347. *The Kinetics of the Reduction of Thallium*(III) *by the Trisdipyridylosmium*(II) *Ion in Aqueous Perchloric Acid.*

By D. H. IRVINE.

The rate of the reaction between thallium(III) and trisdipyridylosmium(II) ion, unlike that between thallium(III) and ferrous ion, increases slightly as the hydrogen-ion concentration is increased. The data can be interpreted by assuming that both unhydrolysed Tl^{3+}, as well as $Tl(OH)^{2+}$, react with $Os(dipy)_3^{2+}$. The values of the respective constants for the two reactions are $3{\cdot}6 \times 10^6 \exp(-6900 \pm 800/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$ and $3{\cdot}6 \times 10^9 \exp(-11{,}500 \pm 1000/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$. Chloride ions show the same retardation of the rate as in the analogous reaction of ferrous ions.

THE kinetics of the reduction of thallium(III) by simple aquated ferrous ion [1,2,3] is slow, the second-order constant at 25° being of the order of 10^{-2} l. mole^{-1} sec.$^{-1}$, and the rate increases as the hydrogen-ion concentration is decreased. Johnson [1] interpreted the results of the hydrogen-ion dependence on the basis that simple ferrous ion reacted with the hydrolysed species of Tl^{3+}, *viz.*, $Tl(OH)^{2+}$ and TlO^{+}, but Ashurst and Higginson [3] pointed out that there is no way of distinguishing from the data between such a mechanism and one in which unhydrolysed Tl^{3+} reacts with the hydrolysed species of ferrous ion.

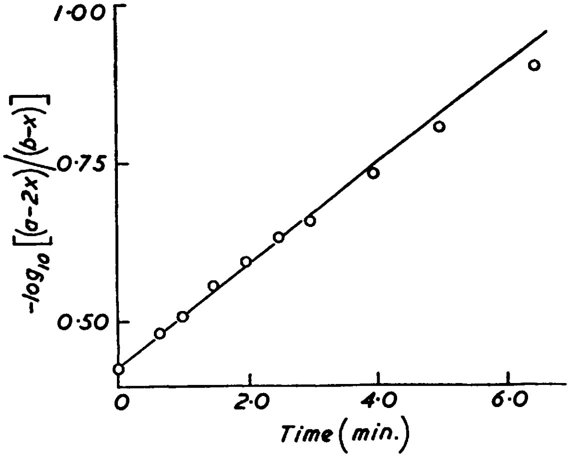
---

[1] Johnson, *J. Amer. Chem. Soc.*, 1952, **74**, 959.
[2] Forchheimer and Epple, *ibid.*, p. 5772.
[3] Ashurst and Higginson, *J.*, 1953, 3044.

In an attempt to find out whether the reduction of thallium(III) by a complex ion presented any essentially different features from its reduction by a simple aquated ion, the reaction between thallium(III) and $Os(dipy)_3^{2+}$ was investigated. Earlier work by George and Irvine[4] on the reduction of thallic ion by the ferrous tris-*o*-phenanthroline ion had suggested a close parallel between this reaction and that between thallium(III) and ferrous ion. However, a further investigation (unpublished results) of the former reaction indicated that the results were not significant as they corresponded to the irreversible oxidation of the ferrous tris-*o*-phenanthroline ion.

The reduction of thallium(III) by $Os(dipy)_3^{2+}$ is reversible in the sense that all the original $Os(dipy)_3^{2+}$ can be recovered after the reaction by addition of a reducing agent. As in the case of the analogous reaction with ferrous ion a departure from second-order kinetics was observed after about 60—70% of reaction. This can be seen in Fig. 1 which shows an example of the simple second-order plot [a = initial concentration of $Os(dipy)_3^{2+}$, b = initial concentration of thallium(III), and x is the amount by which thallium(III) is reduced in time t]. Ashurst and Higginson[3] attribute the departure from second-order kinetics, in the case of the ferrous ion reaction, to the retarding effect of iron(III) formed during the reaction, and presumably a similar explanation is applicable here. In other words, the overall reaction probably involves the following steps:

FIG. 1.



$$Tl^{III} + Os(dipy)_3^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Tl^{II} + Os(dipy)_3^{3+} \quad . \quad . \quad . \quad . \quad (1)$$

$$Tl^{II} + Os(dipy)_3^{2+} \xrightarrow{k_2} Tl^{I} + Os(dipy)_3^{3+} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Dependence of the Rate of the Reaction on the Hydrogen-ion Concentration.—The rate of the reaction between thallium(III) and $Os(dipy)_3^{2+}$ increased slightly as the hydrogen-ion concentration was increased. This behaviour is in contrast with the analogous reaction with ferrous ion where the rate decreased substantially with increased concentration of hydrogen ions. Table 1 shows the results of experiments carried out at 24·5°, with corresponding values for the reaction of ferrous ion for comparison. The values of the observed velocity constants (k_1) in this Table were derived from the slopes of the simple second-order plots. It is clear from Ashurst and Higginson's[3] work that values of k_1 obtained in this way are accurate.

---

[4] George and Irvine, *J.*, 1954, 587.

The data in Table 1 can be explained by assuming that $Os(dipy)_3^{2+}$ reacts with both unhydrolysed Tl^{3+} and $Tl(OH)^{2+}$. On this interpretation the observed velocity constant (k_1) of the reaction is given by the equation

$$k_1 = (k_a[H^+] + k_bK)/(K + [H^+]) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k_a and k_b are the velocity constants for the reaction between $Os(dipy)_3^{2+}$ and Tl^{3+} and $Tl(OH)^{2+}$ respectively, and K is the first hydrolysis constant of thallic ion. A plot of $k_1(K + [H^+])$ against $[H^+]$ from results in Table 1 is shown in Fig. 2. A value of $K(= 6{\cdot}4)$ at this temperature was obtained by interpolation from Johnson's [1] results. The plot is linear and shows that a mechanism in which both Tl^{3+} and $Tl(OH)^{2+}$ react with $Os(dipy)_3^{2+}$ is consistent with the observations.

TABLE 1. *Effect of the hydrogen-ion concentration on the rate of the reaction between* Tl^{III} *and* $Os(dipy)_3^{2+}$.

$[H^+]$	2·99	1·92	0·98	0·52
k_1 (l. mole^{-1} sec.$^{-1}$)	21·7	19·4	17·3	16·6
$10^2k_1'$ (l. mole^{-1} sec.$^{-1}$) for ferrous ion reaction	1·20	1·50	2·20	3·33

Ionic strength = 2·99; Temp. = 24·5°.
The results in row 3 were interpolated from ref. 1.

A similar expression to eqn. (3) can be obtained by assuming that the unhydrolysed Tl^{3+} reacts with $Os(dipy)_3^{2+}$ as well as a conjugate acid species $Os(dipy)_3H^{3+}$. On this basis the velocity constant of the reaction can be expressed by the equation

$$k^1 = \frac{[H^+]}{K + [H]}\left(\frac{k_a'[H^+]}{K_D + [H^+]} + \frac{k_b'K_D}{K_D + [H^+]}\right) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where k_a' and k_b' are the velocity constants for the reaction of Tl^{3+} with $Os(dipy)_3H^{3+}$ and $Os(dipy)_3^{2+}$ respectively and K_D is the dissociation constant of the acid $Os(dipy)_3H^{3+}$.

If $K_D \ll [H^+]$ then eqn. (4) reduces to

$$K_1 = (k_a'[H^+] + k_b'K_D)/(K + [H^+]) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is of the same form as eqn. (3). A decision as to whether equation (3) or equation (4) is a truer representation of the dependence of the rate on the hydrogen-ion concentration could be made by working at low hydrogen-ion concentration. Unfortunately this was not possible because of hydrolysis of thallic ion below a concentration of hydrogen ion of 0·3M. However, E.M.F. measurements on the $Os(dipy)_3^{2+}$–$Os(dipy)_3^{3+}$ couple [5] give no support for the assumption that K_D is much smaller than $[H^+]$ since the E.M.F. of the couple is unaffected by a change of hydrogen-ion concentration in the range 0·001M—0·025M. Accordingly eqn. (3) is preferred.

The Effect of Temperature on the Rate.—The rate of the reaction was measured at 17·5°, 24·5°, and 35·0° at various hydrogen-ion concentrations. A linear plot of $k_1\ (K + [H^+])$ against $[H^+]$ was obtained at each temperature and from these plots values of k_a and k_bK were obtained. Values of K of 5·1, 6·4, and 9·1 at these temperatures respectively were interpolated from Johnson's results,[1] and thence the corresponding values of k_b were determined. The values of k_a and k_b are recorded in Table 2. Expressed according to the Arrhenius equation, the values of k_a and k_b are $3{\cdot}6 \times 10^6$ exp $(-6900 \pm 800/\boldsymbol{R}T)$ and $3{\cdot}6 \times 10^9$ exp $(-11{,}500 \pm 1000/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$ respectively. It is noteworthy that the ratio of 10^3 between the A factors is comparable with

---

[5] Barnes, Dwyer, and Gyarfas, *Trans. Faraday Soc.*, 1952, **48**, 269.

that of 10^4 predicted by Glasstone, Laidler, and Eyring [6] for the reactions between $M_a^{2+} + M_b^{3+}$ and $M_a^{2+} + M_b^{2+}$. The activation energies for the processes are smaller than those for the thallous–thallic exchange [7] and for the reduction of thallium(III) by ferrous ion.

TABLE 2. *Effect of temperature on the rate of the reaction* (*ionic strength* = 2·99).

Temp.	k_a (l. mole^{-1} sec.$^{-1}$)	k_b (l. mole^{-1} sec.$^{-1}$)
17·5°	29·0 ± 2·0	8·4 ± 0·3
24·5	36·0 ± 2·0	14·7 ± 0·3
35·0	53·0 ± 6·0	23·5 ± 0·6

In terms of Zwolinski, Marcus, and Eyring's [8] picture of electron-transfer processes this is presumably due to the smaller degree of reorganisation required by the complex ion in the transition state. The difference in activation energies for the two processes is, however, difficult to understand. Different transfer processes seem to be indicated, though having the osmium(II) in the form of a complex ion presumably rules out the possibility of hydrogen-atom transfer. More data on the reactions of complex ions in solution are highly desirable in order to explain this and other phenomena. There is, for instance, George and Irvine's observation [4] that reactions between complex ions of like charge can proceed with velocity constants greater than 10^5 l. mole ^{1} sec.$^{-1}$.

FIG. 2.

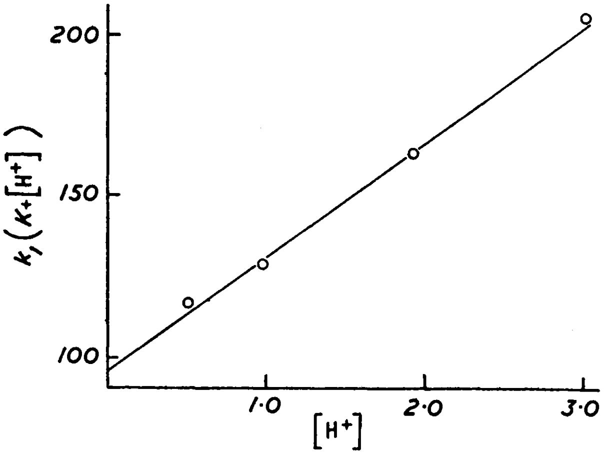


TABLE 3. *Effect of chloride ion on the rate of reaction.*

$10^5[Cl^-]$	9	4·0	7·0	10·0	100·0
k_1 (l. mole^{-1} sec.$^{-1}$)	19·3	6·6	2·9	1·7	very slow

Ionic strength = 2·99; $[H^+]$ = 0·98M; temp. = 27·0°.

The Effect of Chloride Ions.—Table 3 shows the results of experiments carried out in the presence of chloride ions. The retardation of the rate by chloride is similar to that observed in the thallous–thallic exchange reaction [7] and in the reduction of thallium(III) by ferrous ion. As suggested by Harbottle and Dodson [7] this retardation is no doubt due

---

[6] Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," McGraw-Hill, New York, 1941, Chap. 8.

[7] Harbottle and Dodson, *J. Amer. Chem. Soc.*, 1951, **73**, 2442.

[8] Zwolinski, Marcus, and Eyring, *Chem. Rev.*, 1955, **55**, 157.

to the formation of chloro-complexes of thallium(III), but there are insufficient data on these complexes to permit an analysis of the results.

EXPERIMENTAL

Stock Solutions.—Thallium(III) perchlorate was prepared by a method similar to that described by Ashurst and Higginson.[3] Thallium(III) oxide was reprecipitated twice before it was dissolved in 72% "AnalaR" perchloric acid. Total thallium(III) in the solution was determined by adding excess of a standard solution of ferrous sulphate and back-titrating the excess with standard potassium dichromate. The acid concentration of the thallium(III) solution was estimated as described by Johnson.[1]

Trisdipyridylosmium(II) perchlorate was prepared by Burstall, Dwyer, and Gyarfas's method.[9] A stock solution was made up by weight and checked by spectrophotometric titration with a standard solution of "AnalaR" ceric ammonium nitrate.

Sodium perchlorate solution used for adjusting ionic strength was prepared by neutralising "AnalaR" perchloric acid with "AnalaR" sodium hydroxide and filtering.

Conductivity water was used for all solutions; it was obtained by redistilling distilled water, to which a little alkaline potassium permanganate was added, in an all-glass apparatus. The redistilled water was then passed through a column of Permutit "Bio-deminrolit."

Procedure.—Solutions of trisdipyridylosmium(II) being intensely coloured, the reaction was followed spectrophotometrically at a wavelength of 480 mμ, at which the osmium(III) compound has practically no absorption. A simple flow system, in which water from a thermostat was circulated around the spectrophotometer cell holder, enabled the reaction to be carried out at constant temperature.

The recorded values of k_1 are the means obtained from two kinetic runs with two different preparations of thallium(III). The values of k_1 from the two experiments were found to be within 5% of each other.

At the high concentrations of perchlorate used some initial oxidation of the $\mathrm{Os(dipy)_3}^{2+}$ was observed, which appeared to be due largely to some impurity in the sodium perchlorate solution, but a slight amount was also caused by the perchloric acid. Fortunately the oxidation occurred instantaneously, so that the kinetics were not affected if thallium(III) was added last to the reaction mixture. Its only effect then was to alter the initial concentration of $\mathrm{Os(dipy)_3}^{2+}$, and by running a blank before each experiment the extent of the alteration could be determined. In no case did the amount of initial oxidation caused by the perchlorate solutions exceed 15%, so that never more than 15% of the tervalent osmium complex was present at the start of any given reaction.

Because of the low concentration of the reactants used [*ca.* $5{\cdot}0 \times 10^{-5}$M for the osmium compound and 10^{-4}M for thallium(III)] it seemed advisable to check the quantitativeness of the reaction under these conditions. Experiment showed that with $2{\cdot}16 \times 10^{-5}$M-thallium(III) and $4{\cdot}40 \times 10^{-5}$M-$\mathrm{Os(dipy)_3}^{2+}$ and the initial oxidation of $\mathrm{Os(dipy)_3}^{2+}$ in the high perchlorate medium being allowed for, 95% of the osmium compound was oxidised by the thallium(III).

All the experiments were conducted at a constant ionic strength of 2·99.

I thank Professor P. George for helpful criticisms and Professor C. W. L. Bevan for his interest.

UNIVERSITY COLLEGE, IBADAN, NIGERIA.

[*Received, November* 19*th*, 1956.]

---

[9] Burstall, Dwyer, and Gyarfas, *J.*, 1950, 953.