

Table of Contents

Chapter 1

Potential Energy Surfaces of Chemical Reactions	1
1.1 Introduction. Mechanism of Chemical Reaction and Quantum Chemistry	1
1.2 Choice of a Coordinate System and the Representation of a PES	2
1.3 Topography of the PES and Properties of a Reacting System	6
1.3.1 Critical Points	6
1.3.2 The Regions of the Minima on the PES	8
1.3.2.1 Vibrational Spectrum of Molecules	9
1.3.2.2 Calculation of Thermodynamic Functions of Molecules	11
1.3.2.3 Topological Definition of Molecular Structure	13
1.3.2.4 Structural Diagrams.	18
1.3.3 Saddle Points on the PES. Transition States	20
1.3.3.1 Localization of the Transition States on the PES.	21
1.3.3.2 Symmetry Selection Rules for Transition State Structures	23
1.3.3.3 Calculation of Activation Parameters of Reactions and of Kinetic Isotopic Effects	27
1.3.4 Pathway of a Chemical Reaction	30
1.3.4.1 Ambiguity of the Definition	30
1.3.4.2 A More Accurate Definition of the MERP and the Reaction Coordinate	31
1.3.4.3 Symmetry Demands on the Reaction Path	34
1.3.4.4 Chiral and Achiral Pathways of Degenerate Reactions.	36
1.3.5 Empirical Correlations of the Reaction Pathways	39
1.3.5.1 Molecular Vibrations and the Reaction Coordinate.	39
1.3.5.2 The Principle of Least-Motion	41
1.3.5.3 Structural Correlations of the Pathways of Chemical Reactions	42
1.4 Dynamic Approach.	45
1.5 Tunnelling Effects in Chemical Reactions	49
1.6 Description of Nonadiabatic Reactions	53
References	58

Chapter 2

Quantum Chemical Methods for Calculating Potential Energy Surfaces	61
2.1 General Requirements upon the Methods for Calculating Potential Energy Surfaces	61
2.2 Nonempirical (ab initio) Methods. The Hartree–Fock Method	62
2.2.1 Closed Electron Shells	62
2.2.2 Open Electron Shells	64
2.2.3 Basis Sets of Atomic Orbitals	66
2.2.4 Electron Correlation	69
2.2.5 The Problem of Stability of Hartree–Fock Solutions	75
2.3 Semiempirical Methods	76
2.3.1 The Extended Hückel Method	78
2.3.2 Semiempirical Selfconsistent Field Methods	78
2.3.2.1 The CNDO/2 Method	78
2.3.2.2 The MINDO/3 Method	80
2.3.2.3 The MNDO Method	82
2.3.2.4 The AM1 Method	85
References	86

Chapter 3

Effects of the Medium	88
3.1 A General Scheme for Calculating the Solvation Effects	89
3.2 Macroscopic Approximation	90
3.2.1 General Theory	90
3.2.2 Model Hamiltonians in the Macroscopic Approximation	92
3.2.2.1 Model Hamiltonian in the Kirkwood Approximation	93
3.2.2.2 A Model Hamiltonian Based on the Born Formula. Scheme of Solvatons.	93
3.2.2.3 The Scheme of Virtual Charges	95
3.2.2.4 The Theory of Selfconsistent Reactive Field	96
3.3 Discrete Representation of Solvent Molecules. Model Hamiltonians in the Microscopic Approximation.	97
3.4 Specific Features of the Supermolecular Approach in Studies of Solvation Effects	100
3.5 Statistical Methods for Studying Solutions	102
References	104

Chapter 4

Orbital Interactions and the Pathway of a Chemical Reaction	106
4.1 The Role of Frontier Orbitals	106
4.2 Theory of Orbital Interactions	108
4.3 Components of the Interaction Energy of a Reacting System in a Transition State	111
4.4 Isolobal Analogy	113
References	115

Chapter 5

Substitution Reaction.	116
5.1 Nucleophilic Substitution at a Tetrahedral Carbon Atom.	117
5.1.1 The S _N 2 Reactions	118
5.1.1.1 Stereochemistry of the Reactions	118
5.1.1.2 Reaction Coordinate and the Structure of the Transition State	119
5.1.1.3 Energetics and Stoichiometric Mechanism of the Gas-Phase S _N 2 Reactions	121
5.1.1.4 Effect of the Solvent.	125
5.1.1.5 Reactions with Retention of Configuration of the Carbon Atom	128
5.1.2 The S _N 1 Reactions	130
5.2 Electrophilic Substitution at the Tetrahedral Carbon Atom.	132
5.3 Nucleophilic Substitution at the Carbon Atom of the Carbonyl Group	134
5.3.1 The Stoichiometric Mechanism.	134
5.3.2 Homogeneous Catalysis	138
5.3.3 Stereochemistry of the Reaction	142
5.3.3.1 The Direction of Nucleophilic Attack and Orbital Steering	142
5.3.3.2 Stereochemical Control of the Breakdown of the Tetrahedral Adduct	144
5.4 Aromatic Electrophilic Substitution Reactions	147
5.5 Nucleophilic Substitution at the Nitrogen, Phosphorus, and Sulfur Centers	154
5.5.1 Substitution at the Nitrogen Atom of Nitroso- and Nitro-Groups	154
5.5.2 Substitution at the Dicoordinate Sulfur Atom	156
5.5.3 Substitution at Tricoordinate Sulfur and Phosphorus Centers .	158
5.5.4 Substitution at Tetracoordinate Phosphorus	159
5.5.5 Substitution at Pentacoordinate Phosphorus	161

5.5.6 Inclusion of the Polytopal Rearrangements of Intermediates in the Overall Reaction Scheme.	164
References	165
 <i>Chapter 6</i>	
Addition Reactions	170
6.1 Electrophilic Additions to Multiple Bonds.	170
6.2 Nucleophilic Addition to Alkenes.	174
6.3 Nucleophilic Addition to a Triple Bond	177
References	179
 <i>Chapter 7</i>	
Low-Energy Barrier Reactions. Structural Modelling.	181
7.1 The Principle of Correspondence Between Structures of the Initial and the Transition State of Reaction.	181
7.2 Nucleophilic Rearrangements and Tautomerizations	182
7.3 Cyclization Reactions	186
7.4 Topochemical Reactions	188
References	189
 <i>Chapter 8</i>	
Radical Reactions.	190
8.1 Specific Features of the Theoretical Analysis of Radical Reactions	190
8.2 Free-Radical Reactions	191
8.2.1 Bond-Cleavage and Addition Reactions.	192
8.2.2 Radical Substitution Reactions at the Tetrahedral Carbon Atom.	195
8.3 Reactions with Formation of Biradicals.	196
8.4 The Reactions of Carbenes	200
8.4.1 Addition to the Double Carbon–Carbon Bond	201
8.4.2 Insertion into σ -Bonds.	204
References	207
 <i>Chapter 9</i>	
Electron and Proton Transfer Reactions	210
9.1 Electron Transfer Reactions.	210
9.1.1 Single Electron Transfer Reactions in Organic Chemistry	210

9.1.2 Elementary Act of Electron Transfer	211
9.1.3 Theoretical Studies of the Mechanism of $S_{RN}1$ Reactions.	214
9.2 Proton Transfer Reactions	217
9.2.1 Potential Energy Curves and Activation Barriers	219
9.2.2 Stereochemistry	221
9.2.3 Proton Transfer in Systems with the Intramolecular Hydrogen Bonding	222
9.2.4 The Tunnelling Mechanism in Proton Transfer Reactions	227
9.2.5 Double Proton Migrations	231
References	

Chapter 10

Pericyclic Reactions	238
10.1 Reactions of Cycloaddition	239
10.1.1 [2 + 2]-Cycloaddition	239
10.1.2 [4 + 2]-Cycloaddition	242
10.2 Electrocyclic Reactions	246
10.3 Sigmatropic Rearrangements	251
10.4 Haptotropic Rearrangements	254
10.5 Ion-Radical Pericyclic Reactions.	257
References	261
List of Abbreviations	265
Subject Index	267