

ABSTRACT

The solubilities of various mononuclear, dinuclear and tetranuclear cobalt(III) complexes were measured and used to determine the transfer chemical potentials. Single ion values for the complex ions, based on the TATB extrathermodynamic assumption were evaluated and discussed with respect to the effects of ligands, sizes, charges and bridging groups.

The partial molar volumes of some dinuclear cobalt(III) complexes were also determined.

The kinetics of the acid hydrolysis of the tri- μ -hydroxobis[triamminecobalt(III)] ion, $[(\text{NH}_3)_3\text{Co}(\mu\text{-OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$, was studied as a function of temperature, $[\text{H}^+]$ and $[\text{Cl}^-]$. The reaction consists of three distinct steps, the first two of which correspond to cleavage of a hydroxo bridge to produce $\text{cis}-[(\text{NH}_3)_3(\text{H}_2\text{O})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_3]^{4+}$ and the subsequent isomerisation to the *trans*-congener. The kinetic and activation parameters for these two steps correspond to the previously reported values.^{143,196} The third step involves a rate limiting second bridge cleavage to give mononuclear species and was studied at an ionic strength of 1.0 mol dm^{-3} and over the ranges $0.1 \leq [\text{H}^+] \leq 0.5 \text{ mol dm}^{-3}$, $25.1 \leq \theta \leq 35.1^\circ\text{C}$, $0.1 \leq [\text{Cl}^-] \leq 0.5 \text{ mol dm}^{-3}$ and various methanol-water cosolvent mixtures containing up to 40% methanol. The rate of the reaction was first order with respect to $[\text{Cl}^-]$ and involves a $[\text{H}^+]$ -dependent (k_c) and independent (k'_c) pathways. At 25.1°C $k_c = 1.17 \times 10^{-2} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$, with $\Delta H^\ddagger = 51 \pm 14 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -110 \pm 48 \text{ J mol}^{-1} \text{ K}^{-1}$, while $k'_c = 4.4 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ with, $\Delta H^\ddagger = 132 \pm 32 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 136 \pm 105 \text{ J mol}^{-1} \text{ K}^{-1}$. A mechanism for the reaction was proposed based on the variation of rate with $[\text{Cl}^-]$ and methanol content of the solvent as well as analysis of products of the reaction.

The kinetics of the oxidation of L-ascorbic acid by cobalt(III) hexols, $[\text{Co}\{(\mu\text{-OH})_2\text{CoN}_4\}_3]^{6+}$ ($\text{N}_4 = (\text{NH}_3)_4$, $(\text{en})_2$ and tren), dinuclear cobalt(III)

complexes, $[\text{N}_4\text{Co}(\mu\text{-OH})_2\text{CoN}_4]^{4+}$ ($\text{N}_4 = (\text{NH}_3)_4, (\text{en})_2$) and mononuclear cis-diaqua cobalt(III) complexes, $[\text{N}_4\text{Co}(\text{H}_2\text{O})_2]^{3+}$ ($\text{N}_4 = (\text{NH}_3)_4, (\text{en})_2$ and tren) were studied as a function of pH, L-ascorbic acid concentration, temperature, ionic strength and methanol content of the solvent. The kinetic data indicated involvement of the mono-protonated (HA^-) and de-protonated (A^{2-}) ascorbate species in the redox process for the hexols and dinuclear complexes.

For $[\text{Co}\{(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4\}_3]^{6+}$ the rate constants, k_1 and k_2 , at 25°C are $0.22 \pm 0.02 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $(5.51 \pm 0.09) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively and the corresponding activation parameters are: $\Delta\text{H}_1^\ddagger = 103 \pm 7 \text{ kJ mol}^{-1}$, $\Delta\text{S}_1^\ddagger = 89 \pm 22 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta\text{H}_2^\ddagger = 46 \pm 3 \text{ kJ mol}^{-1}$, $\Delta\text{S}_2^\ddagger = 19 \pm 11 \text{ J mol}^{-1} \text{ K}^{-1}$.

For the dinuclear $[(\text{NH}_3)_4\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{4+}$ the rate constants, k_1 and k_2 , at 25°C are $0.20 \pm 0.05 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $(1.47 \pm 0.03) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively and the corresponding activation parameters are: $\Delta\text{H}_1^\ddagger = 137 \pm 43 \text{ kJ mol}^{-1}$, $\Delta\text{S}_1^\ddagger = 204 \pm 142 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta\text{H}_2^\ddagger = 89 \pm 42 \text{ kJ mol}^{-1}$, $\Delta\text{S}^\ddagger = 116 \pm 138 \text{ J mol}^{-1} \text{ K}^{-1}$.

The results indicated that only the HA^- species was involved in the redox process for the mononuclear complexes. The specific rate constants for the species $[(\text{tren})\text{Co}(\text{H}_2\text{O})_2]^{3+}$ and $[(\text{tren})\text{Co}(\text{OH})(\text{H}_2\text{O})]^{2+}$ (k_1 and k_2) are $0.26 \pm 0.09 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $1.25 \pm 0.03 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively at 30°C and the corresponding activation parameters are: $\Delta\text{H}_1^\ddagger = 124 \pm 9 \text{ kJ mol}^{-1}$, $\Delta\text{S}_1^\ddagger = 137 \pm 30 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta\text{H}_2^\ddagger = 82 \pm 2 \text{ kJ mol}^{-1}$, $\Delta\text{S}_2^\ddagger = 26 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$.

The effect of methanol content of the solvent on the rate parameters were discussed with respect to solvation of the initial states and transition states.

The Marcus cross-relationship and Fuoss model for electron transfer were applied to the redox processes to determine the self-exchange rate

constants for the tetranuclear and dinuclear complexes as well as the rate determining step for the reduction of the hexols.