

## The Effects of Some Organic Molecules on the Rate of the Thallium(I)—Thallium(III) Exchange Reaction

OLE FARVER

*The Royal Danish School of Pharmacy, Chemical Laboratory D,  
DK-2100 Copenhagen, Denmark*

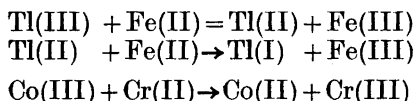
The thallium(I)—thallium(III) electron exchange rate has been measured at 25°C in aqueous perchloric acid at ionic strengths of 1.20 and 3.00 in presence of some organic compounds containing conjugated double bonds.

For 2,2'-bipyridyl a large decrease in exchange rate was observed and attributed to the formation of an unreactive complex with thallium(III). For other amines such as 4,4'-bipyridyl, 4-aminopyridine, and 4-cyanopyridine which are known only to complex weakly with the reactants, no change in the reaction rate was observed. With oxalic acid which forms a rather weak complex with thallium(III), a decrease in the exchange rate was observed which could be quantitatively described by considering the concurrent reduction of thallium(III) through a  $\text{TlC}_2\text{O}_4^+$  species which does not participate in the exchange reaction.

The experimental results are discussed in relation to earlier work on the homogeneous catalysis of the thallium(I)—thallium(III) exchange reaction.

The thallium(I)—thallium(III) exchange reaction is of particular interest in that there is considerable kinetic evidence that it does not occur through the formation of thallium(II) as an intermediate.<sup>1</sup>

We report here a study of the effect of some complexing agents on the Tl(I)—Tl(III) exchange reaction, planned so that we could compare our results with the effect of the same ligands on the two following reactions which are known to involve one-electron changes



### EXPERIMENTAL

*Reagents.* A thallium(I) perchlorate stock solution was prepared by dissolving recrystallised B.D.H. laboratory reagent thallos carbonate in a stoichiometric amount of concentrated perchloric acid. The concentration of Tl(I) was determined iodometrically.

A stock solution of Tl(III) perchlorate was prepared by anodic oxidation of standardised Tl(I) perchlorate in 2 M perchloric acid. The concentration of Tl(III) was determined gravimetrically with 8-hydroxyquinoline as described in Ref. 2.

Tl-204 was bought as  $\text{Tl}_2\text{SO}_4$  at Kjeller in Norway; specific activity, 5 mCi/mg Tl. Labelled thallic perchlorate was prepared by oxidation with bromine followed by precipitation of  $\text{Tl}_2\text{O}_3$  with concentrated ammonia. The oxide was carefully washed with water and redissolved in concentrated perchloric acid.

All organic compounds were purified by recrystallisation.

*Kinetic experiments.* In the reactions with no ligands added and also those involving amine ligands, all components of a reaction mixture except Tl(I) were mixed in brown flasks and the specific activities were measured immediately. The mixtures were then allowed to stand overnight in a thermostat at  $25 \pm 0.05^\circ\text{C}$  and the activities were determined again to ensure that reduction of Tl(III) had not occurred. Tl(I) solutions which also had been thermostated were then added, and aliquots of the reaction mixtures were taken out at fixed times. After separation (see below) the activity of the Tl(III) fraction was determined. As Tl(III) is reduced by oxalic acid, this compound was added after Tl(I).

Tl(I) and Tl(III) was separated by adding 1 ml of the reaction mixture to 10 ml of a half concentrated aqueous ammonia solution containing 0.5 M sodium chromate, 1 M sodium cyanide, and 10 % ethanol. 1 ml thallic perchlorate was immediately added, and this mixture was allowed to stand for 10 min in an ice bath to ensure complete aggregation of thallic chromate. The mixture was then centrifuged, and 10 ml of the supernatant liquid was counted using a Mullard Geiger tube type MX 124 and a conventional counting circuit. The zero time exchange never exceeded 2–3 %.

All kinetic runs were made in duplicate and the deviation between the results was always less than 5 %.

Except for the oxalate containing solutions, plots of  $\ln(1-F)$  — where  $F$  is the fraction of exchange that has occurred — against time were linear for several half lives. The second order rate constants were calculated from these plots in the usual way.

The mathematical treatment of the oxalic acid reactions is described later in this paper.

## RESULTS

*No ligands added.* The rate of exchange in the same media as for the catalytic studies is illustrated by a typical plot (Fig. 1). Table 1 shows the experimentally found rate constants which are in excellent agreement with those reported by previous workers.<sup>3,4</sup>

*2,2'-Bipyridyl.* The stability constants of  $\text{Tl}(\text{bipy})^{3+}$  and  $\text{Tl}(\text{bipy})_2^{3+}$  are reported in the literature.<sup>5</sup>  $K_1 = 10^{9.4}$  and  $K_2 = 10^{6.7}$  at  $25^\circ\text{C}$  in 0.5 M  $\text{NaNO}_3/0.5$  M  $\text{HNO}_3$ .

The exchange experiments were carried out at  $25^\circ\text{C}$  in 0.68 M  $\text{NaClO}_4/0.5$  M  $\text{HClO}_4$ . Table 2 shows the variation in exchange rate with the ligand concentration. The decrease in rate corresponds to the increase in  $\text{Tl}(\text{bipy})^{3+}$  concentra-

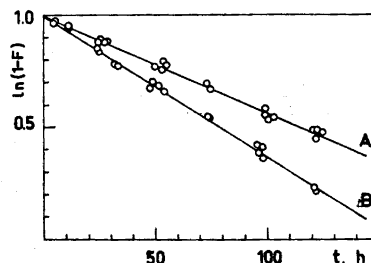


Fig. 1. Plot of  $\ln(1-F)$  against time. Curve A:  $1.15 \times 10^{-3}$  M  $\text{Tl}(\text{ClO}_4)_3$ ,  $4.34 \times 10^{-2}$  M  $\text{TlClO}_4$ , 2.95 M  $\text{HClO}_4$ ,  $I = 3.00$  M. Curve B:  $1.81 \times 10^{-2}$  M  $\text{Tl}(\text{ClO}_4)_3$ ,  $1.81 \times 10^{-2}$  M  $\text{TlClO}_4$ , 1.00 M  $\text{HClO}_4$ ,  $I = 1.20$  M.

Table 1. Results of exchange experiments between Tl(I) and Tl(III) in aqueous perchlorate solutions at 25°C.

| $I$<br>M | $H^+$<br>M | Tl(III)<br>$M \times 10^2$ | Tl(I)<br>$M \times 10^2$ | $t_{\frac{1}{2}}$<br>h | $k$<br>$M^{-1} h^{-1}$ |
|----------|------------|----------------------------|--------------------------|------------------------|------------------------|
| 1.20     | 1.00       | 1.81                       | 1.81                     | 46.5                   | .41                    |
| 1.20     | 1.00       | .906                       | .906                     | 98.0                   | .39                    |
| 1.20     | 1.00       | .516                       | .516                     | 168                    | .40                    |
| 3.00     | 1.50       | .115                       | 4.34                     | 67.5                   | .23                    |
| 3.00     | 2.00       | .115                       | 4.34                     | 64.5                   | .24                    |
| 3.00     | 2.25       | .115                       | 4.34                     | 65.0                   | .24                    |
| 3.00     | 2.50       | .115                       | 4.34                     | 68.0                   | .23                    |
| 3.00     | 2.75       | .115                       | 4.34                     | 70.5                   | .22                    |
| 3.00     | 2.95       | .115                       | 4.34                     | 67.5                   | .23                    |

Table 2. Results of exchange experiments between Tl(I) and Tl(III) in aqueous perchlorate solutions in presence of 2,2'-bipyridyl.  $H^+ = 0.5$  M,  $I = 1.20$  M,  $T = 25^\circ C$ .

| Tl(III)<br>$M \times 10^3$ | Tl(I)<br>$M \times 10^3$ | Bipy<br>$M \times 10^3$ | $t_{\frac{1}{2}}$<br>h | $k$<br>$M^{-1} h^{-1}$ |
|----------------------------|--------------------------|-------------------------|------------------------|------------------------|
| 3.39                       | 3.39                     | 0                       | 265                    | 0.38                   |
| 3.39                       | 3.39                     | 1.70                    | 560                    | 0.18                   |
| 3.39                       | 3.39                     | 3.39                    | 1400                   | 0.07                   |
| 3.39                       | 3.39                     | 5.09                    | very large             | 0                      |
| 3.39                       | 3.39                     | 6.78                    | very large             | 0                      |
| 3.39                       | 3.39                     | 10.22                   | very large             | 0                      |

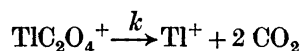
tion. When the concentration of 2,2'-bipyridyl is bigger than that of Tl(III) the rate of exchange is extremely slow.

*4,4'-Bipyridyl, 4-aminopyridine, and 4-cyanopyridine.* All experiments were carried out at 25°C in 1.00 M perchloric acid. The ionic strengths were corrected to 1.20 by adding  $NaClO_4$ . Table 3 gives the experimental results. From this table it is clear that in the concentration range employed here, there is no observable kinetic effect.

Table 3. Results of exchange experiments between Tl(I) and Tl(III) in aqueous perchlorate solutions in presence of 4,4'-bipyridyl, 4-aminopyridine, and 4-cyanopyridine.  $H^+ = 1.00$ ,  $I = 1.20$ ,  $T = 25^\circ\text{C}$ .

| Ligand          | L<br>$M \times 10^2$ | Tl(III)<br>$M \times 10^2$ | Tl(I)<br>$M \times 10^2$ | $t_{\frac{1}{2}}$<br>h | $k$<br>$M^{-1} h^{-1}$ |
|-----------------|----------------------|----------------------------|--------------------------|------------------------|------------------------|
| 4,4'-Bipyridyl  | 8.20                 | 1.81                       | 1.81                     | 48.0                   | .40                    |
|                 | 8.20                 | .906                       | .906                     | 98.0                   | .39                    |
|                 | 8.20                 | .516                       | .516                     | 165                    | .41                    |
| 4-Aminopyridine | 9.06                 | 1.81                       | 1.81                     | 54.5                   | .35                    |
|                 | 9.06                 | .906                       | .906                     | 103                    | .37                    |
|                 | 9.06                 | .516                       | .516                     | 168                    | .40                    |
| 4-Cyanopyridine | 1.43                 | .516                       | .516                     | 172                    | .39                    |
|                 | 2.87                 | .516                       | .516                     | 185                    | .36                    |
|                 | 5.73                 | .516                       | .516                     | 175                    | .38                    |

*Oxalic acid.* A series of experiments were made at  $25^\circ\text{C}$  in 3.00 M perchlorate solutions in which oxalic acid and thallic ion concentrations were held equal. The stability constant of the oxalate complex with Tl(III) has recently been reported.<sup>6</sup>  $K = 860$  at  $25^\circ\text{C}$  in 3.0 M perchlorate solution. No complex formation with Tl(I) was observed. The thallic complex decomposes, however, according to the scheme



with the rate constant  $k = 0.111 \text{ h}^{-1}$  at  $25^\circ\text{C}$  in 3.0 M perchlorate solution.<sup>6</sup>

The experimental results from an exchange experiment are shown in Fig. 2, where the decrease in 204-Tl labelled Tl(III) in a 3.00 M perchloric acid solution is plotted against time. Fig. 2 shows furthermore the expected decrease in labelled Tl(III) in the absence of exchange, as calculated using the first order rate constant given above.

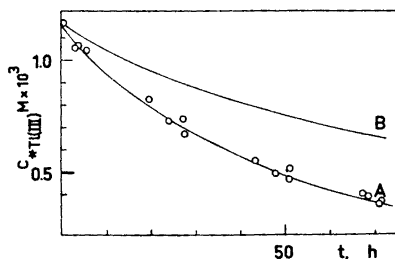


Fig. 2. Decrease in 204-Tl labelled Tl(III) with time.  $1.15 \times 10^{-3} \text{ M Tl}(\text{ClO}_4)_3$ ,  $4.34 \times 10^{-2} \text{ M TlClO}_4$ ,  $1.15 \times 10^{-3} \text{ M}$  oxalic acid,  $2.95 \text{ M HClO}_4$ ,  $I = 3.00 \text{ M}$ . Curve A: experimental results. Curve B: calculated, assuming that no exchange occurred.

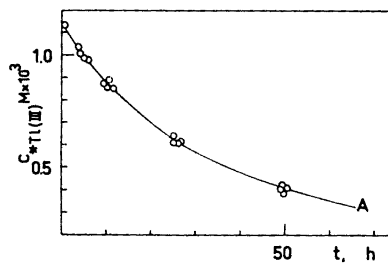
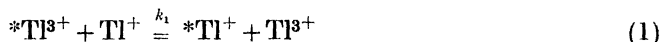


Fig. 3. Decrease in 204-labelled Tl(III) with time.  $1.15 \times 10^{-3} \text{ M Tl}(\text{ClO}_4)_3$ ,  $4.34 \times 10^{-2} \text{ M TlClO}_4$ ,  $1.15 \times 10^{-3} \text{ M}$  oxalic acid,  $1.50 \text{ M HClO}_4$ ,  $I = 3.00 \text{ M}$ . Curve A: calculated, assuming that no exchange occurred. O: experimental points.

Similar experiments were carried out with varying hydrogen ion concentration down to 1.50 M. Below 2.00 M perchloric acid the exchange reaction becomes negligible. This is shown in Fig. 3 where the solid curve represents the decrease in labelled Tl(III) in the absence of exchange and the circles represent experimental points.

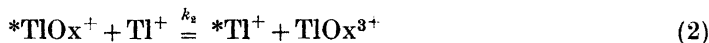
In order to interpret the experimental results the following simple mechanism involving three concurrent reactions was considered.

*Exchange path (1).* A concerted two-electron transfer between the aquo ions according to (1)



Here as in the following, \*Tl means  $^{204}\text{Tl}$  labelled thallium.

*Exchange path (2).* Two-electron transfer between  $Tl^+$  and the oxalate complex,  $TlOx^+$ .



*Path (3).* Decomposition of the  $TlOx^+$  complex.



Let  $x$  and  $y$  be total concentrations of \*Tl(III) and Tl(III),  $r$  and  $s$  concentrations of free  $*Tl^{3+}$  and  $Tl^{3+}$ , and  $a$  and  $c$  initial concentrations of \*Tl(III) and Tl(I), respectively. According to the above reaction schemes, the following two differential equations then apply

$$\frac{dx}{dt} = k_1(s(a-x) - r(c-y)) + k_2((y-s)(a-x) - (x-r)(c-y)) - k_3(x-r)$$

$$\frac{dy}{dt} = k_1(r(c-y) - s(a-x)) + k_2((x-r)(c-y) - (y-s)(a-x)) - k_3(y-s)$$

Furthermore, if the concentrations of Tl(III) and oxalic acid are equal then

$$K = \frac{([TlOx^+] + [*TlOx^+])[H^+]^2}{([Tl^{3+}] + [*Tl^{3+}])([H_2Ox])} \rightarrow \frac{(x-r+y-s)}{(r+s)^2} = 860/[H^+]^2$$

As complexes of Tl(III) are labile, the ratio between non-radioactive and radioactive  $Tl^{3+}$  will always be equal to the ratio between the total concentrations of non-radioactive and radioactive Tl(III)

$$s/r = y/x$$

These four equations were solved numerically by means of a GIER computer. The differential equations were integrated numerically, using Runge-Kutta's method.<sup>7</sup> A program for minimising  $\sum(x_{\text{obs}} - x_{\text{calc}})^2$  as a function of  $k_1$ ,  $k_2$ , and  $k_3$  was written in GIER algol, using the Letagrop procedure.<sup>8</sup> Table 4 gives the results of the calculation. The  $k_1$  values obtained here are within

Table 4. Results of exchange experiments between Tl(I) and Tl(III) in aqueous perchlorate solutions in presence of oxalic acid.  $T=25^{\circ}\text{C}$ .

| Tl(I)<br>$\text{M} \times 10^3$ | Tl(III)<br>$\text{M} \times 10^3$ | $\text{H}_2\text{Ox}$<br>$\text{M} \times 10^3$ | $\text{H}^+$<br>$\text{M}$ | $k_1$<br>$\text{M}^{-1} \text{h}^{-1}$ | $k_2$<br>$\text{M}^{-1} \text{h}^{-1}$ | $k_3$<br>$\text{M}^{-1} \text{h}^{-1}$ |
|---------------------------------|-----------------------------------|---|----------------------------|--|--|--|
| 4.34                            | 1.15                              | 1.15  | 2.95                       | $.237 \pm .005$                        | $.004 \pm .019$                        | $.109 \pm .003$                        |
| 4.34                            | 1.15                              | 1.15  | 2.75                       | $.230 \pm .004$                        | $-.005 \pm .010$                       | $.115 \pm .003$                        |
| 4.34                            | 1.15                              | 1.15  | 2.50                       | $.225 \pm .010$                        | $.004 \pm .029$                        | $.108 \pm .003$                        |
| 4.34                            | 1.15                              | 1.15  | 2.25                       | $.201 \pm .015$                        | $-.005 \pm .012$                       | $.119 \pm .003$                        |
| 4.34                            | 1.15                              | 1.15  | 2.00                       | $.169 \pm .050$                        | $-.007 \pm .034$                       | $.114 \pm .003$                        |

experimental error in good agreement with the values given in Table 1, where no ligands were added. As  $k_2$  is always zero within experimental error, it is concluded that electron transfer under the present conditions only takes place through exchange path (1).

#### DISCUSSION

The thallium(I)–thallium(III) exchange reaction has long been known to be catalysed by platinum metal<sup>2,9</sup> which only affects the rate of the Tl(III)–Fe(II) reaction in a way which can be attributed to the catalysis of the postulated Tl(II)–Fe(II) step.<sup>10</sup> Recently it has been reported<sup>11</sup> that in homogeneous solution 2- and 4-aminopyridine behave similarly to Pt-metal in the Tl(III)–Fe(II) reaction. It has been shown here that under similar conditions these compounds do not affect the rate of the Tl(I)–Tl(III) exchange. For oxalate, in which a conjugated double bond system joins two metal ions, remote attack has been postulated<sup>12</sup> to explain the fast transfer of one electron from the Cr(II)–aqua ion to  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ . We have shown here that oxalic acid does not increase the rate of the concerted two-electron Tl(I)–Tl(III) exchange reaction.

Both nitrate and sulphate ions are known to catalyse the Tl(I)–Tl(III) exchange.<sup>9,13,14</sup> In both cases the experimental data fit the following equation

$$k_{\text{obs}} = k_0 + aC_L + bC_L^2$$

where  $k_0$  is the rate constant with no added ligand and  $C_L$  is total ligand concentration. Brubaker and Mickel<sup>13</sup> showed that the sulphate data also equally well fit a mechanism in which exchange occurs only through the aqua ion path, and through two other paths involving one and three sulphate ions, respectively. In order to do this, it was assumed that the formation constants for  $\text{TlSO}_4^+$  and  $\text{TlSO}_4^-$  are equal. Brubaker *et al.*<sup>14</sup> suggested that the electron transfer occurred through symmetrical bridged intermediates. We find that the early nitrate data can be treated in the same way. In this case the formation constant for  $\text{TlNO}_3^{2+}$  is known to be about equal to the

formation constant for  $\text{TlNO}_3$  (both *ca.* 2 in the concentrated ionic media used here<sup>15</sup>). Thus, in this case the experimental rate constants obey the following expression

$$k_{\text{obs}} = 0.578 + 3.3(\alpha)(1 - \alpha) + 11\alpha^2[\text{NO}_3^-]_{\text{free}}$$

where  $\alpha = [\text{TlNO}_3]/[\text{Tl(I)}]_{\text{tot}} = [\text{TlNO}_3^{2+}]/[\text{Tl(III)}]_{\text{tot}}$ .

Ligands such as chloride and cyanide<sup>16</sup> do not catalyse but inhibit the reaction under conditions where only  $\text{Tl(III)}$  is detectably complexed. At higher concentrations where both  $\text{Tl(I)}$  and  $\text{Tl(III)}$  are complexed, analogous behavior to that of nitrate and sulphate is observed, and has also been interpreted as electron transfer occurring in symmetrical bridged intermediates.

Our results show that ligands which complex only with  $\text{Tl(III)}$  but not with  $\text{Tl(I)}$ , such as 2,2'-bipyridyl and oxalic acid inhibit the rate of exchange, while ligands such as 4,4'-bipyridyl, 4-cyanopyridine, and 4-aminopyridine which under the present conditions interact only weakly or not at all with  $\text{Tl(I)}$  and  $\text{Tl(III)}$  do not affect the rate at all.

We conclude that only ligands which bind appreciably to  $\text{Tl(III)}$  and also  $\text{Tl(I)}$  can increase the rate of exchange, as would be expected for reactions through a symmetrical bridged activated complex.

*Acknowledgement.* The author wishes to express his thanks to Dr. G. M. Nord, Chemistry Department I, University of Copenhagen, for originally having suggested this study, and for many valuable suggestions during the preparation of the manuscript.

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Received May 19, 1971.