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PART I

DISSOCIATION KINETICS OF MAGNESIUM AMINOCARBOXYLATE COMPLEXES

PART II

KINETICS OF THE POTASSIUM FERRATE OXIDATION OF CERTAIN NITROGEN-CONTAINING COMPOUNDS, AND THE APPLICATION OF POTASSIUM FERRATE TO THE DETERMINATION OF CHEMICAL OXYGEN DEMAND

by

Mark G. Cherwin

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TITLE

Part I - Dissociation Kinetics of Magnesium Aminocarboxylate Complexes;

Part II - Kinetics of the Potassium Ferrate Oxidation of Certain Nitrogen-containing Compounds, and the Application of Potassium Ferrate To the Determination of Chemical Oxygen Demand

BY

Mark G. Cherwin

APPROVED	DATE
James D. Carr	12 - 16 - 76
Robert C. Larson	12 - 16 - 76
Michael L. Gross	12 - 16 - 76
Robert S. Marianelli	12 - 16 - 76

SUPERVISORY COMMITTEE

GRADUATE COLLEGE **UNIVERSITY OF NEBRASKA**

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TABLE OF CONTENTS

Page

LIST OF TABLES

Table Page

Table | Page

LIST OF FIGURES

Figure Page

Figure Page

Figure Page

Figure Page

PART I

Dissociation Kinetics of Magnesium Aminocarboxylate Complexes

INTRODUCTION

In the past several years a number of investigations have studied the symmetric, near-symmetric, and enantiomeric exchange reactions of the aminccarboxylate ligands EDTA, PDTA and CyDTA. Structures, names and abbreviations for these ligands are given in Table I. Complexes between these ligands and a variety of metal ions have been used: Calcium (1,2), strontium (3), cadmium (4,5), lead (6,7), nickel (8,9), copper (10), and zinc (11). In the cases of calcium, cadmium, lead and copper, the reactions of all three of these structurally similar ligands have been studied. Only in the cases of calcium and cadmium has the investigation been extended to include the ligand BDTA, a structural intermediate between PDTA and CyDTA. In addition to kinetic studies of this type, the formation of complexes between these ligands and alkali metal ions has also been investigated (12-17).

In many of these studies, dissociative pathways, particularly hydrogen ion catalyzed ones, have been observed in addition to ligand dependent reactions. Certain rate constants for these dissociative pathways for

aminocarboxylate complexes of the alkaline earths have been reported (2,3,18-20), but the paucity of information available for the particular member of this family, magnesium, is surprising.

One of the most frequently used techniques for studies of this type has been polarimetry. This of course necessitates the use of an optically active ligand. It further requires that the reaction be slow enough to allow for both mixing of the reactants and response of the mechanical detection system with which most conventional polarimeters are equipped. The rates of the ligand exchange reactions for magnesium aminocarboxylate complexes are such that the polarimetric technique is well suited to their investigation.

The so-called "Eigen mechanism" for the formation reaction of metal ion complexes proposes that the rate-determining step be the loss of water from the primary coordination sphere of the metal ion after the metal ion has formed an outer-sphere complex with the incoming ligand. Accordingly, metal ions may be classified with respect to their rate behavior in the light of this general mechanism. Extensive work of this nature has been carried out for exchange reactions involving monodentate ligands, but only recently have such investigations been extended to multidentate ligands. Included among these have been the

aminocarboxylates (2,21). Although calcium and strontium have been classified in terms of this mechanism, little is known of the corresponding rate behavior of the magnesium ion. The purpose of the present investigation is to provide this information.

In the present study the polarimetric technique was used to measure the kinetics of the following ligand exchange reactions:

$$\text{CyDTA} + \text{Mg-l-PDTA} \longrightarrow \text{Mg-CyDTA} + \text{l-PDTA} \quad (1)$$

$$\text{CyDTA} + \text{Mg-d-BDTA} \longrightarrow \text{Mg-CyDTA} + \text{d-BDTA} \quad (2a)$$

$$\text{d-CyDTA} + \text{Mg-meso-BDTA} \longrightarrow \text{Mg-d-CyDTA} + \text{meso-BDTA} \quad (2b)$$

$$\text{d-CyDTA} + \text{MgEDTA} \longrightarrow \text{Mg-d-CyDTA} + \text{EDTA} \quad (3)$$

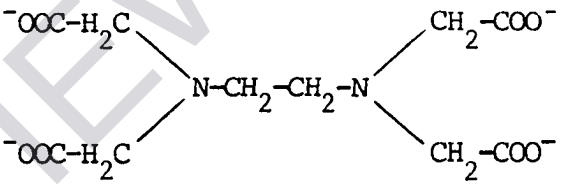
From these measurements, dissociative rate constants are determined. These results are then used to calculate formation rate constants through known equilibrium constants and comparisons are made with "Eigen mechanism" formation rate predictions.

TABLE I.

Structures of Aminocarboxylate Ligands

Ligand	Abbreviation
Ethylenediaminetetraacetate	EDTA or Y-4

Structure:



Ligand	Abbreviation
Propylenediaminetetraacetate	PDTA or P-4

Structure:

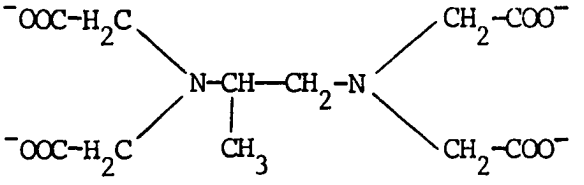
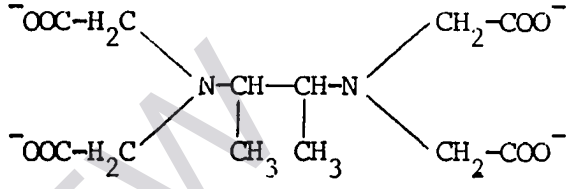


TABLE I. Continued

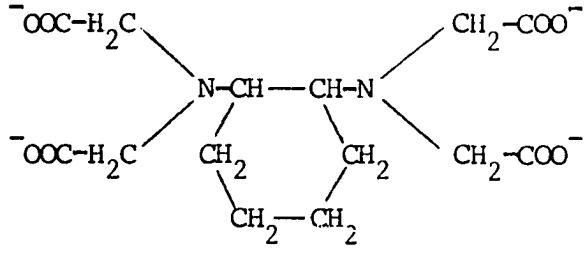
Ligand	Abbreviation
Trans-2,3-Diaminobutane-N,N,N',N'-tetraacetate	BDTA or B-^{4}

Structure:



Ligand	Abbreviation
Trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetate	CyDTA or Cy-^{4}

Structure:



EXPERIMENTAL

Reagents. All solutions were prepared with deionized, distilled water using standard volumetric glassware. Those used over a period of time as stock solutions were stored in polyethylene bottles. Gilman 2 ml and 0.2 ml microburets were used for all titrations and in preparations of stock solutions and reaction mixtures, where such volumes were appropriate. All pH adjustments were made using reagent grade nitric acid or tetramethylammonium hydroxide (TMAOH - Southwestern Chemicals Inc.). Stock magnesium and zinc ion solutions were prepared from the corresponding reagent grade nitrate salts and standardized by titration with standard disodium EDTA solution. All metal ion-ligand titrations were carried out in excess ammonia buffer (pH~10) using eriochrome black T indicator. Ligand solutions were standardized by titration with either standard magnesium or standard zinc solution. The zinc solution was prepared for use in a separate project not included here. Its use as a standard in this work was bred purely of convenience. The magnesium complexes of each of the various ligands were prepared by mixing stoichiometric amounts of stock magnesium ion solution and the appropriate ligand solution. Stock ligand solutions were prepared from their acids: H_4EDTA, H_4-1-PDTA,

H_4-d-BDTA, H_4-meso-BDTA, H_4-d-CyDTA, and H_4-dl-CyDTA. These ligands had been previously prepared and recrystallized by D. G. Swartzfager (2). The ionic strength of the reaction mixtures was not strictly controlled but varied as follows:

Reaction Mixtures		u
Mg-l-PDTA	+ 10-fold excess dl-CyDTA	0.3
Mg-l-PDTA	+ > 10-fold excess dl-CyDTA	0.6
Mg-d-BDTA	+ 10-fold excess dl-CyDTA	0.3
Mg-d-BDTA	+ > 10-fold excess dl-CyDTA	0.4 to 1.7*
Mg-meso-BDTA	+ 10-fold excess d-CyDTA	0.08
MgEDTA	+ 10-fold excess d-CyDTA	0.08
MgEDTA	+ > 10-fold excess d-CyDTA	0.1 to 0.14*

* depending upon actual CyDTA contentration

Apparatus. All reactions were monitored polarimetrically with a Perkin-Elmer Model 141 polarimeter equipped with a thermostatted 10 cm cell. A permanent record of optical rotation as a function of time was made by an attached Sargent model SR recorder. All reactions were carried out at 25 ± 0.2°C; such temperature being maintained by a Lauda MGW waterbath. The optical rotations of all but 11 reactions were monitored at 365 nm using the Hg source with which the

polarimeter was equipped. The other 11 reactions (all between MgEDTA and greater than 10-fold excess d-CyDTA) were monitored using an external Bausch and Lomb Xenon source with attached power supply and grating monochrometer. Since these reactions involved a large excess of optically active attacking ligand, the absolute amount of attacking ligand that would be converted to a complexed form would be small. As a result, the observed change in optical rotation (relative to the equilibrium value) would also be small. Since this change in rotation as a function of time is the experimental parameter of real interest, it was hoped that the more intense Xenon source with continuously variable wavelength would maximize its value. After careful alignment of the source with the optics of the polarimeter, the largest optical rotation value for an equilibrium mixture of the reactants of interest occurred at 345 nm. The improvement in signal strength, hence in optical rotation value, was modest: an increase of approximately 50%.

A minimum of 2 hours was required for polarimeter warm-up, after which time signal drift was inconsequential, even for the longest reactions (4 to 6 hours). Prior to every reaction, both the recorder and digital readout were zeroed against an air blank.

Solution pH measurements were made with a Corning model 12 expanded scale pH meter, equipped with standard Corning pH