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

A Thesis

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for the Degree of Doctor of Philosophy

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 bimetalated 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.

TABLE OF CONTENTS

	<u>Page</u>
<u>CHAPTER 1 : INTRODUCTION</u>	1
<u>REACTIONS OF CHROMIUM-OXALATE COMPLEXES</u>	
1.1 Reactions of the Trisoxalatochromium(III) Anion	1
1.2 Reactions of Other Chromium(III)-Oxalate Complexes	8
1.3 Aquation of the Trisoxalatochromium(III) Anion	10
1.4 Aquation of Other Chromium(III)-Oxalate Complexes and Anation Reactions by Oxalate Ions	16
1.5 Isomerisation of the Bisoxalatodiaquochromium(III) Anion	21
<u>METAL ION CATALYSIS</u>	
1.6 Metal Ion Catalysis of Organic Reactions	23
1.7 Metal Ion Catalysis of Inorganic Reactions	28
1.8 Metal Ion Catalysed Reactions of Chromium(III) Oxalate Complexes	30
<u>SALT EFFECTS IN REACTION KINETICS</u>	
1.9 Ionic Theories	37
1.10 Electrolyte Effects on Reaction Kinetics	39
1.11 Ion Association	41

	<u>Page</u>
<u>SALT EFFECTS ON THE RACEMISATION OF THE TRISOXALATOCHROMIUM(III)</u>	
<u>ANION</u>	
1.12 "Ionic Strength" Interpretation	48
1.13 Ion Association Interpretation	51
1.14 The Present Study	55
<u>CHAPTER 2 : EXPERIMENTAL</u>	56
2.1 Reagents	56
2.2 Apparatus	61
2.3 Spectra	65
2.4 Aquation Studies	65
2.5 Isomerisation Studies	69
<u>CHAPTER 3 : STOICHIOMETRIC MECHANISM OF THE COPPER(II) ION</u>	73
<u>CATALYSED AQUATION OF THE TRISOXALATOCHROMIUM(III)</u>	
<u>ANION</u>	
3.1 Introduction	73
3.2 Stoichiometric Interpretation of Rate Studies	73
3.3 Aquation of the Trisoxalatochromium(III) Ion	75
3.4 Aquation of the Bisoxalatodiaquo-chromium(III) Ion	76
3.5 Aquation of the Tetraquomonoxalatochromium(III) Ion	78
3.6 Spectra Determination of the Aquation Products	82

	<u>Page</u>
<u>CHAPTER 4 : PRELIMINARY EXPERIMENTS ON SALT EFFECTS IN</u>	86
<u>THE AQUATION OF THE TRISOXALATOCHROMIUM(III)</u>	
<u>ION</u>	
4.1 Aquation of the Trisoxalatochromium(III) Ion in Aqueous Solution	86
4.2 Photochemical Decomposition of the Trisoxalato- chromium(III) Ion	88
4.3 Dependence of the Rate of Aquation of the Tris- oxalatochromium(III) Ion on pH	89
4.4 Dependence of the Observed Rate of Aquation of the Trisoxalatochromium(III) Ion on pH in the Presence of Copper Perchlorate	90
4.5 Dependence of the Rate of Aquation on the Anion of the Copper Salt	92
4.6 Dependence of the Rate of Aquation of M_3CrOX_3 on the Cation, M^+ , in the Presence of Copper Perchlorate	93
<u>CHAPTER 5 : COPPER(II) ION CATALYSED AQUATION AND RACEMISATION</u>	96
<u>OF THE TRISOXALATOCHROMIUM(III) ION</u>	
5.1 Experimental	96
(i) Kinetic studies	96
(ii) Stability of pH	97

CHAPTER 5 : (cont'd.)

5.2	(i)	Dependence of the Observed Rate of Aquation on Copper Perchlorate Concentration	98
	(ii)	Dependence of the Observed Rate of Aquation of the Trisoxalatochromium(III) Ion on Copper Perchlorate Concentration at Constant Ionic Strength	99
	(iii)	Effect of Temperature on the Rate and Formation Constants of the Aquation of the Trisoxalatochromium(III) Ion in the Presence of Copper Perchlorate	133
5.3		The Copper Sulphate Catalysed Aquation of the Trisoxalatochromium(III) Anion	142
5.4		Dependence of the Rate of Racemisation of the Trisoxalatochromium(III) Ion on Copper Salt Concentration at 0.1°C. A re-analysis of Shooter's ⁷⁴ Data	156
5.5		Prediction of the Dependence of the Observed Rate of Aquation on Trisoxalatochromium(III) Ion Concentration	163
5.6		Summary	164

<u>CHAPTER 6 : THE COPPER(II) ION CATALYSED AQUATION OF THE</u>	169
<u>TRISOXALATOCHROMIUM(III) ANION. EFFECT OF pH</u>	
<u>ON THE OBSERVED RATE OF AQUATION</u>	
6.1 Introduction	169
6.2 Hydrolysis of the Copper(II) Ion	170
6.3 The Dependence of the Observed Rate of Aquation of the Trisoxalatochromium(III) Ion on pH in the Presence of 0.01M Copper Perchlorate	175
6.4 The Detection of Copper-Hydroxy Polymer Formation	195
<u>CHAPTER 7 : ISOMERISATION OF THE BISOXALATODIAQUOCHROMIUM(III)</u>	197
<u>ION</u>	
7.1 The Rate of Isomerisation of the Bisoxalatodiaquo- chromium(III) Ion in Aqueous Solution	197
7.2 The Dependence of the Observed Rate of Isomerisation of the Bisoxalatodiaquochromium(III) Ion on Sodium Perchlorate Concentration	198
7.3 Copper(II) Ion Catalysed Isomerisation of the Bisoxalato- diaquochromium(III) Ion	201
(i) Experimental	201
(ii) The Dependence of the Rate of Isomerisation on Copper Perchlorate Concentration	203

<u>CHAPTER 7 : (cont'd.)</u>	
(iii) The Dependence of the Rate of Isomerisation on Copper Sulphate Concentration	210
7.4 Summary	214
<u>CHAPTER 8 : SUMMARY AND CONCLUSIONS OF THE COPPER(II) ION CATALYSED REACTIONS OF SOME CHROMIUM-OXALATO COMPLEXES</u>	218
<u>CHAPTER 9 : THE DETECTION OF ION PAIR FORMATION BETWEEN METAL IONS AND THE TRISOXALATOCHROMIUM(III) ION USING USING CIRCULAR DICHROISM STUDIES</u>	230
9.1 Introduction	230
9.2 Previous Attempts of Detection	231
9.3 Circular Dichroism Studies of the Trisoxalatochromium(III) Ion	234
(i) Experimental	234
(ii) Circular Dichroism Spectrum of (+) CrOX_3^{3-}	234
(iii) Circular Dichroism Spectrum of (+) CrOX_3^{3-} in the Presence of Metal Salts	235
<u>APPENDIX : KINETIC DATA</u>	

APPENDIX : COMPUTER PROGRAMS

BIBLIOGRAPHY :

ACKNOWLEDGEMENTS :