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Inner-Sphere Electron-Transfer in the Reduction of Dioxalatodiaquoruthenium(III) by Ti(III)

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Previously, we showed that Ti(III) reductions of Ru(III) oxidant involving certain classes of ligands follow outer-sphere reaction mechanisms [1], while Ti(III)-reduction of Ru(III) complexes containing other classes of ligands follow inner-sphere reactions that have either substitution [2] or electron-transfer [3] as the rate-determining process. We now report that $Ru(C_2O_4)_2(H_2O)_2^-$ is reduced by Ti^{3+} with a rate faster than any Ru(III)–Ti(III) process previously reported.

Apparatus and reagent were generally as previously described [1–3]. *Sodium diaquodioxalatoruthenium(III) trihydrate*: μ-Tetracetatodiruthenium chloride (0.2 g) was dissolved in 250 ml of water containing 0.4 g of sodium oxalate. The solution was refluxed under a slow stream of oxygen for four hours. The resulting yellow solution was reduced to a volume of 20 mL and then passed through a Sephadex G10 column. A solid product separated out on cooling the eluate in an ice bath. The product was recovered by filtration and air-dried. *Anal.*: (% found/% calculated for $Na[Ru(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$): Ru, 26.1/25.9; C, 11.5/12.3; H, 2.4/2.6; $C_2O_4^{2-}$, 44.6/45.2.

A similar procedure, starting with a solution of oxalic acid rather than one of sodium oxalate, produced the corresponding free acid. *Anal.*: (% found/% calculated for $H_3O[Ru(ox)_2(H_2C)_2]\cdot 2H_2)$: Ru, 27.8/27.5; C, 12.2/13.1; H, 3.0/3.0; $C_2O_4^{2-}$, 47.3/48.0.

In 1.0 *M* LiCl–0.1 *M* HCl, the UV–visible spectrum of the product showed peaks at ($\epsilon \times 10^{-2}$ cm *M*): 490(0.02), 360(120), 290(23) and 275(38) nm. Evans method gave a magnetic moment of 2.0 B.M. and cyclical voltammetry gave a reduction potential of −0.35 volts *vs.* the Ag/AgCl electrode in 0.9 *M* LiCl–0.1 *M* HCl.

Addition of Ti(III) to solution of the Ru(III) complex caused a rapid change in spectrum. Spectrophotometric titration showed that 1.0 mol of Ru(III) was consumed per mol of Ti(III). The rate of the reaction was followed (1 *M* LiCl–HCl, 25 °C) at 425 nm using a computer linked Durrum stopped-flow spectrometer.

The measured second-order rate constant is four orders of magnitude larger than would be expected for Ti(III) reduction of an oxidant of this reduction potential *via* an outer-sphere reaction [1]. It is clear that this redox reaction involves the inner-sphere mechanism.

As in the case [2] of Ti(III) reduction of $Ru(NH_3)_5C_2O_4^+$ and of $Ru(NH_3)_4C_2O_4^+$, the second order rate constant was found to be independent of acid (0.008 $M < [H^+] < 0.012$ M). The value of that rate constant was, however, determined to be $(4.0 \pm 0.1) \times 10^4$ M^{-1} s^{-1}, twice as large as in the prior cases. Substitution reactions of Ti^{3+} are generally held to have associative character. The negative value of the charge of the present oxidant would be expected to cause a more rapid rate of formation of the binuclear complex which is an intermediate in the inner sphere mechanism. Rates of substitution of mononegative ions on Ti^{3+} range from 10^{-4} to 10^{-6} M^{-1} s^{-1}, with $HC_2O_4^-$ being 4×10^{-5} M^{-1} s^{-1}. The overall rate of the redox reaction surely involves at least partial control by the substitution process, but the increase of rate on change of charge type is less than would be expected for full substitution rate control. Partial control of rate by the electron-transfer process cannot be ruled out.

References

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