

ABSTRACT

Some substitution and electron-transfer reactions involving cyanide complexes of manganese(III) and ruthenium (II) in acidic solution have been investigated in two separate studies.

In the first, a detailed investigation of the spectra of potassium hexacyanomanganate(III) in aqueous cyanide solution was carried out and the reaction which this complex undergoes on acidification with perchloric acid was followed spectrophotometrically at 380nm and an ionic strength of 0.50M ($\text{NaClO}_4/\text{HClO}_4$). This reaction, which has been interpreted as an acid-catalyzed aquation, followed a rate law:

$$\text{rate} = k_{\text{obs}} [\text{Mn}(\text{CN})_6^{3-}]$$

The data obtained showed a dependence of k_{obs} on the acidity and fitted the equation

$$k_{\text{obs}} = k_0 + k_1 [\text{H}^+]$$

which suggested both acid-independent and acid-dependent pathways for the aquation. The product of the reaction has been identified by its absorption spectrum as the hydroxopentacyanomanganate(III) species, $[\text{Mn}(\text{CN})_5\text{OH}^{3-}]$.

A kinetic study was also made of the reaction of the aquation product with hydroxylamine at 25.0°C and ionic strength 0.50M to give Mn^{2+} , HCN and N_2 as products. This

reaction was found to show a first-order dependence on complex ion, but a less than first-order dependence on the hydroxylammonium ion concentration, this being present in excess. The data obtained, which followed a rate law:

$$\text{rate} = \frac{k [\text{Mn}(\text{CN})_6^{3-}] [\text{NH}_3^+\text{OH}]}{1 + K [\text{NH}_3^+\text{OH}]}$$

has been interpreted in terms of an equilibrium ion-pair formation prior to the redox step. A possible mechanism is discussed.

A study has also been made of the nitrous acid catalyzed conversion of potassium hexacyanoruthenate(II) to a ruthenium cyanonitrosyl complex in varying concentrations of nitric acid (1-6M). Kinetic data was obtained by following product formation by direct spectrophotometry at 450nm and 25.0°C. Rate measurements proved the reaction to be first-order in nitrous acid when this was present in limiting concentrations, but independent of this reagent when present in excess.

The kinetic data is consistent with a redox equilibrium between Ru(II), Ru(III) and HNO_2 , HNO_3 , being established in solution prior to the reaction of ruthenium(III) complex with nitrogen dioxide to give a cyanonitrosyl complex. Depending on the nitrous acid concentration present, either reaction can be made rate determining. Possible mechanisms are discussed.