

**Pressure Effect on the Rate of Outer-sphere Electron-transfer within the Ion-pair  
between  $\mu$ -Ethylenediaminetetra-acetato-di- $\mu$ -oxo-bis[oxomolybdate(v)]  
and  $\mu$ -Hyperoxo-bis[penta-amminecobalt(III)] Ions**

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*Summary* The title reaction gave large positive activation volumes for both the precursor (ion-pair) formation constant and the first-order electron-transfer rate constant within the ion-pair; this result was interpreted mainly in terms of the change in solvation state in each process.

THE pressure effect on outer-sphere electron-transfer reactions in aqueous solution was discussed theoretically by Stranks.<sup>1</sup> However, only limited experimental data are available for electron-exchange reactions proceeding by the outer-sphere mechanism, *i.e.* between aqua-thallium(I) and -thallium(III),<sup>2</sup> hexa-aqua-iron(II) and -iron(III), and tris-(ethylenediamine)-cobalt(II) and -cobalt(III).<sup>1,3</sup> All these electron-transfer reactions are between positively charged reactants, and gave negative activation volumes ( $-13$  to *ca.*  $-20$   $\text{cm}^3 \text{mol}^{-1}$ ), which were successfully interpreted by Stranks' theory. However, details of the experimental studies are unpublished.

We have recently found that  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values of the outer-sphere redox reactions differ significantly on changing the charge of the oxidants used for oxidising negatively charged molybdenum(V)<sup>4,5</sup> and vanadium(IV) complexes.<sup>6</sup> The change in solvation state on forming the encounter complex and the overall charge of the encounter complex were considered to be important factors which must be reflected in the activation volume.

We report here the activation volume of the outer-sphere electron-transfer reaction between binuclear complexes with opposite charges, *i.e.* between  $[\text{Mo}_2^{\text{V}}\text{O}_4(\text{edta})]^{2-}$  ( $\text{H}_4\text{-edta}$  = ethylenediaminetetra-acetic acid) and  $[(\text{NH}_3)_5\text{Co}^{\text{III}}-$

$(\mu\text{-O}_2^-)\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$  in the range 0.1—294 MPa. The reaction was monitored at 670 nm (absorption peak of the  $\mu$ -hyperoxo-complex)<sup>4</sup> by the usual method with a Union Giken RA-401 spectrophotometer equipped with a high-pressure cell compartment. The first-order rate constant with respect to the binuclear  $\text{Co}^{\text{III}}$  complex ( $k_{\text{obs}}$ ) was plotted against the concentration of the dimeric  $\text{Mo}^{\text{V}}$  complex, which was in large excess over the  $\text{Co}^{\text{III}}$  complex. The concave curves (Figure) were analysed with the aid of reciprocal plots,  $k_{\text{obs}}^{-1}$  *vs.*  $[\text{Mo}_2]^{-1}$ , to give the rate law (equation 1) where  $K_{\text{IP}}$  and  $k_e$  are the ion-pair formation

$$k_{\text{obs}} = 2K_{\text{IP}}k_e[\text{Mo}_2]/(1 + K_{\text{IP}}[\text{Mo}_2]) \quad (1)$$

constant and the first-order electron-transfer rate constant within the ion-pair, respectively. The factor 2 in the numerator shows that the oxidation of the first  $\text{Mo}^{\text{V}}$  ion in the dimer is the rate-determining step which is followed by a rapid oxidation of the second  $\text{Mo}^{\text{V}}$ .<sup>4</sup> Analysis of the pressure dependence of both  $K_{\text{IP}}$  and  $k_e$  gave the volume of activation ( $\Delta V^\ddagger$ ) and the compressibility of activation ( $\Delta\beta^\ddagger$ ):  $\Delta V_{\text{IP}}^\ddagger = 23.7 \pm 3.0$   $\text{cm}^3 \text{mol}^{-1}$ ,  $\Delta\beta_{\text{IP}}^\ddagger = (-6.2 \pm 2.2) \times 10^{-2}$   $\text{cm}^3 \text{mol}^{-1} \text{MPa}^{-1}$ ,  $\Delta V_e^\ddagger = 12.1 \pm 1.9$   $\text{cm}^3 \text{mol}^{-1}$ , and  $\Delta\beta_e^\ddagger$  *ca.* 0  $\text{cm}^3 \text{mol}^{-1} \text{MPa}^{-1}$  at 41.1 °C and  $[\text{H}^+] = I = 0.1$  M ( $\text{HClO}_4$ ).

The present overall volume change on activation,  $(\Delta V_{\text{IP}}^\ddagger + \Delta V_e^\ddagger) = 36$   $\text{cm}^3 \text{mol}^{-1}$ , is among the largest pressure effects ever observed for the reaction of metal complexes in aqueous solution. It is generally believed that two factors are important for the volume change on activation, the volume change of the substrate itself and the change in

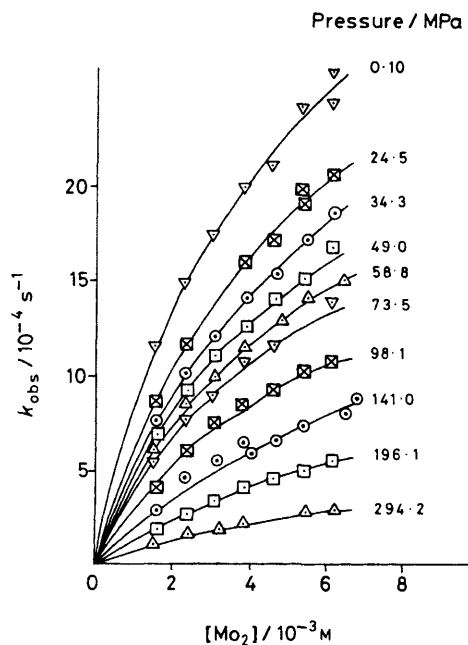


FIGURE. Dependence of the first-order rate constant ( $k_{\text{obs}}$ ) on  $[\text{Mo}_2^{\text{V}}\text{O}_4(\text{edta})^{2-}]$  at various pressures for the oxidation of  $[\text{Mo}_2^{\text{V}}\text{O}_4(\text{edta})^{2-}]$  with  $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\mu\text{-O}_2)\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}([\mu\text{-O}_2^-] = 1 \times 10^{-4} \text{ M}, [\text{H}^+] = 1 = 0.1 \text{ M}, 41.1 \text{ }^\circ\text{C})$ .

the solvation state.<sup>7</sup> The change in volume of the substrate on ion-pair formation would be very small. The large positive  $\Delta V_{\text{IP}}$  must be due to the change in the hydration sphere accompanied by the formation of an ion-pair with a +3 charge from the two separated ions with charges of +5 and -2. Water molecules of hydration would be released to increase the apparent volume of the system. A highly charged ion has a highly ordered hydration sphere, which is apparently in a considerably compressed state. The compressibility is dependent on the pressure, and the negative  $\Delta\beta_{\text{IP}}$  reflects the participation of highly charged particles. The observed  $\Delta V_{\text{IP}}$  and  $\Delta\beta_{\text{IP}}$  values imply that  $K_{\text{IP}}$  should increase on further increase in pressure above 300 MPa.

The positive  $\Delta V_e^\ddagger$  reflects an increase in volume on the formation of the transition state within the precursor ion-pair. Since no bond cleavage and bond formation take place in the activation process of the outer-sphere electron transfer, a value as high as  $+12 \text{ cm}^3 \text{ mol}^{-1}$  is difficult to interpret in terms of the volume change of the substrate itself. Neither does Stranks' theory on solvent rearrangement in the hydration sphere give a satisfactory explanation. The sign of  $\Delta V_e^\ddagger$  may be interpreted by considering the change in dipole moment of the precursor complex on going to the transition state. Its magnitude, however, seems to be too great to be thus accounted for. Details will be discussed elsewhere.

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<sup>6</sup> M. Nishizawa, Y. Sasaki, and K. Saito, manuscript in preparation.

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