

## Measurement of the Rate Constant for Through-bridge Intra-molecular Electron Transfer in the Intermediate of a Ru<sup>III</sup>-Ti<sup>III</sup> Redox Reaction involving 3-Formylpentane-2,4-dione as Bridging Ligand

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The rate constant (25 °C; 1 M-LiCl) for electron transfer through the bridging ligand in the kinetic intermediate bis(pentane-2,4-dionato)ruthenium(III)- $\mu$ -(3-formylpentane-2,4-dionato)titanium(III)(OH)<sup>2+</sup> is 21 s<sup>-1</sup>.

Electron-transfer (E.T.) processes that involve  $t_{2g}$  orbitals as both donor and acceptor orbitals have been investigated both in mixed-valence compounds and also in redox processes in solution. In only one case known to us has an E.T.-rate constant been measured for the mixed-valence compounds.<sup>1</sup> Ru<sup>III</sup>-Ti<sup>III</sup> redox reactions that involve either carboxylate or thiocyanate ligands on Ru<sup>III</sup> give rise to inner-sphere E.T., but the rate-limiting step is substitution on Ti<sup>III</sup>, so that only a lower limit of the intramolecular E.T. rate can be estimated.<sup>2</sup> We have now found an Ru<sup>III</sup>-Ti<sup>III</sup> system in which we can measure the rate of intramolecular E.T. So far as we know, this is the first report of the first-order rate constant of inner-sphere  $t_{2g}$ - $t_{2g}$  E.T. in a solution-phase redox intermediate.

Straightforward procedures were used to prepare and characterize bis(pentane-2,4-dionato)(3-formylpentane-2,4-dionato)ruthenium(III), Ru(pd)<sub>2</sub>(fpd). The half-wave reduction potential, in 0.9 M-LiCl-0.1 M-HCl, is -0.16 V vs. the normal hydrogen electrode (N.H.E.).

We have already established<sup>3</sup> a correlation of the rate of outer-sphere reduction of Ru<sup>III</sup> complexes by TiOH<sup>2+</sup> to the driving-force of such reactions. We estimate, using this correlation and the potential of Ru(pd)<sub>2</sub>(fpd), that the rate constant (25 °C; 0.9 M-HCl-0.1 M-HCl) for reduction of this oxidant by TiOH<sup>2+</sup> would be 1 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. We measured the rate constant for the reaction of TiOH<sup>2+</sup> with tris(pentane-2,4-dionato)ruthenium(III), Ru(pd)<sub>3</sub>, as oxidant to be 2 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. This value agrees with that predicted by the reduction potential of Ru(pd)<sub>3</sub> (-0.28 V vs. N.H.E.) using the established correlation.

The reaction of Ru(pd)<sub>2</sub>(fpd) with Ti<sup>III</sup> was studied at 25.0 °C, in LiCl-HCl solutions of 1.0 M total chloride concentration. Polarographic and spectrophotometric experiments show that there is a redox process in which one mol (within 5%) of Ru<sup>III</sup> is reduced per mol of Ti<sup>III</sup> added. An isosbestic point was noted at 385 nm. After about 15 min, the isosbestic point was absent, owing to decomposition of the Ru<sup>II</sup> product.<sup>4</sup>

The kinetics of the reaction were measured with the concentration of Ti<sup>III</sup> at least ten times larger than that of Ru<sup>III</sup>, by following absorbance changes at a fixed wavelength between 400 and 510 nm (usually 440 nm), using a Durrum

stopped-flow spectrophotometer. Two relaxations, with half-times of tens of milliseconds, were observed.† The rate laws were as given in equations (1) and (2).

$$k_{\text{obs}} = k_a + k_b [\text{Ti}^{\text{III}}]/[\text{H}^+] \quad (1)$$

$$k'_{\text{obs}} = k_c \quad (2)$$

$$k_a = 2.9 \text{ s}^{-1}, k_b = 28 \text{ s}^{-1}, k_c = 21 \pm 3 \text{ s}^{-1}$$

Rate constants for both processes are several orders of magnitude larger than the measured rate constant for reduction of Ru(pd)<sub>3</sub>, or the predicted outer-sphere rate constant for reduction of Ru(pd)<sub>2</sub>(fpd) by TiOH<sup>2+</sup>. The increase in redox rate brought about by substitution of a formyl group on to the ring indicates that the present reaction involves an inner-sphere mechanism with E.T. through the bridging ligand rather than through space.

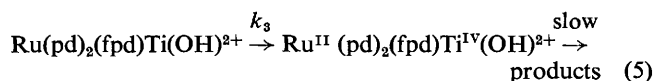
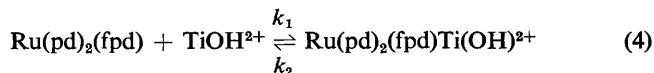
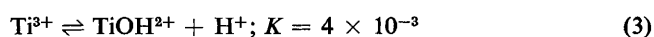
We have measured the rate of formation of mono(pentane-2,4-dionato)titanium(III). The rate constant (25 °C; 1.0 M-LiCl) for reaction of Ti<sup>3+</sup> with the enol form of pentane-2,4-dione is  $2.4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This is comparable with the rate constant for the titanium-dependent relaxation we observe during reduction of Ru(pd)<sub>2</sub>(fpd). The similarity of the rate constants‡ leads us to conclude that the reductant-dependent relaxation is due to formation of the binuclear intermediate.

The second relaxation is too slow to be a substitution process, but much too rapid to correspond to break-up of the Ru<sup>II</sup> product.<sup>4</sup> The data force us to conclude that the second relaxation ( $k'_{\text{obs}}$ ) corresponds to intramolecular E.T. through the bridging ligand.

† The faster relaxation accounted for most of the absorbance change. Further characterization of the intermediate was not feasible. We thank R. N. Bose for discussion of a related system that he is now studying in this laboratory. In that system, characterization of the intermediate is feasible.

‡ Analogy with substitution on iron(III) implies that the rate of substitution on TiOH<sup>2+</sup> should be 10–10<sup>3</sup>-times faster than substitution on Ti<sup>3+</sup>: D. P. Fay, A. R. Nichols, and N. Sutin, *Inorg. Chem.*, 1971, **10**, 2096.

A mechanism that is consistent with our data is given in equations (3)—(5), and this requires that equations (6) and (7) should apply, where  $[\text{Ti}^{\text{III}}]$  is the total concentration of titanium(III) in solution.



$$k_{\text{obs}} = (k_1 + k_3) + \frac{k_1 K [\text{H}^+]}{[\text{H}^+] + K} - k'_{\text{obs}} \quad (6)$$

$$k'_{\text{obs}} = k_3 k_1 K [\text{Ti}^{\text{III}}] / \{(k_2 + k_3) ([\text{H}^+] + K) + k_1 K [\text{Ti}^{\text{III}}]\} \quad (7)$$

Plots of observed rate constants, multiplied by  $(1 + K/[\text{H}^+])$  against  $[\text{Ti}^{\text{III}}]$  and against  $[\text{H}^+]$  gave straight lines. Using the quoted value for  $K$ , the values  $k_1 = 4.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $k_3 = 21 \text{ s}^{-1}$ , and  $k_2 = 5 \text{ s}^{-1}$  were obtained from slopes and

intercepts of these plots. These values are consistent§ with all our data.

Our observation is that the intramolecular E.T. rate constant is measurable in this system, whereas for inner-sphere E.T. involving carboxylate bridging ligands E.T. is more rapid than substitution. This implies that there is a significant activation barrier to E.T. through the bridging ligand.¶ A requirement of coplanarity of the formyl group and the pentanedionate ring would account for such a barrier.

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§ The value of the  $k_1/k_2$  ratio is large but not unreasonably so, in comparison with  $\text{Ti}^{\text{III}}$  stability constants. A mechanism involving substitution on  $\text{Ti}^{3+}$  and competition between E.T. and an acid-base reaction would also fit the data. The E.T. rate constant would be the same for both mechanisms.

¶ Other  $t_{2g}-t_{2g}$  E.T. reactions are rate-limited by chemical changes on one of the reactants prior to E.T.: F. H. Kristine and R. E. Shepard, *Inorg. Chem.*, 1981, **20**, 215.