

Contents

1	The Carbon Dioxide Molecule	1
1.1	Introduction	1
1.2	Electronic Properties of CO ₂	2
1.2.1	Ground State of Carbon Dioxide	2
1.2.2	Lowest Excited States of Carbon Dioxide	6
1.3	Main Features of Carbon Dioxide Reactivity	8
1.3.1	Carbon Dioxide as O-Nucleophile	9
1.3.2	Carbon Dioxide as C-Electrophile	10
1.3.3	Amphoteric Reactivity of Carbon Dioxide	11
1.4	Carbon Dioxide Radical Anion, CO ₂ ⁻	12
1.5	Carbon Dioxide Radical Cation, CO ₂ ⁺	19
1.6	Spectroscopic Techniques Applied to the CO ₂ States	20
1.6.1	IR Spectroscopy	20
1.6.2	UV Spectrum of Carbon Dioxide	22
1.6.3	Nuclear Magnetic Resonance (NMR) Spectroscopy	26
	References	27
2	CO₂ Coordination to Metal Centres: Modes of Bonding and Reactivity	35
2.1	Mode of Bonding of Carbon Dioxide to Transition-Metal Centres	35
2.2	XRD Structure of η^2 -C ₂ O Mononuclear Metal Complexes	37
2.3	XRD Structural Data for η^1 -C Metal Complexes	41
2.4	XRD Structural Characterization of O-End-On Complexes	43
2.5	Multinuclear Complexes	43
2.5.1	Side-On Bonded Complexes	43
2.5.2	O-End-On Bonded Complexes	44
2.6	Spectroscopic (IR and ¹³ C-NMR) Data for the Complexes Correlated to the Various Modes of Bonding of CO ₂	47
2.6.1	Infrared Data Relevant to Transition Metal Complexes	47

2.6.2	NMR Data for Transition Metal Complexes	49
2.7	Fluxionality of the CO ₂ Molecule Coordinated to Transition Metal Systems	51
2.8	Interaction of CO ₂ with Metal Atoms in Low-Temperature Solid-Inert-Gas Matrices	55
2.9	Interaction of Metal Cations with CO ₂ in the Gas Phase	57
2.10	Reactions of Coordinated CO ₂	58
2.10.1	Reaction of Coordinated CO ₂ with Electrophiles and O-Transfer from CO ₂ to Produce CO	59
2.10.2	Reactions of Coordinated CO ₂ with Nucleophiles	63
2.11	Conclusions	64
	References	64
3	Interaction of CO₂ with Electron-Rich Moieties	71
3.1	Reaction with the Hydride Ion	71
3.2	Reaction with Hydroxide and Alkoxide Species	72
3.3	Reaction with Carbanions	73
3.4	Reaction with Amines	74
	References	82
4	Insertion of CO₂ into E–X Bonds	85
4.1	Carbon Dioxide Insertion into M–H Bonds	85
4.2	CO ₂ Insertion into M–OH Bonds	91
4.3	CO ₂ Insertion into M–C Bonds	95
4.4	CO ₂ Insertion into M–OR Bonds	97
4.5	Insertion into M–O ₂ Bonds	98
4.6	CO ₂ Insertion into M–N Bonds	102
4.6.1	Insertion into Transition Metal Amides	102
4.6.2	Insertion into Main Group and Post-Transition Metal Amides	108
4.6.3	Insertion into Amides of Non-Metallic Elements	112
4.7	CO ₂ Insertion into M–P Bonds	115
4.8	CO ₂ Insertion into C–C Bonds	117
4.9	CO ₂ Insertion into C–N Bonds	120
4.10	Insertion into Other E–X Bonds	127
4.10.1	Insertion into M–M Bonds	127
4.10.2	Insertion into Si–H Bonds	128
4.10.3	Insertion into C–H Bonds	129
4.11	Conclusions	131
	References	131
5	Interaction of CO₂ with C–C Multiple Bonds	143
5.1	Introduction	143
5.2	Oxidative Coupling with CO ₂	144
5.3	Carboxylation of Olefins	147
5.4	Carboxylation of Alkynes	156

5.5	Carboxylation of Allenes	164
5.6	Carboxylation of Conjugated Dienes	169
	References	176
6	Reaction Mechanisms in the Direct Carboxylation of Alcohols, Polyols, Cyclic Ethers, and Cyclic Amines to Afford Monomeric Compounds and Polymeric Materials	183
6.1	Utilization of Organic Carbonates and Conventional Synthetic Routes	183
6.2	Direct Carboxylation of Alcohols	185
6.2.1	Thermodynamic and Kinetic Issues	185
6.2.2	Reaction Mechanism	187
6.3	Direct Carboxylation of Diols and Polyols	210
6.4	Oxidative Carboxylation of Olefins to Afford Cyclic Carbonates	213
6.5	Carboxylation of Cyclic Ethers	216
6.5.1	Synthesis of Monomeric Cyclic Carbonates	217
6.5.2	Synthesis of Polycarbonates	221
6.6	Formation of Polyurethanes: Carboxylation of Cyclic Amines	223
6.7	Conclusions	225
	References	226
7	Carbon Dioxide Conversion in High Temperature Reactions	237
7.1	Introduction	237
7.2	CO ₂ as Oxidant	238
7.2.1	OCM Promoted by CO ₂	238
7.2.2	Oxidative Dehydrogenation of Alkanes	243
7.2.3	Oxidative Dehydrogenation of Ethylbenzene to Styrene	254
7.2.4	CO ₂ (Dry) Reforming of Methane	265
7.3	Hydrogenation of CO ₂	277
7.3.1	Reverse Water Gas Shift Reaction (RWGS)	278
7.3.2	CO ₂ Hydrogenation to Methanol and DME	278
7.3.3	Catalytic Systems for CO ₂ Hydrogenation	280
7.3.4	Reaction Mechanism for CO ₂ Hydrogenation	285
7.4	Conclusions	295
	References	296
8	One- and Multi-electron Pathways for the Reduction of CO₂ into C1 and C1+ Energy-Richer Molecules: Some Thermodynamic and Kinetic Facts	311
8.1	Introduction	311
8.2	Key Steps and Aspects in CO ₂ Reduction	312
8.3	One-Electron Transfer to CO ₂ vs Multi-electron Transfer	321

8.4	Competitive Coordination of CO ₂ and H ⁺ to a Catalytic Centre and Their Reduction	322
8.5	Sequential “One-Electron Plus One-Proton” Pathways in Multi-electron Reduction of Bound CO ₂	326
8.6	Photochemical and Photoelectrochemical Reduction of CO ₂	332
8.7	Perspective Electrochemical, Photochemical and Photoelectrochemical Reduction of CO ₂	339
	References	340
9	Enzymatic Conversion of CO₂ (Carboxylation Reactions and Reduction to Energy-Rich C1 Molecules)	347
9.1	Introduction	347
9.2	CO ₂ Fixation in Biosynthesis	348
9.2.1	Calvin–Benson–Bassham-Cycle	349
9.2.2	Reductive TCA (Arnon–Buchanan) Cycle	350
9.2.3	Reductive Acetyl-CoA (Wood–Ljungdahl) Pathway	350
9.2.4	Acyl-CoA Carboxylation Pathways	351
9.3	Carboxylation Reactions	353
9.3.1	Bio-Carboxylation of Aromatic and Hetero-Aromatic Compounds	353
9.3.2	Bio-Carboxylation of Epoxides	357
9.4	Reduction Reactions	358
9.4.1	Carbon Monoxide Dehydrogenases	358
9.4.2	Formate Dehydrogenases	360
9.4.3	Formaldehyde Dehydrogenase	360
9.4.4	Alcohol Dehydrogenases	361
9.4.5	Production of Acetic Acid	361
9.4.6	Reduction of CO ₂ to Carbon Monoxide or Formate	362
9.4.7	Bioconversion of Carbon Dioxide into Methanol	364
	References	366
10	Thermodynamics and Applications of CO₂ Hydrates	373
10.1	Introduction	373
10.2	Structure of Gas Hydrates	376
10.2.1	Formation of Gas Hydrates from a Microscopic Perspective	376
10.2.2	Crystal Structures of Gas Hydrates	378
10.2.3	Characteristics of CO ₂ Hydrates	381
10.3	Physical Properties of CO ₂ Hydrates	382
10.3.1	Mechanical Properties	384
10.3.2	Thermal Properties	384
10.3.3	Other Physical Properties	386
10.4	Phase Equilibrium of CO ₂ Hydrate	386

10.4.1	Experimental Methods to Study Hydrate Phase Equilibria	386
10.4.2	Pressure–Temperature Phase Diagram of $\text{CO}_2 + \text{H}_2\text{O}$ System	389
10.5	Applications of CO_2 Hydrates	390
10.5.1	Formation of CO_2 Hydrate	390
10.5.2	Dissociation of CO_2 Hydrate	391
10.5.3	CO_2 Capture and Sequestration	392
10.5.4	Replacement of CH_4 by CO_2 in Naturally Occurring Hydrates	395
10.5.5	CO_2 Hydrates in Refrigeration Processes	396
	References	399
	Index	403