MECHANISTIC STUDIES OF STEPWISE REDUCTIONS OF THE DI-μ-CYANOBIS[TETRACYANOFERRATE(III)] ION IN AQUEOUS SOLUTION

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ABSTRACT

Mechanistic studies of stepwise reductions of the di-µ-cyanobis-[tetracyanoferrate(III)] ion in aqueous solution.

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Although the dimeric di-µ-cyanobis[tetracyanoferrate(III)] ion was discovered in the early 1900's there is limited related literature available. The complex possesses many interesting qualities both on the fundamental as well as the biological level. Due to the fact that the complex contains two iron(III) centers, the kinetic and mechanistic behaviour of the complex when reacted with various reducing agents such as thiosulfate, thiourea, thiocyanate and L-cysteine have been investigated.

In this study we have investigated the kinetics and mechanism of the reactions of the dimeric complex Di-µ-cyanobis[tetracyanoferrate(III)] ion, $[Fe_2(CN)_{10}]^{4-}$ with various reducing agents such as sodium meta-bisulfite, L-ascorbic acid and hexacyanoferrate(II) ion, using mainly spectrophotometric (stopped-flow and diode array) techniques.

Sulfite reacts with the complex ion $[Fe_2(CN)_{10}]^{4-}$ via four steps: each of the first two fast stages involves an electron transfer then the production of a mixed-valence sulfito-'complex adduct' via the attack of the $SO_3^{-\cdot}$ and

$HSO_3^{-\cdot}$ radicals. The third stage is slow and involves another electron transfer to produce $[Fe_2(CN)_9(CNHSO_3)]^{6-}$ or $[Fe_2(CN)_9(CNSO_3)]^{7-}$. The fourth stage is the hydrolysis that possibly cleaves the 2 CN bridges to produce $[Fe(CN)_5SO_3]^{5-}$. The first three stages are sulfite dependent. The rate constants for the first electron transfer (first stage) were 1.08 ± 0.03 $mol^{-1}\ dm^3\ s^{-1}$ and 50.8 ± 4.3 $mol^{-1}\ dm^3\ s^{-1}$ at 30.5 °C for the bisulfite and sulfite species respectively. The rate constants for the second electron transfer (second stage) were (0.085 ± 0.003) $mol^{-1}\ dm^3\ s^{-1}$ and 4.35 ± 0.34 $mol^{-1}\ dm^3\ s^{-1}$ at 30.5 °C for the bisulfite and sulfite species respectively. And finally the rate constants for the cleavage (third stage) were (0.22 ± 0.01) x 10^{-1} $mol^{-1}\ dm^3\ s^{-1}$ and 0.22 ± 0.04 $mol^{-1}\ dm^3\ s^{-1}$ at 29.9 °C for the bisulfite and sulfite species respectively. The enthalpy of activation for all three stages were all positive values while the entropy of activation were negative for the bisulfite species and positive for the sulfite species.

The mechanism is thought to involve the formation of an ion-triplet consisting of the complex, the metal cation and sulfite. The effect of the catalysis by alkali metal cations was observed, and the reactivity was found to be $Li^+ < Na^+ < K^+ < Cs^+$. This was ascribed to the decrease in the enthalpies of hydration as one descends the group since deaquation is necessary to facilitate formation of an ion-triplet and electron-transfer between reacting anions. The ion-triplet formation constant, K_{IT}, also

increases down the group for the same reason. Detailed calculations based on ion-triplet mechanism determined the rate constant of electron-transfer: $k_{et1} = 2.44 \pm 0.25\ mol^{-1}\ dm^3\ s^{-1}$ and $k_{et2} = 92.3 \pm 2.8\ mol^{-1}\ dm^3\ s^{-1}$ at 30.5 °C for the bisulfite and sulfite species respectively.

The outer-sphere reduction of the complex with L-ascorbic acid was revisited to give a more accurate determination of kinetic and stoichiometry data. It was determined that this reaction proceeds via three stages, the first stage is approximately ten times faster than the second. It is proposed that the first two stages are successive one-electron transfer reactions resulting in the reduction of the two iron (III) centers followed by the much slower third stage, which is the hydrolysis of the iron (II) dimeric complex to yield aquapentacyanoferrate(II). The rate constants for the first electron transfer (first stage) are $(3.82 \pm 0.09) \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ and $(5.10 \pm 0.93) \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ at 24.8 °C for the HA^- and A^{2-} species respectively. The rate constants for the second electron transfer (second stage) were $(5.52 \pm 0.11) \times 10^1\ dm^3\ mol^{-1}\ s^{-1}$ and $(12.6 \pm 1.1) \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ at 24.8 °C for the HA^- and A^{2-} species respectively.

Using the Marcus cross-relationship, the self exchange rate constants, $k_{11} = 2.35 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ for the $[Fe_2(CN)_{10}]^{4-/5-}$ redox couple, and $k_{11} = 9.23 \times 10^{11}\ dm^3\ mol^{-1}\ s^{-1}$ for the $[Fe_2(CN)_{10}]^{5-/6-}$ redox

couple, were determined. These rate constants were indicative of an outer-sphere electron transfer mechanism.

Ion-triplet based calculations determined k_{et1} = (2.20 ± 0.12 x 10^2) $dm^3 mol^{-1} s^{-1}$ and k_{et2} = (5.3 ± 2.0) x 10^8 $dm^3 mol^{-1} s^{-1}$ at 24.8 °C for the HA^- and A^{2-} species respectively.

The outer-sphere reduction of the complex with the hexacyanoferrate(II) ion proceeds via two steps: the initial stage involving the predictable electron transfer and thus the production of the mixed valence complex species. The final stage is thought the involve the decomposition of the dimer complex to form iron(II) ion which undergoes slow oxidation and further reaction with the hexacyanoferrate(II) to give the complex $Fe^{III}[Fe^{II}(CN)_6]^-$. The rate constants for the first stage were found to be (176 ± 7) x 10^2 $dm^3 mol^{-1} s^{-1}$ and (19.7 ± 0.6) x 10^2 $dm^3 mol^{-1} s^{-1}$ at 25.9°C for the mono and di-protonated species respectively.

The activation parameters of $\Delta H^\#$ and $\Delta S^\#$ for the initial stage were determined to be (22.7 ± 5.7), (32.6 ± 1.8) kJ mol^{-1} and (-86.9 ± 18.5), (-72.8 ± 5.8) J $mol^{-1} K^{-1}$ for the mono and di-protonated species respectively.

Ion-triplet based calculations determined k_{et1} = (102.4 ± 4.3) $mol^{-1} dm^3 s^{-1}$ and k_{et2} = (13.01 ± 0.35) $dm^3 mol^{-1} s^{-1}$ at 26.0°C for the mono and di-protonated species respectively.

Preliminary investigations were carried out to study the electron-transfer reactions between the complex and the monomeric species aquapentacyanoferrate(II) as well as the mixed-valence complex species and aquapentaamminecobalt(III). Both reactions appeared to be of an outer-sphere nature.