INORGANIC
REACTION MECHANISMS

J. O. EDWARDS

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An Introduction

JOHN O. EDWARDS

Brown University

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THE PHYSICAL INORGANIC CHEMISTRY SERIES

Robert A. Plane and Michell J. Sienko, Editors

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Editors' Foreword

In recent years few fields of chemistry have expanded at a rate to match that of inorganic chemistry. Aside from the stimulus afforded by the demand for new materials, a primary cause for the resurgence has been the application of physics and physical chemistry concepts to inorganic problems. As a result, both researchers active in the field and students entering the field need to become as thoroughly familiar with physical concepts as with descriptive information. However, there is presently no single point of view sufficiently general to organize the entire discipline. Instead, various points of view have arisen corresponding to the most powerful methods of attack in each research area. The synthesis of these different points of view constitutes the present series of monographs. Each monograph is contributed by an inorganic chemist active in a particular research area and reflects the methods of approach characteristic to that area. The operational procedure has been to invite able scientists to write where their interests lead them.

The series fulfills several functions. Through flexible selection of several of the monographs to supplement the introductory volume, it can be used as a textbook for an advanced inorganic chemistry course that makes full use of physical chemistry prerequisites. As a series in total, it is a reference treatise of inorganic chemistry systematized by

physical principles. Finally, each monograph by itself represents a specialist's introduction to a specific research field.

It is hoped that the authors contributing to this series have succeeded in directing attention to unsolved problems and that their efforts will be repaid by continued research advances in inorganic chemistry.

M. J. SIENKO
R. A. PLANE

Ithaca, New York
February 1963

Preface

This book was written at the invitation of Mr. William A. Benjamin, and it is one of the series edited by Professors M. J. Sienko and R. A. Plane. As such it is designed to fit the needs of undergraduate seniors and beginning graduate students. The level is that of an introduction to the interesting and rapidly expanding field of inorganic reaction mechanisms.

In writing this book, the author assumes that the reader will have a general knowledge of inorganic and organic chemistries plus at least a year of physical chemistry, including both kinetics and thermodynamics. The first three chapters are general discussions of background material. The next six chapters are concerned with either specific types of mechanisms or specific groups of compounds. Some unsolved problems are mentioned in the last chapter.

In a book of this nature, it is possible neither to cover all of the variety of mechanisms known nor to cover any of them in great detail. A compromise in the choice of topics was made by the author, who has tried to achieve some variety plus some depth. Consequently it has been necessary to leave out many interesting studies, such as the fine work of Basolo and Wojcicki on carbonyl exchanges.

This book could not have been completed without the help of many people. Professors M. J. Sienko and R. A. Plane, of Cornell, Professor Cooper Langford, of Amherst, Mr. Joseph Epstein, of the

Army Chemical Center, and Professor Khairat M. Ibne-Rasa, of Brown, have made suggestions as to the scientific content. Miss Lois Nyberg, Mrs. Ruth C. Edwards, and particularly Mrs. Alda O. Kirsis have helped with the wording and grammar. Brown University has made available the necessary time, and Professors John Ross and Richard L. Carlin have significantly helped by taking over many of my lectures. For their forbearance while his mind was solely on the book, the author is grateful to his family and his students.

<div align="right">JOHN O. EDWARDS</div>

Providence, Rhode Island
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Introduction

1-1 THE SUBJECT OF THIS BOOK

The field of inorganic reaction mechanisms is not a new one, for as early as the turn of the century several chemists were studying the kinetics of oxidation-reduction and acid-base reactions. In the succeeding years, particularly around 1930, acid-base catalysis was investigated rather carefully. These early investigations were carried out mostly by physical chemists, who employed only kinetics on simple aqueous mixtures and were interested mainly in testing the theories current at that time. During the same period, the organic chemists were becoming interested in detailing the pathways that atoms take during the course of a reaction. The now popular field of physical organic chemistry thus sprang into being, and interest in organic mechanisms is currently widening into the area of biochemical reactions.

In recent years, the inorganic chemists have become aware of the large array of systems available to them for study, both by the kinetic methods of the physical chemist and by the detailed stereochemical techniques of the organic chemist. It would be unfair, however, to assume that the relatively late entry of the pure

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inorganic chemist into the area of mechanisms showed a lack of interest. In fact, until the complex pattern of structures and bondings in inorganic molecules was partially resolved, there was little that the inorganic chemist could do in the area of mechanisms except for reaction kinetics. The nature of bonding in inorganic compounds is not yet fully resolved, and there are many structures to be worked out. There is no doubt, however, that the field of reaction mechanisms for inorganic compounds is receiving considerable attention at present.

Before discussion of actual cases, there are several points that must be mentioned to establish between the reader and the author a common set of definitions and symbols. This chapter deals with such points.

The *inorganic reactions* with which we shall deal involve compounds other than those containing carbon-hydrogen or carbon-carbon bonds at the reaction site. Because of the quality and quantity of previous work on organic compounds, it will be necessary to use organic examples for comparative purposes. Also, it has often been necessary (for stability, structural, electronic, or analytical reasons) for the inorganic chemist to use organic substituents in his systems, and such cases will be included here. Primarily, however, the cases will be noncarbon compounds.

By *reaction mechanism*, we mean the detailed, stepwise pattern of atomic and electronic motions that take place while reactants change to products. Heavy reliance on chemical kinetics will be necessary, because in inorganic systems many rapid equilibria are possible before the transition state. Other clues to mechanism are obtained through isotope-tracer studies, stereochemical investigations, medium effects (including both solvents and electrolytes), and linear free-energy relations.

1-2 STOICHIOMETRY

In all studies of mechanism, one of the first and certainly most important pieces of data needed is the *stoichiometry* of the reaction. There are two ways to interpret this word and both are correct. The more limited way, and this is the one we shall employ here, is that stoichiometry refers to the number of particles (atoms, molecules, and ions) in the balanced chemical equation representing the chemical reaction. In many cases, where more than a single reaction occurs, stoichiometry may refer more broadly to how much

reactant(s) goes to what product(s) and to the extent to which the various reactions compete.

The need for correct stoichiometry (equation balancing) is a point that most students do not fully recognize. One cannot quantitatively treat or discuss a reaction without first having balanced the equations for this reaction. It is also worth noting that identification of all products of the reaction can be useful in elucidation of mechanism. A single product suggests a single transition state involving atom transfer, whereas multiple products usually occur where the mechanism involves molecular fragmentation and competing transition states.

1-3 EQUILIBRIA

The relationship between the yield in a reaction at infinite time and the yield at some specific time during the course of the reaction is one that has not been carefully handled in some cases. Since this interrelation between thermodynamics and kinetics will be used in the chapters following, it is appropriate that the matter be covered here.

Thermodynamics is the area of physical chemistry that deals with the spontaneity of a chemical reaction. The first step in considering the potential yield of a reaction is to set up an expression of the type

$$K_c = \frac{[M]^m[N]^n \cdots}{[A]^r[B]^b \cdots} \tag{1-1}$$

where K_c is a temperature-dependent constant, brackets denote concentrations, and the other symbols are derived from the balanced chemical equation

$$aA + bB \cdots \rightleftharpoons mM + nN \cdots$$

Only at equilibrium will Eq. (1-1), called the *equilibrium-constant expression*, apply, for only in that state does the given ratio of concentrations become equal to the constant K_c. This constant can be calculated from the free energies of the reactants and products.

The equilibrium-constant formulation, which was first recognized by Guldberg and Waage in 1864, is commonly called the *law of mass action*. These workers stated that the extent of a reaction is proportional to the molar concentration of each reacting substance raised to a power equal to the number of molecules of

that substance taking part in the reaction. A more general statement is: the product of the concentrations of the products of a reaction, each raised to a power equal to the number of partaking molecules, divided by the product of the concentrations of the reactants, each raised to its analogous power, is equal to a constant at any given temperature.

For example, the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

in the gas phase reaches an equilibrium position corresponding to the mass expression

$$K_c = \frac{[HI]^2}{[I_2][H_2]} \tag{1-2}$$

where K_c has the value 45.9 at 490°C. Using this value, one can calculate percentage yields and the like at this temperature. It is important to remember that most equilibrium constants have dimensions; thus the value obtained for K_c will usually depend on the concentration units employed.

The equilibrium-constant expression has been given in terms of concentrations. Since the *activity* of a material (which might be defined as its effective concentration) is often different from its concentration, it is more strictly correct to use activities in the equilibrium expression. Use of concentrations may be satisfactory in certain cases, as for neutral molecules in dilute phases; in other cases, such as with ionic solutes, it is imperative that activities be employed.

Since the concentration of water is in great excess in most aqueous solutions studied, the activity of water is constant. This activity can, therefore, be placed in the constant of mass expression; one does not find the water concentration (or activity) expressed as such along with other concentration terms. An example will be given below.

Consider also the solubility-product expression for lead sulfide

$$K_{sp} = [Pb^{++}][S^-] \tag{1-3}$$

The reaction is

$$PbS(s) \rightleftharpoons Pb^{++} + S^-$$
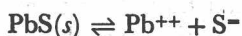
where the solid material is in equilibrium with the aqueous ions.