

Chemical Kinetics and
Inorganic Reaction Mechanisms
Second Edition

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*To my wife Ema
our son Miroslav
and our grandson Lovro*

FOREWORD

The serious study of the reaction mechanisms of transition metal complexes began some five decades ago. Work was initiated in the United States and Great Britain; the pioneers of that era were, in alphabetical order, F. Basolo, R. E. Connick, J. O. Edwards, C. S. Garner, G. P. Haight, W. C. E. Higginson, E. L. King, R. G. Pearson, H. Taube, M. L. Tobe, and R. G. Wilkins. A larger community of research scientists then entered the field, many of them students of those just mentioned. Interest spread elsewhere as well, principally to Asia, Canada, and Europe.

Before long, the results of individual studies were being consolidated into models, many of which traced their origins to the better-established field of mechanistic organic chemistry. For a time this sufficed, but major revisions and new assignments of mechanism became necessary for both ligand substitution and oxidation-reduction reactions. Mechanistic inorganic chemistry thus took on a shape of its own.

This process has brought us to the present time. Interests have expanded both to include new and more complex species (*e.g.*, metalloproteins) and a wealth of new experimental techniques that have developed mechanisms in ever-finer detail. This is the story the author tells, and in so doing he weaves in the identities of the investigators with the story he has to tell. This makes an enjoyable as well as informative reading.

Professor Ašperger is to be commended for preparing an authoritative and contemporary volume in the field. Modern studies are emphasized, and the readers are led straight to the frontier after the fundamentals are presented. The final chapter, *Some Recent Publications in the Scientific Spotlight*, is innovative. Eleven contemporary metal systems are shown, most in terms of synthesis and structure. Challenges can be found here for the mechanistic chemist.

James H. Espenson

Iowa State University
Ames, Iowa, USA
January 2003

PREFACE

This book is the thoroughly revised English version of the first Croatian edition published in 1999 by the Croatian Academy of Sciences and Arts in Zagreb under the title *Kemijska kinetika i anorganski reakcijski mehanizmi* (*Chemical Kinetics and Inorganic Reaction Mechanisms*). Since three years have passed from the appearance of the Croatian edition, the entire text has been rewritten. Thus, the thermodynamic and kinetic chapters have been raised to a higher level. New material has been added in an effort to make the English edition “up-to-date.” For instance, Ahmed Zewail’s laser technique for observation of the motions of atoms and molecules during chemical changes (Nobel Prize for chemistry, 1999) is now described. The thermally induced spin crossover phenomenon found in the solid state, as well as in solutions of the complexes of iron(II), iron(III) and cobalt(II), is presented. The molecular bistability leading to metal complexes with short memory effects has been depicted. Special attention has been paid to platinum complexes as antitumor agents. The antitumor activity of germanium complexes and of metallocenes is described and the mechanism of the antitumor activity is discussed. The second generation of cisplatin analogs is presented. Attention has been also paid to the antitumor activity of metallocenes. Metallocene chemistry is presently a very promising field of inorganic chemistry. Metallocene complexes of titanium and zirconium are mentioned and their important role in the manufacture of polymers is stressed. The role of ferrocene derivatives as effective nucleophilic catalysts in kinetic resolutions of many useful organic reactions is included in the text. New achievements in the chemistry of dendrimers (cascade molecules) are described.

During the writing of the book several papers relevant to the book’s subject were published. Although a time distance is usually needed for proper appreciation of recent papers, the author discusses a few of them in Chapter 15 – “Recent publications in the scientific spotlight”. The selection of these papers is very arbitrary, and limited to the author’s own interest and judgement, and the available space. The first initiative in this respect came from the author’s regular reading of the *Chemical & Engineering News*, and he acknowledges this incentive.

The book is a monograph aimed primarily at young researchers (graduate students) in the field of inorganic reaction mechanisms. The first part of the book (about 110 pages) is devoted to chemical kinetics necessary for the study

of any reaction mechanism, whether inorganic or organic. Understanding of this part requires a knowledge of inorganic, organic and physical chemistry at the undergraduate level. Graduate students of any chemical subject, as well as graduate students of chemical engineering, pharmaceutical and even medical sciences might find this part useful. It is written in a way easily acceptable to graduate students of various basic interests. The remaining part of the book is devoted to the study of reaction mechanisms of transition metal complexes. These compounds contain metals such as iron, copper, cobalt, *etc.*; their reactions are not only the domain of inorganic, but also of organic chemists and biochemists (hemin, hemoglobin, cytochromes, chlorophylls, cobalamins, *etc.*), so the interest in the subject of the book should actually be much broader than one would expect from its title.

The idea of writing such a book was born after I taught at a graduate course in inorganic reaction mechanisms at Northwestern University, Evanston, Illinois, in 1970. The majority of my students were inorganic chemists, but some declared themselves as organic chemists, interested in reaction mechanisms in general. With pleasure I adjusted my course to such an audience, because I have never appreciated the 19th century division into chemistry of “dead matter” (inorganic) and chemistry of substances isolated from living organisms (organic).

Since then, many years passed until in 1997 I started to work on the Croatian version of the book, having in mind that Croatian chemists should publish also in Croatian, otherwise further development of the Croatian chemical terminology would be seriously impeded, a problem that is faced by many small nations. When the book appeared in 1999, I received several suggestions to prepare its English version, which has now been done.

I am greatly obliged to Professor Vladimir Simeon for suggesting numerous improvements and for editing the manuscript. Besides, Professors Vl. Simeon and Tomislav Cvitaš, contributed several pages to Chapter 1 (mostly pertaining to quantum mechanics and to statistical thermodynamics), and conformed the definitions and usage of physical quantities, symbols and terminology to the current standards recommended by IUPAC. Thanks are due to my colleagues, Professors Zlatko Mihalić, Leo Klasinc and Nenad Trinajstić, who read the manuscript and gave many useful remarks and suggestions. Professor N. Trinajstić was the editor of the first (Croatian) edition. I am also grateful to Mrs. Greta Prajdić, BSc, for careful technical editing and to Mrs. Tamara Jovanović, BA, who corrected my English.

Smiljko Ašperger

Zagreb, October 2002

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