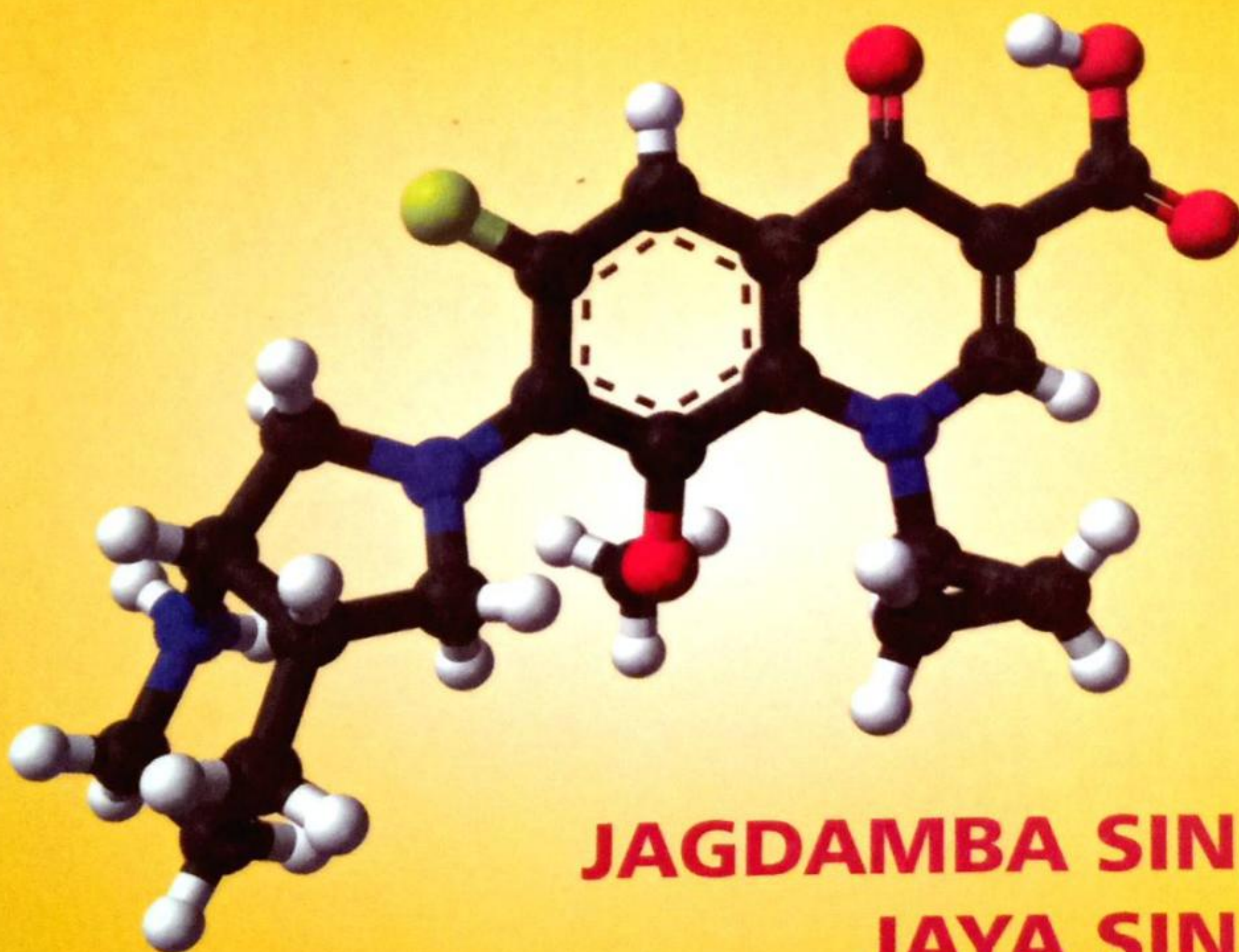


NEW AGE

FOURTH EDITION

PHOTOCHEMISTRY AND PERICYCLIC REACTIONS



JAGDAMBA SINGH
JAYA SINGH



NEW AGE INTERNATIONAL PUBLISHERS

Contents

<i>Preface to the Fourth Edition</i>	(v)
<i>Preface to the First Edition</i>	(vi)
<i>Acknowledgements</i>	(ix)

CHAPTER 1 Pericyclic Reactions 1-16

1.1	Introduction	1
1.2	Construction of π Molecular Orbitals of Ethylene and 1, 3-Butadiene	3
1.3	Symmetry in π Molecular Orbital	6
1.4	Filling of Electrons in π Molecular Orbitals in Conjugated Polyenes	8
1.5	Construction of Molecular Orbitals of Conjugated Ions and Radicals	9
1.6	Frontier Molecular Orbitals	13
1.7	Excited States	13
1.8	Symmetries in Carbon-Carbon Sigma Bond	14
1.9	Theory of Pericyclic Reactions	14
	<i>Glossary</i>	15
	<i>Further Reading</i>	15
	<i>Problems</i>	16

CHAPTER 2 Electrocyclic Reactions 17-57

2.1	Introduction	17
2.2	Conrotatory and Disrotatory Motions in Ring-opening Reactions	18
2.3	Conrotatory and Disrotatory Motion in Ring-closing Reactions	20
2.3.1	Open Chain Conjugated System having $4n\pi$ Conjugated Electrons	21
2.3.2	Open Chain Conjugated System having $(4n + 2)\pi$ Conjugated Electrons	22
2.4	Frontier Molecular Orbital (FMO) Method	23
2.4.1	Cyclisation of $4n\pi$ Systems	24
2.4.2	Electrocyclic Ring-Opening in which Polyene has $4n\pi$ Electrons	29
2.4.3	Cyclisation of $(4n + 2)\pi$ Systems	31

2.4.4	Electrocyclic Ring-opening in which Polyene has $(4n + 2)\pi$ Electrons	34
2.4.5	Selection Rules and Microscopic Reversibility	37
2.5	Correlation Diagram	39
2.5.1	Correlation Diagram of the Electrocyclic Reaction in which Polyene has $4n\pi$ Electrons	39
2.5.2	Correlation Diagram of Electrocyclic Reaction in which Polyene has $(4n + 2)\pi$ Electrons	43
2.6	The Woodward—Hoffmann Rule for Electrocyclic Reactions	46
2.6.1	Woodward—Hoffmann Rule for Electrocyclic Thermal Reactions	46
2.6.2	Photochemical Electrocyclic Reactions	46
2.7	Hückel-Mobius (H-M) Method or Perturbation Molecular Orbital (PMO) Method	50
	<i>Glossary</i>	52
	<i>Further Reading</i>	53
	<i>Problems</i>	53

CHAPTER 3 Cycloaddition Reactions 58–110

3.1	Introduction	58
3.2	Theory of Cycloaddition Reactions: FMO Method	60
3.2.1	[2 + 2] Cycloaddition Reactions	61
3.2.2	[4 + 2] Cycloaddition Reactions	63
3.3	Correlation Diagrams of Cycloaddition Reactions	80
3.3.1	Orbital Symmetry in Cycloaddition	80
3.3.2	Correlation Diagram of [4 + 2] Cycloaddition Reaction	82
3.4	The Woodward-Hoffmann Rule for Cycloaddition Reactions	85
3.4.1	The Woodward-Hoffmann Rule in 4 + 2 Cycloadditions	85
3.4.2	Woodward-Hoffmann Rule in 2 + 2 Cycloadditions	86
3.5	Hückel-Mobius Method	86
3.6	Cycloreversion or Retrocycloaddition Reactions	88
3.7	[4 + 2] Cycloadditions of Cations and Anions	91
3.8	Cycloadditions involving more than [4 + 2] Electrons	92
3.9	Some Anomalous [2 + 2] Cycloadditions	93
3.10	Chelotropic Reactions	96
3.10.1	[2 + 2] Chelotropic Cycloadditions	97
3.11	Chelotropic Elimination	98
3.12	1, 3-Dipolar Cycloadditions	99
3.12.1	Stereochemistry of 1, 3-Dipolar Cycloadditions	101
	<i>Glossary</i>	105
	<i>Further Reading</i>	105
	<i>Problems</i>	106

CHAPTER 4 Sigmatropic Rearrangement		111-159
4.1	Introduction and Classification	111
4.1.1	Classification of Sigmatropic Rearrangements	111
4.1.2	Name of the Rearrangement	112
4.2	Mechanism of Sigmatropic Rearrangement	115
4.2.1	Sigmatropic Shifts of Alkyl Group	120
4.2.2	Selection Rules for Sigmatropic Rearrangement	124
4.3	Other Sigmatropic Shifts	125
4.3.1	Cope Rearrangement	125
4.3.2	Claisen Rearrangement	132
4.4	[2, 3] Sigmatropic Rearrangements	140
4.5	Some Other $[m, n]$ Sigmatropic Rearrangements	143
4.6	The Woodward-Hoffmann Rule for Sigmatropic Rearrangement	144
4.6.1	The Woodward-Hoffmann Rule for (m, n) Sigmatropic Rearrangement where Migrating Group is not Hydrogen	144
4.6.2	The Woodward-Hoffmann Rule for (m, n) Sigmatropic Rearrangement where Migrating Group is Hydrogen	146
4.7	Hückel—Mobius Method in Sigmatropic Rearrangements	148
4.8	Modified and Degenerate Cope Rearrangement	150
4.9	Fluxional Molecules	153
	<i>Glossary</i>	154
	<i>Further Reading</i>	155
	<i>Problems</i>	155

CHAPTER 5 Group Transfer Reactions		160-167
5.1	Ene Reactions	160
5.2	Group Transfer Reactions given by Diimide	164
	<i>Glossary</i>	166
	<i>Further Reading</i>	166
	<i>Problems</i>	166

CHAPTER 6 Introduction and Basic Principles of Photochemistry		168-191
6.1	Energy of a Molecule	168
6.2	Photochemical Energy	171
6.2.1	Photochemical Excitation of the Molecule	172
6.3	Electronic Transitions	174
6.3.1	Types of Electronic Excitation and Molecular Orbital View of Excitation	175
6.4	Spin Multiplicity	180

6.5	Nomenclature of Excited States	182
6.6	The Fate of the Excited Molecule—Physical Processes: Jablonski Diagram	183
6.7	Photolytic Cleavage	188
6.8	Laws of Photochemistry	190
	6.8.1 Grotthuss-Draper Law	190
	6.8.2 Einstein's Law of Photochemical Equivalence	190
6.9	Quantum Yield or Quantum Efficiency	190
	6.9.1 The Reasons for High Quantum Yield	191
	<i>Further Reading</i>	191
	<i>Problems</i>	191

CHAPTER 7 Photochemistry of Carbonyl Compounds 192–236

7.1	α -Cleavage or Norrish Type I Process	192
	7.1.1 Norrish Type I Process given by Acyclic Saturated Ketones	192
	7.1.2 Norrish Type I Reaction of Saturated Cyclic Ketones	198
	7.1.3 Norrish Type I Process given by Cyclopentanones	204
	7.1.4 α -Cleavage given by Cyclobutanones	206
7.2	β -Cleavage Reaction	211
7.3	Intramolecular Hydrogen Abstraction (γ -Hydrogen Abstraction)	215
7.4	Hydrogen Abstraction from Other Sites	220
	7.4.1 β -Hydrogen Abstraction	221
	7.4.2 δ - and ϵ -Hydrogen Abstraction	221
	7.4.3 Hydrogen Abstraction from Distant Sites	222
7.5	Formation of Photoenols or Photoenolisation	223
7.6	Intermolecular Hydrogen Transfer: Intermolecular Photo Reduction	224
7.7	Photocycloaddition Reaction (Paterno-Büchi Reaction)	226
	7.7.1 Addition to Electron-Rich Alkenes	226
	7.7.2 Addition to Electron Deficient Alkenes	227
	7.7.3 Oxetane Formation with Dienes and Alkynes	229
	7.7.4 Intramolecular Paterno-Büchi Reaction	231
7.8	$ 2+2 $ Cycloaddition Reaction of Enones with Alkenes	232
	<i>Glossary</i>	234
	<i>Further Reading</i>	234
	<i>Problems</i>	235

CHAPTER 8 Photo Rearrangements 237–269

8.1	Photo Rearrangement of Cyclopentenone	237
8.2	Cyclohexanone Rearrangements	238
	8.2.1 Lumiketone Rearrangement	238
	8.2.2 Di- π -Methane Type Rearrangement	241

8.3	Rearrangement of Dienones	243
8.4	Photo Rearrangements of β, γ -Unsaturated Ketones	251
8.4.1	1,2-Acyl Shift (Oxa-Di- π -methane Rearrangement)	252
8.4.2	1,3-Acyl Shift	253
8.5	Aza-Di- π -Methane Rearrangement	258
8.6	Di- π -Methane (DPM) Rearrangement	259
8.7	Rearrangements in Aromatic Compounds	265
	<i>Glossary</i>	267
	<i>Further Reading</i>	267
	<i>Problems</i>	268
CHAPTER 9 Photo Reduction and Photo Oxidation		270-276
9.1	Photo Reduction of Carbonyl Compounds	270
9.2	Photo Reduction of Aromatic Hydrocarbons	271
9.3	Photochemical Oxidations	272
9.4	Photo Oxidation of Alkenes and Polyenes	273
	<i>Glossary</i>	275
	<i>Further Reading</i>	276
	<i>Problems</i>	276
CHAPTER 10 Photochemistry of Alkenes, Dienes and Aromatic Compounds		277-308
10.1	Photochemistry of Alkenes	277
10.2	<i>Cis-Trans</i> Isomerisation of Alkenes	278
10.2.1	<i>Cis-Trans</i> Isomerisation of Alkenes by Direct Irradiation	278
10.2.2	Sensitised <i>Cis-Trans</i> Isomerisation	280
10.3	Dimerisation of Alkenes	281
10.3.1	Intramolecular Dimerisation	284
10.4	Photochemistry of Conjugated Dienes	286
10.4.1	Photochemistry of Conjugated Dienes in Solution	287
10.5	Photoisomerisation of Benzene and Substituted Benzene	290
10.5.1	1,2-Alkyl Shift	293
10.5.2	Mechanism of 1, 3-Alkyl Group Shift	294
10.6	Photoaddition of Alkenes to Aromatic Benzenoid Compounds	295
10.6.1	1,2-Cycloaddition Reactions	295
10.6.2	1,3-Photoaddition of Benzene	297
10.6.3	1,4-Photoaddition of Benzenes	298
10.7	Addition of Oxygen	300
10.8	Aromatic Photosubstitution	300
10.8.1	Type A Reactions	301
10.8.2	Type B Substitutions	303
10.8.3	Radical Substitutions	303

10.9	Photochemistry of Diazo Compounds	304
10.10	Photochemistry of Azides	305
	<i>Glossary</i>	306
	<i>Further Reading</i>	306
	<i>Problems</i>	307
CHAPTER 11 Photo Substitution Reactions at sp^3 Hybrid Carbon Having at Least One Hydrogen		309–319
11.1	Introduction	309
11.2	Barton Reaction	309
11.3	The Hoffmann Loeffler Freytag Reaction	314
11.4	Photolysis of Hypohalites	317
	<i>Glossary</i>	318
	<i>Further Reading</i>	318
	<i>Problems</i>	318
CHAPTER 12 Photochemistry in Natural Products		320–329
12.1	Photo Rearrangement or Isomerisation	320
12.2	Photochemistry of Natural Products Containing Bicyclo [3, 1, 0] Hexane-2-One Residue	322
12.3	Photochemistry of Natural Products having β , γ -Unsaturated Ketone Group	324
12.4	Photochemistry of Natural Products having Epoxy Ketone System	324
12.5	Dye-Sensitised Photooxygenations	325
12.6	Photochemistry of Saturated Ketones	329
CHAPTER 13 Photochemistry in Nature and Applied Photochemistry		330–353
13.1	Photochemical Reactions in the Atmosphere	330
13.2	Chemistry of Vision	335
13.3	Photography	339
13.4	Light-Absorbing Compounds	343
13.5	Photochromism	347
13.6	Photoimaging	349
13.7	Photochemistry of Polymers	350
	<i>Problems</i>	353

CHAPTER 14 Problems and Their Solutions

354-469

CHAPTER 15 Quenching of Excited States and Investigation of Reaction Mechanism

470-514

15.1	Introduction	470
15.2	Quencher and Quenching of Excited States	471
15.2.1	Excimers	472
15.2.2	Exciplex	473
15.3	Quenching Processes and Quenching Mechanism	475
15.3.1	Electron-transfer Quenching	476
15.3.2	Heavy Atom Quenching	476
15.3.3	Quenching by Molecular Oxygen (Triplet State) and Paramagnetic Species	477
15.4	Electronic Energy Transfer	477
15.5	Investigation of Reaction Mechanism	480
15.6	Quantitative Methods	480
15.6.1	Identification of Products	480
15.6.2	Intermediates	481
15.7	Isotopic Labelling	487
15.8	Lowest Energy Excited State	488
15.9	Reactive Excited States	489
15.10	Quantitative Methods	490
15.10.1	Quantum Yield	490
15.10.2	Experimental Determination of the Quantum Yield	492
15.10.3	Procedure of Determining Quantum Yield of a Photochemical Reaction	495
15.11	Lifetime of the Reaction Intermediate for Lifetime of the Excited State	495
15.12	Rate Constants and their Relation with the Lifetime of Reactive Excited States (Triplet State)	496
15.13	Rate Constants and their Relation with the Lifetime of Reactive Singlet Excited States	500
15.14	Determination of Rate Constants of Photochemical Reactions	503
15.14.1	Rate of Unimolecular Photochemical Reactions from Singlet Excited State	504
15.14.2	Rate of Unimolecular Photochemical Reactions from the Triplet State	505
15.14.3	Rate of Bimolecular Reaction from Triplet State	507
15.15	Effect of Light Intensity on the Rate of Photochemical Reactions	511
	<i>Problems</i>	
	<i>Index</i>	514

515-519