Contents

Editors' Foi	reword	v
Preface		vii
Chapter 1	INTRODUCTION	1
1-1	The Subject of this Book	1
1-2	Stoichiometry	2
1-3	Equilibria	2 3
1-4	Reaction Rate	5
1-5	Transition-State Theory	8
1-6	Order and Reaction Mechanism	10
1-7	Symbols	11
Chapter 2	BINDING STRENGTH AND REACTION RATES: ACIDS, BASES, AND SOLVENTS	14
2-1		14
2-1		15
	General-Acid Catalysis	17
2-3		18
2-1		20
2-3	Staustical Corrections	20
		ix

X—CONTENTS

2-6	Lewis Theory	22
2-7	Other Definitions	24
2 -8	General Influence of Solvents	25
2-9	Physical Properties of Solvents	26
	Chemical Nature of Solvents	28

BINDING STRENGTH AND REACTION Chapter 3 **RATES: LINEAR FREE-ENERGY RELA-**TIONS 31 3-1 Linear Free-Energy Relations 32 3-2 Assumptions 36

3-3	Mathematical Form	37
3-4	Examples of LFER	37
3-5	Problems with LFER	40

3-6	Intermediates	45
3-7	Kinetic Isotope Effects	46

3-7 Kinetic Isotope Effects

Chapter 4 NUCLEOPHILIC DISPLACEMENTS 51 Types of Mechanism 4-1 51 4-2 Rate Scales 53 4-3 Rate Factors 54 4-4 Orders of Nucleophilic Character 57 4-5 **Displacements on Phosphorus** 59

- Displacements in Planar Complexes 4-6 63 68
- 4-7 Discussion

Chapter 5 NONRADICAL MECHANISMS FOR **PEROXIDE REACTIONS**

5-1	Nucleophilic Displacements	73
5-2	Peroxyanions as Nucleophiles	81
5 -3	Peroxyanions as Leaving Groups	82
5-4	Peroxide Decomposition	84

73

5-5 Hypohalite Reactions 88

	CONTEN	тs—xi
Chapter 6	REPLACEMENTS IN OCTAHEDRAL	
	COMPLEXES	90
6-1	Labile and Inert Complexes	90
6-2	Crystal-Field Stabilization	92
6-3	General Aspects	95
6-4	Dissociation vs. Displacement	100
6-5		103
≻6-6	Chromium(III) Compounds	107
6-7		112
Chapter 7	ELECTRON-TRANSFER REACTIONS	
	OF COMPLEXES	115
7-1	Electron-Transfer Theory	115
7-2	Outer-Sphere Exchange Reactions	118
7-3	Bridge Mechanism	120
* 7-4		125
7-5		127
7-6	Noncomplementary Reactions	128
7- 7	Replacement through Redox Mechanism	132
Chapter 8	REACTIONS OF OXYANIONS	137
8-1	Factors Affecting Rates	137
8-2	Ŷ.	142
8-3	Exchange between Phosphate and Water	145
	Induced Reactions	146
8-5	Chromate-Arsenite Reaction	149
8-6	Urea-Formation Reaction	151
Chapter 9	FREE RADICAL REACTIONS	154
- 9-1	Steady-State Approximation	155
9-1 9-2	Decomposition of Persulfate	155 155
9-2 9-3		155
	Chain Reactions	158
9-1 9-5	Hydrogen-Bromine Reaction	163
9-6		166
9-7	Persulfate-Peroxide Reaction	170
	· ····································	170

8

xii—Contents

Chapter 10	SOME UNSOLVED PROBLEMS	174
10-1	General Problems	174
10-2	Constituents of a Rate Law	175
10-3	Trace-Metal Catalysis	176
10-4	Problems in Phosphorus Displacements	177
10-5	Replacements in Coordination Compounds	180
10-6	Nitrosation Reactions	181
10-7	Some Reactions to Study	183



185