ABSTRACT

Kinetic Studies of the reduction of the di-μ-cyanobis[tetracyanoferrate(III)] ion in aqueous solution.

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The kinetics of the reduction of the dimeric species, di-μ-cyanobis[tetracyanoferrate(III)] ion, by the one electron sulfur containing reductant, thiourea and the hexaaquatitanium(III) species were investigated.

In the presence of thiourea, the dimeric species undergoes rapid one electron reduction to form the mixed-valence species Fe^{II} - Fe^{III}, followed by a slower substitution reaction leading to two moles of mononuclear Fe- complexes. The formation of the mixed-valence complex consists of a single kinetic step which was followed by stopped-flow technique and a subsequent slower step was followed by conventional spectrophotometric technique.

Spectrophotometric titration, shows that two moles of thiourea were incorporated into one mole of the dimer complex, forming two moles of mononuclear thiourea substituted monomer, $[Fe(CN)_5tu]^{3-}$, which is ultimately reoxidised by the ambient oxygen in solution to form two moles of the Fe(III) monomer.

In the first stage of the reaction, which involves formation of the mixed-valence species, the pseudo-first order rate constant was found to be linearly dependent at low concentrations of thiourea but, a zero order effect

is observed at high concentrations. The rate constant, k_1 for the formation of the ring-opened species was calculated and found to be $(2.12 \pm 0.34) \times 10^{-2}$ s^{-1} at 24.9 °C. A similar trend is observed for the second stage and the rate constant, k_3 calculated for the formation of the aqua mixed-valence species was $(1.09 \pm 0.04) \times 10^{-3}$ s^{-1} at 24.9 °C.

The effect of temperature on the redox rate was investigated and the activation parameters were calculated as $\Delta H_1^{\neq} = (40.9 \pm 6.1)$ kJ mol^{-1} $\Delta S_1^{\neq} = (-139 \pm 8)$ J mol^{-1} K^{-1}); ($\Delta H_3^{\neq} = (93 \pm 5)$ kJ mol^{-1}, $\Delta S_3^{\neq} = (-10.1 \pm 0.9)$ J mol^{-1} K^{-1}) for the corresponding k_1 and k_3 steps, respectively.

The addition of the titanium(III) solution to the dimer results in the rapid disappearance of the complex peak at 560 nm giving rise to a distinct peak at *ca* 390 nm which is indicative of an iron(II,II) species. Spectrophotometric titration shows that two moles of the titanium(III) species react with one mole of the dimeric complex. The reaction with titanium(III) shows a similar trend to that of thiourea/dimer reaction, consisting of two stages.

The first stage was found to be monophasic and was considered to be a one electron reduction of the first iron(III) centre leading to the formation of the mixed-valence species. The pseudo-first order rate constant was found to be dependent on the concentration of titanium(III). The second stage involves the reduction of the other iron(III) centre leading to the formation of the iron(II,II) dimeric species. The titanium(III) species will become oxidised forming the insoluble titanium(IV) species. An inverse hydrogen ion dependence was observed for both stages.

The rate constants, k_1 which involves the hydroxotitanium(III) species and k_2 involving the hexaaquatitanium(III) species were calculated

as (12.20 ± 0.01) $dm^3\ mol^{-1}\ s^{-1}$ and (1.98 ± 0.21) $dm^3\ mol^{-1}\ s^{-1}$ at 25 °C respectively. The corresponding rate constants, k_3 and k_4 (for the reaction path involving the hydroxo species and hexaaqua species respectively) were calculated as (0.70 ± 0.01) $dm^3\ mol^{-1}\ s^{-1}$ and (3.8 ± 0.01) x 10^{-2} $dm^3\ mol^{-1}s^{-1}$ at 25 °C for the second stage.

The reaction of the dimer with thiourea shows catalytic effect in the presence of Cu(II) ions at concentrations greater than 1ppm. The amount of copper(II) found in the redox systems studied, was less than 0.07 ppm. At this low concentration of copper(II), practically no effect on the redox system was observed.