Contents

1. Ion-Molecule Reactions and Their Role in Radiation Chemistry 1

1.1 Historical Background 1
1.2 Rationale of Outline 5
References 6

2. Unimolecular Processes; the Nature and Structure of Ionic Intermediates in Radiolysis 8

2.1 Introduction 8
2.2 Theoretical Prediction of Ionic Unimolecular Reactions 8
2.3 Ionic Fragmentation 10
2.3.1 Experimental Determination of Ionic Fragmentation Processes 10
2.3.2 Ionic Fragmentation in Alkanes and Cycloalkanes at Elevated Densities 11
2.3.3 Ionic Fragmentation in Unsaturated Hydrocarbons at Elevated Densities 14
2.3.4 Ionic Fragmentation in Polar Organic Compounds at Elevated Densities 14
2.4 Effect of Internal Energy on Ionic Fragmentation Processes 15
2.5 Ionic Structures 17
2.5.1 Experimental Determination of Ionic Structures 17
2.6 Ionic Isomerization Reactions 21
2.6.1 The Effects of Energy and Pressure 21
2.6.2 Isomerization of Alkyl Carbonium Ions 24
2.6.3 Isomerization in Other Hydrocarbon Ions 30
2.6.4 Isomerization of Oxygenated Ions 32
2.6.5 Isomerization of $C_3H_8N^+$ Ions 35
References 35

3. Ion Lifetimes and the Fate of Unreactive Ions 40

3.1 Introduction 40
3.2 Neutralization of Ions and Ion Lifetimes 40
3.2.1 Gas Phase 40
3.2.2 Liquid Phase 44
3.3 Reactions of Ions in Competition with Neutralization 45
3.3.1 Ion-Molecule Reactions in the Liquid Phase 45
3.3.2 The Effects of Traces of Foreign Compounds on Ion-Molecule Reaction Mechanisms 52
References 58

4. Kinetics and Mechanisms of Ion-Molecule Reactions **64**

4.1 Ion-Molecule Collisions 64
4.1.1 Collision Rates 64
4.2 Mechanisms of Ion-Molecule Reactions 72
4.2.1 The Lifetime of the Ion-Molecule Complex 72
4.2.2 Factors Influencing Reaction Rates 79
4.2.3 Factors Influencing the Importance of Competing Reaction Channels 79
4.2.4 Mechanisms of Charge Transfer Reactions 82
4.3 Theoretical Prediction of Ion-Molecule Reaction Products 83
References 85

5. Proton Transfer Reactions **90**

5.1 Proton Affinities 90
5.2 The Rates of Proton Transfer Reactions 96
5.2.1 Cations 96
5.2.2 Anions 99
5.3 Mechanisms of Proton Transfer Reactions 103
5.3.1 H^+ *versus* H Transfer 103
5.3.2 Charge Transfer as a Competing Reaction Channel 105
5.3.3 Competition with Displacement, Condensation, or Clustering Reactions 105
5.4 Dissociation of Protonated Molecules 108
5.4.1 Protonated Alkanes 109
5.4.2 Protonated Cycloalkanes 110
5.4.3 Protonated Unsaturated Hydrocarbons 111
5.4.4 Protonated Polar Molecules 111
5.5 Conclusions 113
References 113

6. Negative Atom and Two-Atom Transfer Reactions **120**

6.1 Introduction 120
6.2 Reactions in Hydrocarbon Systems 120
6.2.1 Hydride Transfer Reactions 120
6.2.2 Dual Channel Reactions: One- and Two-Particle Transfer Reactions 129
6.2.3 Resonance H^- and H_2^- Transfer Reactions 135
6.2.4 H^- Transfer Reactions of Negative Ions 135
6.3 Reaction in Silanes 136
6.4 Halide Ion Transfer Reactions 137
6.4.1 Reactions in Perfluoroalkanes 137
6.4.2 F^- Transfer Reactions between Negative Ions and Inorganic Molecules 138
References 138

7. Condensation Reactions **142**

7.1 Introduction 142
7.2 Condensation Reactions in Olefinic Systems 142
7.2.1 Effect of Density 143
7.2.2 Structure and Isomerization Reactions of Olefinic Condensation Ions 147
7.3 Condensation Reactions in Aromatic Systems 149
7.4 Condensation Reactions in Alkane Systems 152
7.5 Condensation Reactions in Polar Organic Compounds: Elimination Reactions 155
7.6 Associative Detachment 161
References 161

8. Association or Clustering Reactions 165

8.1 Introduction 165
8.2 Equilibrium in Association and Clustering Reactions. Determinations of Enthalpy and Entropy Changes of the Reactions 169
8.3 Rates of Association and Clustering Reactions 174
8.4 Structures of Clusters 178
8.5 Reactions of Association Ions and Clusters; Implications for the Radiolysis 181
8.6 Association and Clustering Reactions in Particular Systems 185
8.6.1 Polar Organic Compounds 185
8.6.2 Aromatic Hydrocarbons 190
8.6.3 Alkanes 191
8.6.4 Inorganic Systems 192
References 193

Index 199