



The
**Molecular
World**



**Chemical Kinetics
and Mechanism**

edited by Michael Mortimer
and Peter Taylor

CONTENTS

PART 1 CHEMICAL KINETICS

Clive McKee and Michael Mortimer

USE OF THE CD-ROM PROGRAM: KINETICS TOOLKIT	10
1 INTRODUCTION	11
1.1 A general definition of rate	14
2 A CLOSER LOOK AT CHEMICAL REACTIONS	18
2.1 Individual steps	19
2.2 Summary of Section 2	23
3 RATE IN CHEMICAL KINETICS	24
3.1 Kinetic reaction profiles	24
3.2 <i>Rate of change of concentration of a reactant or product with time</i>	27
3.3 A general definition of the rate of a chemical reaction	31
3.4 Summary of Section 3	33
4 FACTORS DETERMINING THE RATE OF A CHEMICAL REACTION	35
4.1 A simple collision model	35
4.2 An experimental approach	38
4.3 Summary of Section 4	40
5 DETERMINING EXPERIMENTAL RATE EQUATIONS AT A FIXED TEMPERATURE	42
5.1 <i>Practical matters</i>	42
5.2 A strategy	43
5.3 Reactions involving a single reactant	44
5.3.1 A preliminary half-life check	44
5.3.2 The differential method	47
5.3.3 The integration method	52

5.4	Reactions involving several reactants	57
5.4.1	The isolation method	57
5.4.2	The initial rate method	60
5.5	Summary of Section 5	63
6	THE EFFECT OF TEMPERATURE ON THE RATE OF A CHEMICAL REACTION	65
6.1	The Arrhenius equation	65
6.2	Determining the Arrhenius parameters	67
6.3	The magnitude of the activation energy	73
6.4	Summary of Section 6	78
7	ELEMENTARY REACTIONS	80
7.1	Molecularity and order	80
7.2	Reactions in the gas phase	81
7.3	Reactions in solution	85
7.4	Femtochemistry	86
7.5	Summary of Section 7	91
8	REACTION MECHANISM	92
8.1	Evidence that a reaction is composite	92
8.2	A procedure for simplification: rate-limiting steps and pre-equilibria	94
8.3	Confirmation of a mechanism	100
8.4	Summary of Section 8	103
	SUMMARY OF PART 1	104
	LEARNING OUTCOMES FOR PART 1	105
	QUESTIONS: ANSWERS AND COMMENTS	108
	EXERCISES: ANSWERS AND COMMENTS	120
	FURTHER READING	131
	ACKNOWLEDGEMENTS	132

PART 2: THE MECHANISM OF SUBSTITUTION

Edited by Peter Taylor from work authored by Richard Taylor

1	ORGANIC REACTIONS	135
1.1	Why are organic reactions important?	135
1.2	Classification of organic reactions	136
2	REACTION MECHANISMS	139
2.1	Reaction mechanisms: why study them?	139
2.2	Breaking and making covalent bonds	144
2.2.1	Radical reactions	145
2.2.2	Ionic reactions	147
2.3	Summary of Sections 1 and 2	148
3	IONIC SUBSTITUTION REACTIONS	150
3.1	Nucleophiles, electrophiles and leaving groups	150
3.2	The scope of the S_N reaction	154
3.2.1	Nucleophiles	154
3.2.2	Leaving groups	156
3.3	How far and how fast?	161
3.3.1	How far?	161
3.3.2	How fast?	163
3.4	Summary of Section 3	164
4	S_N2 AND S_N1 REACTION MECHANISMS	166
4.1	Introduction	166
4.2	Kinetics and mechanism of S_N reactions	167
4.2.1	A concerted mechanism	168
4.2.2	Two-step associative mechanism	168
4.2.3	Two-step dissociative mechanism	169
4.2.4	Which mechanism is at work?	171
4.3	Summary of Section 4	174
5	S_N2 VERSUS S_N1	175
5.1	The effect of substrate structure	175
5.2	The effect of the nucleophile	177
5.3	Summary of Section 5	178
6	CONCLUDING REMARKS	179
	LEARNING OUTCOMES FOR PART 2	180
	QUESTIONS: ANSWERS AND COMMENTS	182
	ACKNOWLEDGEMENTS	185

PART 3: ELIMINATION: PATHWAYS AND PRODUCTS

Edited by Peter Taylor from work authored by Richard Taylor

1	INTRODUCTION: β-ELIMINATION REACTIONS	189
1.1	The mechanisms of β -elimination reactions	191
1.2	Summary of Section 1	193
2	THE E2 MECHANISM	194
2.1	The scope of the E2 mechanism	194
2.2	The stereochemistry of the E2 mechanism	195
2.3	Isomeric alkenes in E2 reactions	198
2.3.1	Which isomer will predominate?	199
2.3.2	Which direction of elimination?	200
3	THE E1 MECHANISM	203
3.1	Summary of Sections 2 and 3	206
4	ELIMINATION VERSUS SUBSTITUTION	208
4.1	Substrate structure	208
4.1.1	Unimolecular versus bimolecular mechanism	209
4.2	Choice of reagent and other factors	209
4.2.1	Choice of leaving group	210
4.2.2	Temperature	210
4.2.3	Summing up	210
4.3	Summary of Section 4	211
5	OTHER USEFUL ELIMINATION REACTIONS	212
5.1	Dehalogenation and decarboxylative elimination	212
5.2	Preparation of alkynes by elimination reactions	213
5.3	Summary of Section 5	214
	LEARNING OUTCOMES FOR PART 3	215
	QUESTIONS: ANSWERS AND COMMENTS	216
	ACKNOWLEDGEMENTS	224

CASE STUDY: SHAPE-SELECTIVE CATALYSIS USING ZEOLITES

Craig Williams and Michael Gagan

1	INTRODUCTION	227
1.1	Natural zeolites	227
1.2	Synthetic zeolites	228
2	STRUCTURE, PROPERTIES AND CLASSIFICATION OF ZEOLITES	230
2.1	Basic structures	230
2.2	Zeolite properties	232
2.3	Zeolites as catalysts	234
2.4	Zeolite classification	235
2.5	Small-pore zeolites	237
2.6	Medium-pore zeolites	238
2.7	Large-pore zeolites	239
3	SHAPE SELECTIVITY	242
3.1	Mass-transport discrimination	242
3.2	Transition-state selectivity	245
3.3	Molecular traffic control	245
4	APPLICATIONS OF SHAPE SELECTIVITY	246
4.1	<i>Para</i> selective alkylation of aromatic hydrocarbons	246
4.2	Selective xylene isomerization	246
4.3	Some other selective alkylation reactions of aromatic compounds	247
4.4	Methanol to gasoline	248
5	ZEOLITES AS ENZYME MIMICS	250
6	MESOPOROUS ALUMINOSILICATE STRUCTURES	251
7	CONCLUSION	255
	ACKNOWLEDGEMENTS	256
	INDEX	257
	CD-ROM INFORMATION	262