fig. 2. McKay's plot of $\log(x_\infty - x)$ *vs.* time t at $[\mathrm{Tl(I)}]=[\mathrm{Tl(III)}]=0.01$ M, $[SO_4^{2-}]=0.02$ M, $[H^+]=0.50$ M, $\mu=3$ M, and 50 °C.
(a) $[\mathrm{Ce(IV)}]=0$, (b) $[\mathrm{Ce(IV)}]=0.001$ M

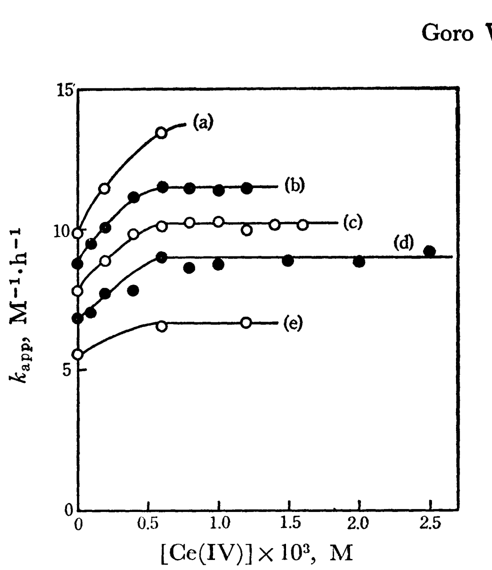

Fig. 3. Dependence of k_{app} upon [H$^+$] and [Ce(IV)] at [SO$_4^{2-}$]=0.02 M, μ=3 M, and 50 °C.
(a) [H$^+$]=0.41 M, (b) [H$^+$]=0.50 M, (c) [H$^+$]=0.70 M, (d) [H$^+$]=1.00 M, (e) [H$^+$]=1.50 M

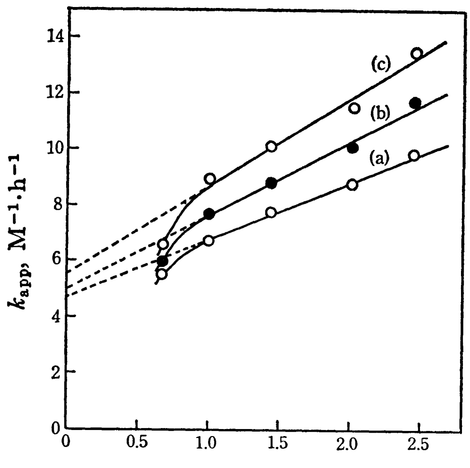

Fig. 4. Linear relationships between k_{app} and [H$^+$]$^{-1}$ at various [Ce(IV)] at [SO$_4^{2-}$]=0.02 M, μ=3 M, and 50 °C.
(a) [Ce(IV)]=0, (b) [Ce(IV)]=0.2×10^{-3} M, (c) [Ce(IV)]=0.6×10^{-3} M

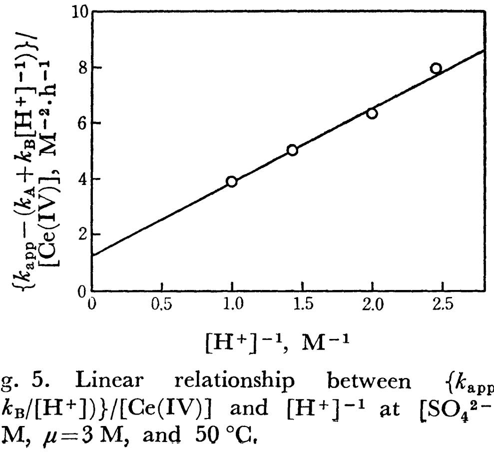

Fig. 5. Linear relationship between $\{k_{app}-(k_A+k_B/[H^+])\}/[Ce(IV)]$ and [H$^+$]$^{-1}$ at [SO$_4^{2-}$]=0.02 M, μ=3 M, and 50 °C.

The results obtained in the concentration range [H$^+$]=0.4–1.5 M and [Ce(IV)]=0–2.5×10^{-3} M are illustrated in Fig. 3. We see that k_{app} increases with decreasing [H$^+$] at constant [Ce(IV)] and with increasing [Ce(IV)] at constant [H$^+$] when [Ce(IV)] is less than 0.6×10^{-3} M. Above this concentration, k_{app} is saturated to a limiting value at respective [H$^+$].

i. When [Ce(IV)]$\leqq$0.6×10^{-3} M: Linear relationships of k_{app} with [H$^+$]$^{-1}$ at [Ce(IV)]=0, 0.2×10^{-3}, and 0.6×10^{-3} M are shown in Fig. 4, and another linear relationship of (k_{app}-intercept in Fig. 3)/[Ce(IV)] with [H$^+$] in Fig. 5. The following equation of k_{app} is thus established as functions of [H$^+$] and [Ce(IV)], where k_A, k_B, k_C, and k_D are constants.

$$k_{app}=\left(k_A+\frac{k_B}{[H^+]}\right)+\left(k_C+\frac{k_D}{[H^+]}\right)[Ce(IV)] \tag{7}$$

From the intercepts and slopes of these straight lines, the values of the individual rate constants at 50 °C can be determined as:

$$k_A = 4.70\ M^{-1}\,h^{-1}$$
$$k_B = 2.13\ h^{-1}$$
$$k_C = 1.30\times10^3\ M^{-2}\,h^{-1}$$
$$k_D = 2.61\times10^3\ M^{-1}\,h^{-1}$$

At least four sets of reactants, *viz.* oxidant, reductant, reductant, and catalyst, may be involved in parallel in the electron transfer reaction between thallium(I) and thallium(III) species; k_B and k_D may be connected with the hydrolyzed species of one of its participants. The sulfate ion is an accelerating ligand, bonding with thallium(I) and/or thallium(III).[11,12]

ii. When [Ce(IV)] exceeds 0.6×10^{-3} M: At increased cerium(IV) concentrations, k_{app} gradually deviates from the linearity in Eq. 7 but reaches a saturated value at respective acid concentrations.

According to the results of irradiation of ultraviolet rays on thallium(I)-thallium(III) system,[25] the rates of exchange of the following are very fast.

$$^*Tl(I) + Tl(II) \rightleftarrows {}^*Tl(II) + Tl(I) \quad (k_I) \tag{8}$$
$$^*Tl(II) + Tl(III) \rightleftarrows {}^*Tl(III) + Tl(II) \quad (k_{III}) \tag{9}$$
$$k_I = 1.8\times10^8\ M^{-1}\,h^{-1} \text{ at } 25°C$$
$$k_{III} = 3.6\times10^8\ M^{-1}\,h^{-1} \text{ at } 25°C$$

The acceleration of electron transfer in the thallium(I)-thallium(III) system by cerium(IV) is due to the initial occurrence of thallium(II) through Reaction 1, followed by the rapid exchanges through Reactions 8 and 9. Thus, the increased rate due to cerium(IV) might be proportional to [Tl(II)], which is approximately expressed as follows.

$$[Tl(II)] = \frac{k_1[Tl(I)][Ce(IV)]}{k_{-1}[Ce(III)]+k_2[Ce(IV)]} \tag{10}$$

As [Ce(IV)] increases, [Tl(II)] increases at first, and attains a limiting value [Tl(II)]=(k_1/k_2)[Tl(I)]. This may qualitatively correspond to the saturation phenomenon of k_{app} at higher [Ce(IV)] as seen in Fig. 3.

How are the Two Electrons Transferred? The two-electron transfer system between thallium(I) and thallium(III) is also known to be accelerated by the addition of a minute amount of iron(II),[22,26] which is a one-electron-reductant. In this case, the smaller the concentration of iron(II), the larger the acceleration, as long as [Fe(II)]$>6.8\times10^{-5}$ M. A rate equation for the fact has been proposed.[26]

The reduction of thallium(III) by iron(II) was not affected by the addition of thallium(I) at all but retarded by the addition of iron(III).[22] Thus, the reduction was deduced to proceed in the following paths.

$$\text{Tl(III)} + \text{Fe(II)} \rightleftarrows \text{Tl(II)} + \text{Fe(III)} \quad (11)$$

$$\text{Tl(II)} + \text{Fe(II)} \rightarrow \text{Tl(I)} + \text{Fe(III)} \quad (12)$$

Thallium(II) is produced as an intermediate, and since Reaction 12 is rate-determining, Reaction 11 maintains partial equilibrium. It can therefore be reasonably said that the addition of iron(III) diminishes [Tl(II)] and consequently the total rate, but the addition of thallium(I) has no effect on the total rate.

It is worthwhile investigating the effect of the addition of iron(III) on the rate of thallium(I)-thallium(III) electron transfer reaction. If this electron transfer were to exactly undergo an initial production of thallium(II), as expressed by

$$\text{Tl(I)} + \text{Tl(III)} \rightleftarrows \text{Tl(II)} + \text{Tl(II)}, \quad (13)$$

the addition of iron(III) should interfere with Reaction 13 on account of the promotion of the backward reaction of Reaction 11, resulting in the retardation of thallium(I)-thallium(III) electron transfer, which would have otherwise occurred through Reactions 8 and 9.

The results of addition of various metal ions to the thallium(I)-thallium(III) system are listed in Table 1. Although the concentration of iron(III) added in the reaction system seems to be high enough to interfere with the production of thallium(II) markedly, no actual retardation effect on the rate of the electron transfer but only a slight acceleration was observed. Attention should be paid to the fact that iron(III) has no ability to oxidize thallium(I) to thallium(II) and as a consequence to thallium(III), on account of its oxidation potential.

This suggests that the two electrons are transferred not through double one-electron transfer steps but mostly through a single step of two-electron transfer without thallium(II) species as the intermediate, when neither one-electron-oxidant nor one-electron-reductant exists in the thallium(I)-thallium(III) system; the chemical equation is as follows.

$$^*\text{Tl(I)} + \text{Tl(III)} \rightarrow {}^*\text{Tl(III)} + \text{Tl(I)} \quad (14)$$

A tentative check by ESR method for the occurrence of thallium(II) was negative in a mixture of thallium(I) and thallium(III) species, while thallium(II) was detected in the presence of one-electron-oxidant.[31] Since chromium exists in such oxidation states as II, III and IV, chromium(II) is known to reduce thallium(III) to thallium(I) as a two-electron-reductant, resulting in chromium(IV) which forms a binuclear complex with an unreacted chromium(II).[32,33] This supports the possibility of the direct two-electron transfer mechanism between thallium(I) and thallium(III) in the absence of one-electron catalyst.

It might be concluded that thallium(I)-thallium(III) electron transfer reaction proceeds mainly *via* a single step of two-electron transfer in the absence of catalyst and *via* two steps of stepwise one-electron transfer in the presence of a one-electron-oxidant or a one-electron-reductant.

Table 1. Effects of metal ions on the rate of Tl(I)-Tl(III) electron transfer reaction at [Tl(I)]=[Tl(III)]=0.01 M, [H$^+$]=0.5 M, μ=1.57 M, and at 50°C

[Added ion], M	k_{app}, M^{-1} h^{-1}
None	2.77
Cu^{2+} 0.01	2.77
Fe^{3+} 0.1	2.98, 2.89, 2.65
Hg^{2+} 0.01	2.88

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