METAL ION CATALYSIS OF SUBSTITUTION AND REARRANGEMENT REACTIONS OF SOME COMPLEX OXALATES OF CHROMIUM(III)

A Thesis

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by

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ABSTRACT

The metal ion catalysed aquation of the trisoxalatochromium(III) ion has been studied in the presence and absence of added electrolytes with emphasis on the copper(II) ion catalysed aquation. The interpretation of the observed catalytic effects of the copper(II) ion, has been attempted in terms of ion association. The proposed scheme, for the aquation, involves metallation of the $CrOX_3^{3-}$ species to account for the promoting effect of the copper(II) ions. The specific rates of aquation and the formation constants of the various species formed between the copper(II) ion and the $CrOX_3^{3-}$ ion have been obtained using curve fitting techniques. Further, the dependence of the formation constants and the specific rates of aquation on temperature has been shown to yield realistic thermodynamic and activation parameters for the proposed model.

Increasing the pH was found to have an accelerating affect on the aquation of the trisoxalatochromium(III) ion at constant copper ion concentration. This has been discussed, using ion association, in terms of catalysis of the aquation reaction by hydrolysis products of the copper(II) ion, in particular the $CuOH^+$ ion.

The catalysed and uncatalysed isomerisation of the bisoxalato-chromium(III) ion has been investigated in the presence and absence of various electrolytes and the kinetic data has been rationalised in terms of an ion association model.

It has also been proposed, from comparisons of studies on the copper(II) ion catalysed aquation and racemisation of the trisoxalato-chromium(III) ion, that a copper(II) ion associates with the $CrOX_3^{3-}$ ion through three carboxyl oxygen atoms, one from each oxalate group to form a monometallated species. Further comparison of these studies has led us to postulate, in the aquation, that a second copper(II) ion, proposed to associate with the monometallated species, associates with two carbonyl oxygen atoms of one of the oxalate groups of the $CrOX_3^{3-}$ ion. This, and the comparison of the specific rates of aquation of the monometallated and bimetallated species, led us to the conclusion that aquation occurs by a rapid one ended dissociation of an oxalate ligand followed by a rate determining loss of the oxalate group.

A number of other results of relevance to the substitution and rearrangement reactions of chromium(III)-oxalate complexes, have also been included.

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