

E.V.Dehmlow, S.S.Dehmlow

# Phase Transfer Catalysis

Third, Revised and  
Enlarged Edition



Weinheim · New York · Basel · Cambridge · Tokyo

# Contents

<b>1</b>	<b>Ion Pairs and Ion Pair Extraction . . . . .</b>	<b>1</b>
1.1	Introduction: The Nature of Phase Transfer Catalysis . . . . .	1
1.2	Ion Pairs in Organic Media . . . . .	3
1.3	Extraction of Ion Pairs from Aqueous Solution . . . . .	6
1.3.1	Principles . . . . .	6
1.3.2	Influence of the Solvent . . . . .	10
1.3.3	Influence of the Onium Cation . . . . .	12
1.3.4	Influence of the Anion . . . . .	14
1.4	Crown Ethers, Cryptates, and Other Chelating Agents as Extractants .	22
1.5	Solid–Liquid Anion Exchange . . . . .	25
<b>2</b>	<b>Mechanism of Phase Transfer Catalysis . . . . .</b>	<b>29</b>
2.1	Mechanistic Investigations . . . . .	29
2.1.1	Mechanism under Neutral Conditions . . . . .	29
2.1.2	Mechanisms in the Presence of Alkali Metal Hydroxides . . . . .	39
2.1.3	Mechanisms in the Presence of Other Bases . . . . .	49
2.2	Empirical Catalyst Evaluations . . . . .	50
2.3	Unusual and Polymer-Supported Catalysts . . . . .	61
2.4	Extraction into the Water Phase (“Inverse PTC”) . . . . .	63
2.5	Cation Extraction . . . . .	63
2.6	Extraction by Anionic Complex Formation or Hydrogen Bonding .	64
<b>3</b>	<b>Practical Applications of Phase Transfer Catalysis . . . . .</b>	<b>65</b>
3.1	General Experimental Procedures . . . . .	65
3.1.1	The Common Catalysts . . . . .	65
3.1.2	Reaction Conditions . . . . .	71
3.1.2.1	Solvent . . . . .	72
3.1.2.2	Stirring . . . . .	72
3.1.2.3	Amount of Catalyst . . . . .	72
3.1.2.4	Stability of the Catalyst . . . . .	73
3.1.2.5	Choice of Catalyst . . . . .	75
3.1.2.6	Separation and Regeneration of the Catalyst . . . . .	75
3.1.2.7	Miscellaneous . . . . .	76
3.1.3	General Remarks on Reactions in the Presence of Additional Bases .	77
3.1.4	Polymer-Bound Catalysts . . . . .	79
3.1.5	Optically Active Catalysts; Enantioselective Reactions . . . . .	80
3.2	Formation of Halides . . . . .	93
3.2.1	Halide Exchange . . . . .	93
3.2.2	Exchange for Fluoride . . . . .	97

3.2.3	Halides from Alcohols, Ethers, and Diazomethanes . . . . .	101
3.3	Preparation of Nitriles . . . . .	103
3.4	Ester Formation . . . . .	106
3.5	Miscellaneous Displacements . . . . .	117
3.6	Thiols and Sulfides . . . . .	122
3.7	Preparation of Ethers . . . . .	126
3.8	<i>N</i> -Alkylations . . . . .	136
3.9	<i>C</i> -Alkylation of Activated CH Bonds . . . . .	149
3.9.1	Alkylation of Arylacetonitriles . . . . .	149
3.9.2	Alkylation of Other Activated Cyanides and Isocyanides . . . . .	156
3.9.3	Alkylation of Malonic Esters . . . . .	158
3.9.4	Alkylation of Benzyl Ketones and Arylacetic Esters and Amides . .	159
3.9.5	Alkylation of Other Doubly Activated CH Bonds . . . . .	164
3.9.6	Alkylation of Carbonyl and Other Less Activated Derivatives . .	166
3.9.7	Alkylation of Hydrocarbons . . . . .	168
3.10	Alkylation and Acylation of Ambident Anions . . . . .	170
3.11	Isomerizations and H/D Exchange . . . . .	184
3.12	Additions across Multiple CC Bonds . . . . .	187
3.12.1	Additions to Acetylenes . . . . .	187
3.12.2	Michael Additions . . . . .	190
3.12.3	Additions across Nonactivated Double Bonds . . . . .	197
3.13	Addition to C=O and C=N Bonds . . . . .	199
3.13.1	Benzoin Condensation . . . . .	199
3.13.2	Aldol-Type Reactions . . . . .	199
3.13.3	Other Types of Reactions . . . . .	204
3.14	$\beta$ -Eliminations . . . . .	209
3.15	Hydrolysis Reactions . . . . .	215
3.15.1	Miscellaneous Hydrolysis Reactions . . . . .	215
3.15.2	Saponification of Esters . . . . .	218
3.16	Generation and Conversion of Phosphonium and Sulfonium Ylides .	222
3.16.1	Wittig Reactions . . . . .	222
3.16.2	Horner (PO-Activated) Olefination . . . . .	226
3.16.3	Sulfonium Ylide and Oxosulfonium Ylide Reactions . . . . .	233
3.17	Nucleophilic Aromatic Substitution . . . . .	237
3.18	Miscellaneous Reactions in the Presence of Bases . . . . .	245
3.18.1	Diazo-Group Transfer . . . . .	245
3.18.2	$\gamma$ -Elimination . . . . .	246
3.18.3	Preparation of Acid Fluorides and Anhydrides . . . . .	246
3.18.4	Rearrangements . . . . .	248
3.18.5	Radical Reactions . . . . .	251
3.18.6	Reactions with Carbon Tetrahalides and Hexahaloethane . . . . .	251

---

3.18.7	Special Reactions of Certain Sulfur Compounds . . . . .	254
3.18.8	Generation of Nitrenes . . . . .	255
3.18.9	PTC Reactions of Diazonium Salts . . . . .	256
3.18.10	Hydrazones by and in PTC . . . . .	258
3.18.11	Electrochemistry . . . . .	258
3.18.12	Other Reactions . . . . .	259
3.19	Organometallic PTC Applications . . . . .	260
3.19.1	Extraction of Metals, Metal Salts, and Metal Carbonyls . . . . .	260
3.19.2	Metal-Organic Reactions of Sulfur Compounds . . . . .	261
3.19.3	Preparation of Complexes, Ligand Exchange . . . . .	262
3.19.4	Carbonylations . . . . .	264
3.19.5	Metal-Organic Coupling Reactions . . . . .	268
3.19.6	Isomerizations and Other Reactions . . . . .	270
3.20	$\alpha$ -Eliminations . . . . .	271
3.20.1	Generation and Addition Reactions of Dichlorocarbene . . . . .	271
3.20.2	Other Reactions of Dichlorocarbene and Trichloromethylide Anion . . . . .	287
3.20.3	Dibromocarbene . . . . .	303
3.20.4	Other Dihalocarbenes . . . . .	309
3.20.5	Other Carbenes . . . . .	315
3.21	Reduction Reactions . . . . .	321
3.21.1	Complex Hydrides and Diborane . . . . .	321
3.21.2	Dithionite . . . . .	330
3.21.3	Alkali Metals and Hydrides . . . . .	331
3.21.4	Metal Carbonyls . . . . .	331
3.21.5	Hydrogenations and Transfer Hydrogenations . . . . .	333
3.21.6	Other Reducing Agents . . . . .	334
3.22	Oxidation Reactions . . . . .	335
3.22.1	Oxidation with Permanganate . . . . .	335
3.22.2	The Role of Hydrogen Peroxide and Alkyl Hydroperoxides in PTC Reactions . . . . .	344
3.22.3	Reactions with Potassium Superoxide . . . . .	349
3.22.4	Chromate . . . . .	359
3.22.5	Hypochlorite/Hypobromite . . . . .	361
3.22.6	Potassium Hexacyanoferrate(III) . . . . .	365
3.22.7	Periodate . . . . .	366
3.22.8	Peroxy Acids . . . . .	368
3.22.9	Oxygen as Oxidant . . . . .	369
3.22.10	Peroxymono- and Peroxydisulfate . . . . .	373
3.22.11	Other Oxidizing Agents . . . . .	374
<b>References</b>		<b>379</b>
<b>Subject Index</b>		<b>481</b>