

Inorganic Reaction Mechanisms

无机反应机理

MARTIN L. TOBE AND JOHN BURGESS

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Preface

The aim of this book is to present an overall view of inorganic reaction mechanisms—substitution, dissociation, addition, electron transfer, intramolecular processes, and their various combinations and extensions—over essentially the whole of the Periodic Table. Although there is the expected dominance of transition metal complexes, compounds of the *sp*-block elements receive appropriate coverage, and occasional mention is made of the lanthanides and actinides. Similarly, the majority of substrates considered are classical inorganic compounds and complexes, but there is full coverage of organometallic systems, including consideration of mechanistic details of homogeneous catalysis, due attention to bioinorganic systems, and a sprinkling of examples from such areas as pharmacology and geochemistry. We restrict ourselves to reactions in solution, covering non-aqueous and mixed aqueous as well as aqueous, and indeed devoting a chapter specifically to medium effects. Although of course we concentrate very much on work published in recent years, we do in places refer to earlier, sometimes much earlier, work in order to sketch the background and context of current research and opinions. The philosophy adopted in this book is that the emphasis is placed on the individual acts of the reaction. The evidence considered will be that gathered, mainly from kinetics but also from stereochemistry and spectroscopy, from studies of systems chosen because they offer the least number of ambiguities and because they throw the most light upon the details of the mechanism. This approach is to be contrasted with many modern reaction mechanism texts, where the emphasis is on mechanism as a guide to synthesis and where reactions that are relevant to the problems of synthesis are given priority.

The breadth of coverage indicated in the preceding paragraph obviously precludes depth in the treatment of many areas of the subject. Obviously we have selected areas of particular importance or interest to us for fuller treatment. Other areas, many of considerable significance, have had to be merely touched on, with references to suitable reviews or recent key papers. In general the text is copiously, though obviously far from comprehensively,

referenced—fully comprehensive reviews have been cited wherever possible. We have not hesitated to cite a number of elderly reviews and books. Sometimes seminal or long-established versions provide the best perspectives, especially when written soon after the blossoming of a field by an author centrally involved in the original work. Often the clearest exposition appears before the i-dotting and t-crossing takes over. Fortunately for all interested in inorganic kinetics and mechanisms, the progress of the subject has been methodically and comprehensively chronicled, between January 1969 and mid-1991, in a series of reports. This series comprises the seven *Specialist Periodical Reports on Inorganic Reaction Mechanisms* published by the Chemical Society (latterly the Royal Society of Chemistry), and their continuation, under the title *Mechanisms of Inorganic and Organometallic Reactions* (eight volumes), published by Plenum Press.

The present book grew out of Martin Tobe's 1972 book of the same title, namely *Inorganic Reaction Mechanisms*. A quarter of a century has elapsed since its appearance, during which time the subject of reaction mechanisms in inorganic chemistry has developed from healthy adolescence to mature middle age. The philosophy underlying this book has remained the same, but the size has perforce increased markedly to reflect the enormous increase in data—and perhaps more modest increase in understanding. It was first planned over a decade ago, when Professor Tobe wished to update the text, but felt (quite wrongly!) unable to deal adequately with all the topics to be covered, and therefore co-opted the surviving author to deal with several areas. Tragically, Martin Tobe died early in 1993, and it has been left to the present writer to bring the book to publication. Fortunately Professor Tobe had almost completed the revision and updating of his sections of the manuscript at the time of his death, and had discussed in detail the form and treatment of the other sections of the book with the surviving author. The approach, content, and arrangement of the whole book thus reflect his views, with several sections enshrining his final long-pondered interpretations. It has taken a regrettably long time to finalize the manuscript, but it is hoped that in such sections the original author's aims, approach, and views have been preserved, and that the surviving author's updating has not been detrimental. Of course all errors and omissions, in these and all other parts of the final text, are the surviving author's responsibility.

This book is intended to present the subject matter as outlined above to academics who lecture or research in this and related fields, and to research workers and final-year undergraduates specializing in this topic. It is also hoped that it will be useful to a variety of scientists—academic, industrial, and public service—from other areas who need a detailed introduction to one or more of its main subject areas.

The long and chequered history of the present volume has left us indebted to a large number of people. We cannot hope to attempt to acknowledge them all individually here, but can only mention a selection. Firstly, we would like to acknowledge the influence and inspiration of the University College chemistry school of an earlier generation. In the preface to the 1972

version of *Inorganic Reaction Mechanisms* Martin Tobe singled out Sir Christopher Ingold and Sir Ronald Nyholm; the present writer would like to acknowledge his enormous debt to Reg Prince, himself a product of the Ingold-Hughes school at University College, for introducing him so interestingly, enthusiastically, and enjoyably to inorganic kinetics and mechanisms. We have both been very grateful for the camaraderie of the Inorganic Mechanisms Discussion Group of the Royal Society of Chemistry, which kept us abreast of current developments over many years. Turning to book production, I am very grateful to Alexandra Seabrook, Tina Cadle, Shuet-Kei Cheung, and Pauline Gillett of Addison-Wesley-Longman for their advice, assistance, encouragement, and patience. They deserve all credit and congratulations on finally coaxing a manuscript from an author eternally reluctant to stop 'improving' it. Finally, particular thanks to Rosalie Tobe for her help and support, and especially for her confidence in the surviving author.

John Burgess

Leicester

Abbreviations

Most ligand abbreviations and, where necessary, formulae are defined in the text or in tables at their point of appearance. Abbreviations for frequently encountered ligands in text, tables, figures, and formulae follow.

aq	water—of hydration <i>or</i> bulk solvent
bipy ^a	2,2'-bipyridyl
cod	cyclo-octadiene
cp	cyclopentadienyl
*cp	pentamethylcyclopentadienyl
cy	cyclohexyl
cyclam	1,4,8,11-tetraazacyclotetradecane (formula 1 in Chapter 4, p. 148)
cyt	cytochrome
dmf/DMF	<i>N,N</i> -dimethylformamide (as ligand/solvent)
dmsO/DMSO	dimethyl sulphoxide (as ligand/solvent)
edta	ethane-1,2-diamine-tetraacetate (formula 12 in Chapter 7, see p. 325)
etmalt	ethylmaltol(ate) (formula 16 in Chapter 4, see p. 192)
en	ethane-1,2-diamine
fc	ferrocene
imid	imidazole
L	ligand (generally monodentate)
LL (LLL ...)	general bidentate (terdentate ...) ligand
M ⁿ⁺ aq	hydrated metal ion
nta	nitrilotriacetate
Nu/nucl	nucleophile
OAc	acetate (ethanoate)
OTf	triflate (trifluoromethylsulphonate)

^a This abbreviation always stands for the 2,2'-compound—its 4,4'-isomer is abbreviated as 4,4'-bipy.

ox	oxalate (ethanedioate)
phen	1,10-phenanthroline
py	pyridine
pz	pyrazine
sep	sepulchrates ^b
terpy	terpyridyl
X ⁻	halide (Cl ⁻ , Br ⁻ , I ⁻) unless specified otherwise

^b Formulae for this and other encapsulating ligands will be found in Chapter 9, as formula 50 in Section 9.5.4.2.

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