The Volume of Activation of the Thallous–Thallic Electron-exchange Reaction

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IN homogeneous solution, electron-transfer rates are strongly influenced by a free energy "rearrangement barrier" arising from the contraction of the co-ordination and solvation spheres of one reactant, usually that of lower oxidation number, and the expansion of these spheres of the other reactant.[1] When a bridged, or inner-sphere, transition state is involved, expulsion of at least one ligand from the co-ordination sphere of one reactant must also occur. These rearrangement processes should be

detected most directly by the measured volume of activation, $\Delta V_{\ddagger}$, for an electron-transfer process. Measurements on electron-exchange reactions should have special significance since they proceed with a zero standard free energy change but there appears to be no reported $\Delta V_{\ddagger}$ value for any such reaction.

We now report the determination of $\Delta V_{\ddagger}$ for the electron-exchange reaction $Tl^{3+}_{aq} + {}^{204}Tl^{+}_{aq} \rightleftarrows Tl^{+}_{aq} + {}^{204}Tl^{3+}_{aq}$ as deduced from the variation of the second-order rate constant, k, for this reaction with applied pressure, p, according to the relation:

$$\left(\frac{\partial \ln k}{\partial p}\right)_{T} = -\frac{\Delta V_{\ddagger}}{RT}.$$

This pressure dependence is shown in Figure 1 for reactions conducted in 1·10M-perchloric acid at 30° and for some preliminary measurements in 4·50M-perchloric acid media. Values of the rate constant, k_p, have all been corrected for the small (*ca.* 4·2% at 1000 atm.) increase in Tl^{III} and Tl^{I} concentrations caused by the contraction of the solvent under pressure. In 1·10M-HClO$_4$, the limiting slope of the log$_{10}$ (k_p/k_1) against p relation corresponds to a limiting volume of activation,

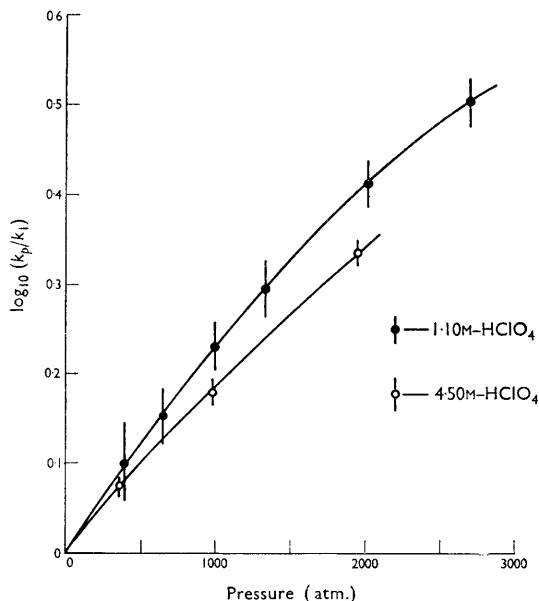$\Delta V_{0\ddagger} = -13·2(\pm 1·0)$ ml. mole^{-1}. Within experimental error, the same value of $\Delta V_{0\ddagger}$ is observed at 4·50M-HClO$_4$.† The nonlinearity of the rate-pressure relation at high pressure is rather typical of many ionic reactions.

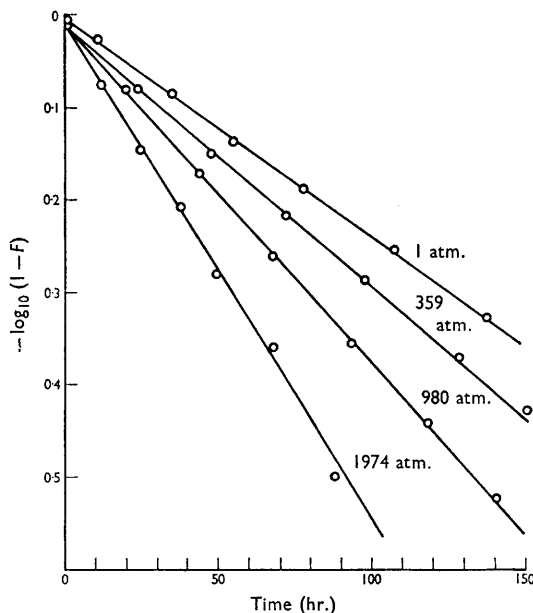FIGURE 2. *Exchange plots for the* Tl^{I}–Tl^{III} *electron exchange reaction in* 4·50M-*perchloric acid*; T = 30°.

The exchange reaction was followed by conventional isotopic procedures based on the precipitation of thallous chromate to separate the oxidation states of thallium. Figure 2 illustrates the excellent reproducibility achieved for the exchange runs, in this instance for 4·50M-HClO$_4$ media. Each experimental point on these graphs represents an *independent* determination, from a *separate* pressure vessel, of the fraction of exchange for the reaction time indicated. Reaction mixtures were contained in polypropene tubes fitted with Teflon plugs and check experiments showed that at atmospheric pressure, the observed rate constant had the same value (0·76 $\pm$ 0·03 mole^{-1} hr.$^{-1}$ in 1·10M-HClO$_4$, 0·195 $\pm$ 0·003 mole^{-1} hr.$^{-1}$ in 4·50M-HClO$_4$; at 30°) with glass or polypropene reaction vessels. Furthermore, experiments at 1335($\pm$20) atm. confirmed that (k_p/k_1) was independent of (i) the exposed surface area of either glass or polypropene in the reaction vessel,

FIGURE 1. *Pressure dependence of the* Tl^{I}–Tl^{III} *electron exchange reaction in* 1·10M- *and* 4·50M-*perchloric acid at* 30°.

† Latest measurements indicate that the 4·5M-HClO$_4$ curve actually lies somewhat nearer to the 1·1M-HClO$_4$ curve than shown in Figure 1. Full details of the experimental procedure, together with the results of the completed pressure-dependence for the 4·50M-HClO$_4$ system and other check experiments, will be published elsewhere.

and (ii) the concentrations of either thallium(I) or thallium(III). These experiments therefore exclude the possibility that pressure-induced heterogeneous catalysis of the electron-exchange reaction might account for the observed acceleration.

The effect of increased pressure upon the hydrolysis equilibrium

$$Tl_{qa}^{3+} + H_2O \rightleftarrows TlOH_{aq}^+ + H_{aq}^+$$
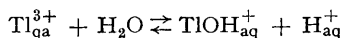
must be considered in an interpretation of $\Delta V_0^{\ddagger}$ since both Tl_{aq}^{3+} and $TlOH_{aq}^{2+}$ undergo electron exchange with Tl_{aq}^+ [N.B. $k(Tl^{3+}-Tl^+) = 0.45$ mole^{-1} hr.$^{-1}$ and $k(TlOH^{2+}-Tl^+) = 0.21$ mole^{-1} hr.$^{-1}$ at 30° in a 3M-perchlorate medium[2]]. The value of $\Delta \bar{V}$ for the hydrolysis reaction, as written, may be estimated as $+20 \pm 3$ ml. mole^{-1}.[3] Whereas in 1.1M-HClO$_4$ at 1 atm. TlOH^{2+} represents 7% of the total thallium(III) concentration, at 2000 atm. this percentage would therefore fall to ca. 1.4%. Assuming similar pressure dependences for both rate constants, then the reaction pathway via TlOH^{2+} may contribute only 3—1% to the observed rate in the pressure range studied. We consider therefore that the value of $\Delta V_0^{\ddagger} = -13.2$ ml. mole^{-1}, observed at both 1.10M- and 4.50M-HClO$_4$, refers to electron exchange between the aquated Tl^{3+} and Tl$^+$ cations.

The value of $\Delta V_0^{\ddagger} = -13.2$ appears to exclude the possibility of an inner-sphere transition state involving expulsion of an aquo-ligand. Values of $\Delta V^{\ddagger}$ observed for known inner-sphere transition states are all positive[4] and as high as $+14$ ml. mole^{-1}. In these instances, a negative contribution to $\Delta V^{\ddagger}$ from the increased electrostriction arising from a more highly charged transition state does not seem to be important, as the value of $\Delta V^{\ddagger}$ is largely independent of charge type. In the present instance therefore, we might tentatively ascribe the large negative $\Delta V_0^{\ddagger}$ value to a large contraction of hydration water about Tl_{aq}^+ as well as to outer-sphere interactions through a hydrogen-bridged transition state. A two-electron transfer should involve a much larger negative $\Delta V^{\ddagger}$ than a one-electron transfer and we incline to the opinion that the former process is operating in the transition state for the T_{aq}^+–Tl_{aq}^{3+} system. We are currently studying high-pressure effects on other electron-exchange reactions involving substitution-inert cations like Co(en)$_3$$^{3+}$ to place these tentative conclusions on a firmer basis.

[1] See for example: R. A. Marcus, Ann. Rev. Phys. Chem., 1965, 15, 155.
[2] R. W. Dodson and E. Roig, J. Phys. Chem., 1961, 45, 2175.
[3] R. M. Noyes, J. Amer. Chem. Soc., 1964, 86, 971.
[4] J. P. Candlin and J. Halpern, Inorg. Chem., 1965, 6, 1086.