

ABSTRACT

Electron Transfer Reactions involving the di- μ -cyano-bis[tetracyanoferrate(III)] Ion in Aqueous Solutions.

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The kinetics of the reduction of the di- μ -cyano-bis[tetracyanoferrate(III)] ion by L-ascorbic acid and three sulphur containing reducing agents, thiosulphate, sulphite and L-cysteine were studied in acidic solution.

The reactions of the complex with the reducing agents can be divided into two groups. Both L-cysteine and L-ascorbic acid react in a similar manner, in the sense that both reduce the two iron centres to form the di- μ -cyano-bis[tetracyanoferrate(II)]. On the other hand the sulphur oxoanions, thiosulphate and sulphite, only reduce one of the iron(III) centres to form the mixed valence complex $\text{Fe}_2(\text{CN})_{10}^{5-}$.

The reduction of the complex by L-ascorbic acid occurs in three stages, resulting in the formation of aquapentacyanoferrate(II). The reaction is a successive reduction of the two iron(III) centres followed by hydrolysis of the di- μ -cyano-bis[tetracyanoferrate(II)] to form the aquapentacyanoferrate(II) ion. It was found that, of the three possible reactive species present from the dissociation of L-ascorbic acid, the ascorbate dianion, A^{2-} , is the most reactive, while the undissociated acid was unreactive under our conditions. The rates of reduction of the first iron(III) centre to form the mixed valence complex, $\text{Fe}_2(\text{CN})_{10}^{5-}$, were found to be $(3.50 \pm 0.06) \times 10^3$ and $(1.28 \pm 0.79) \times 10^8$ $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ at 19.0 °C for the HA^- and A^{2-} terms respectively. For the second reduction the rate constants were found to be $(1.51 \pm 0.04) \times 10^3$ and $(0.61 \pm 0.04) \times 10^8$ $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ at 19.1 °C for the HA^- and A^{2-} terms

respectively. The reaction mechanism involves the alkali metal cations acting as a bridge in the formation of an ion pair.

L-cysteine reacts with the complex in two steps, which are the consecutive reduction of the two iron(III) centres. It appears that at low pHs the first reduction is too fast to be separable under our conditions but at higher pHs the two steps can be separated. At low pH the reduction of $\text{Fe}_2(\text{CN})_{10}^{5-}$ by L-cysteine is quite facile. There are two reactive cysteine species under our conditions, $^-\text{SCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$ and $\text{SHCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$. The first species is much more reactive than the second ; $k_1 = (1.51 \pm 0.33) \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $k_2 = 26.83 \pm 1.17 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 25.0° C . The activation parameters were calculated to be: $\Delta H_1^\ddagger = 57.5 \pm 4.5 \text{ kJ mol}^{-1}$, $\Delta H_2^\ddagger = 24.3 \pm 4.5 \text{ kJ mol}^{-1}$, $\Delta S_1^\ddagger = -24.5 \pm 18.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta S_2^\ddagger = 57.5 \pm 18.0 \text{ J K}^{-1} \text{ mol}^{-1}$.

The reactions with thiosulphate and sulphite/bisulphite results in the reduction of one iron centre with subsequent substitution and/or hydrolysis reactions. Thiosulphate reduces the complex to $\text{Fe}_2(\text{CN})_{10}^{5-}$ then does a substitution reaction resulting in the formation of thiosulphatopentacyanoferrate(II) and (III) complexes. The first reaction, that is the reduction, is quite complex. It proceeds in two steps both of which are thiosulphate dependent. The first step shows a saturation effect while the other shows a first order effect. The mechanism involves a metal ion assisted formation of a thiosulphate adduct of the complex, $[\text{Fe}_2(\text{CN})_9(\text{CNS}_2\text{O}_3)]^{6-}$. The rate constant for formation of this adduct is $0.131 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ while electron transfer occurs with a rate constant of $0.127 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 24.2° C . The entropy of activation values for the various rate constants are all negative implying stable transition states.

The rate of substitution of thiosulphate on $[\text{Fe}_2(\text{CN})_{10}]^{5-}$ was found to be $(4.73 \pm 0.08) \times 10^{-3} \text{ s}^{-1}$ (25.2° C) for the ring opening of the mixed valence dimer to form $[\text{Fe}_2(\text{CN})_{10}(\text{S}_2\text{O}_3)]$.

The reaction with aqueous sulphite is somewhat similar to the thiosulphate. The SO_3^{2-} species is more reactive than the HSO_3^- while SO_2 is unreactive. However both species reacts in the same manner. There is an adduct formation followed by an outer sphere electron transfer. The $[\text{Fe}_2(\text{CN})_9(\text{CNSO}_3)]^{6-}$ or $[\text{Fe}_2(\text{CN})_9(\text{CNHSO}_3)]^{5-}$ then undergoes hydrolysis forming $[\text{Fe}_2(\text{CN})_{10}]^{5-}$. The rate constant for adduct formation was $0.88 \pm 0.01 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at $30.9 \text{ }^\circ\text{C}$ for the bisulphite species and $17.34 \pm 0.03 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at $30.9 \text{ }^\circ\text{C}$ for the sulphite species. The rate constants for electron transfer were $(7.53 \pm 0.01) \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $2.47 \pm 0.08 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at $30.9 \text{ }^\circ\text{C}$, for the bisulphite and sulphite species respectively. A somewhat low value of 9.3 kJ mol^{-1} was obtained for the HSO_3^- pathway of the electron transfer step.

Apart from the similarity between the L-ascorbic acid and L-cysteine and between thiosulphate and aqueous sulphite reactions, the only common feature of all reductants was the effect of the alkali metal cations. The reactivity was found to be $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{NH}_4^+ < \text{Cs}^+$. The mechanisms for the different reductants are proposed on the basis of the formation of an ion pair triplet involving the reductant, the complex and the metal ion.

The transfer chemical potentials studies of two new complexes, $(\text{Ph}_4\text{P})_4\text{Fe}_2(\text{CN})_{10}$ and $(\text{PNP})_4\text{Fe}_2(\text{CN})_{10}$, showed that there was stabilisation of both the salts and the complex ion, $\text{Fe}_2(\text{CN})_{10}^{4-}$, on going from pure water to the highest cosolvent composition.