

Contents

<i>Preface</i>	<i>iii</i>
<i>Contributors</i>	<i>xi</i>
<i>Abbreviations</i>	<i>xiii</i>
1. Oxidation Catalysis by Metalloporphyrins: A Historical Perspective	1
<i>Roger A. Sheldon</i>	
1. Structure and Reactivity of Dioxygen	1
II. Introduction to Hemoproteins	3
III. Early Historical Development	5
IV. Cytochrome P450-Dependent Monooxygenases	8
V. Model Metalloporphyrins: Biomimetic Chemistry	13
VI. Beyond Biomimetics: Suprabiotic Chemistry	20
VII. Concluding Remarks	22
References	23
Additional Reading	27

2. Mechanisms of Reaction of Hypervalent Oxochromium, Iron, and Manganese Tetraphenylporphyrins with Alkenes	29
<i>Dražen Ostović, Gong-Xin He, and Thomas C. Bruice</i>	
1. Introduction	29
11. Chromium Porphyrins	30
111. Iron Porphyrins	42
IV. Manganese Porphyrins	57
References	62
3. Theoretical Studies of Oxometalloporphyrins and Their Reactions with Organic Substrates	69
<i>Karl Anker Jørgensen</i>	
1. Introduction	69
11. Quantum Chemical Methods	71
111. Geometric and Electronic Structures of Oxometalloporphyrins	75
IV. Influence of Axial Ligands (Proximal Effects)	81
V. Mechanism of Oxygen Transfer to Alkenes, Alkanes, and Aromatics	83
VI. Comments	93
Notes and References	94
4. Cytochrome P450 Model Systems	99
<i>Daniel Mansuy and Pierrette Battioni</i>	
1. Introduction	99
11. Oxidations Catalyzed by Cytochrome P450-Dependent Monooxygenases	103
111. Biotechnological Catalysts Based on Yeasts Expressing Human Liver Cytochromes P450	111
IV. Homogeneous Metalloporphyrin Systems Mimicking Cytochrome P450	113
V. Biomimetic Oxygenations Catalyzed by Supported Metalloporphyrins	120
VI. Conclusion and Perspectives	122
References	125
5. Ligninase and Related Model Systems	133
<i>Bernard Meunier</i>	
1. Introduction	133
11. Lignin: Biosynthesis and Structure	134

111. Enzymatic Systems	137
IV. Model Systems of Ligninase	142
V. Concluding Remarks	149
References	150
6. Heme Proteins in Prostaglandin Biosynthesis	157
<i>V. Ullrich and Hans H. Ruf</i>	
1. Introduction	157
11. Prostaglandin Endoperoxide Synthase	160
111. Prostacyclin Synthase	171
IV. Thromboxane Synthase	175
V. Common Principles of Heme Thiolate Catalysis	183
References	186
7. Synthetic Aspects of Porphyrin and Metalloporphyrin Chemistry	193
<i>Tilak P. Wijesekera and David Dolphin</i>	
1. Introduction	193
11. Structure and Properties of Porphyrins and Metalloporphyrins	195
111. Synthesis of Porphyrins	201
IV. General Synthetic Methods	206
V. Metallations and Demetallations of Porphyrins	218
VI. Biomimetic Metalloporphyrin Catalysts	221
References	231
8. Asymmetric Oxidation with Chiral Porphyrin Catalysts	241
<i>Yoshinori Naruta</i>	
1. Introduction	241
11. Catalyst Design and Synthesis	243
111. Asymmetric Oxidation of Olefins	248
IV. Asymmetric Oxidation of Saturated Hydrocarbons	253
V. Asymmetric Oxidation of Sulfides	254
References	256
9. Metalloporphyrin-Catalyzed Oxidation of Hydrocarbons with Dioxygen	261
<i>Teresa Mlodnicka</i>	
1. Introduction	261
11. Autoxidation of Hydrocarbons	262

III. Reductive Oxygen Activation	275
IV. Cooxidation	277
V. Concluding Remarks and Future Prospects	286
References	287
10. Reactions of Alkanes with Dioxygen: Toward Suprabiotic Systems	297
<i>James E. Lyons and Paul E. Ellis, Jr.</i>	
I. Introduction	297
11. Biomimetic Oxidation	298
111. The Suprabiotic Approach	302
IV. Catalysis by Electron-Deficient Metalloporphyrins	306
V. Electron-Deficient Metalloporphyrins as Catalysts for Reactions with O ₂	311
VI. Future Suprabiotic Catalysts	316
VII. Conclusion	319
Abbreviations	319
References	320
11. Supported Metalloporphyrin Models for Heme-Catalyzed Oxidations	325
<i>John R. Lindsay Smith</i>	
I. Background	325
11. Methods Used to Anchor Metalloporphyrins	327
III. Summary of Supported Metalloporphyrins and the Properties of an Ideal Oxidation Catalyst	340
IV. Oxidations Catalyzed by Polymer-Supported Metalloporphyrins	341
V. Oxidations Catalyzed by Metalloporphyrins on Inorganic Supports	352
VI. Future Developments of Supported Metalloporphyrin-Catalyzed Oxidations	358
Abbreviations	360
References	361
<i>Epilogue: Future Prospects</i>	369
<i>Glossary</i>	375
<i>Index</i>	381