

Index

A

Acceptor, 9
Acetogenic bacteria, 361
Acrylic acid, 152
Acyl-CoA carboxylation pathways, 351–353
Adiabatic excitation, 8
Adventitious water, 103
Alcohol dehydrogenase (ADH) enzyme, 358
Alcoholysis of urea, 208
Alkylative/arylate carboxylation, 157
Alkyl esters of acrylic acids, 151
Alkylmagnesium amides, 109
Alkyne cyclotrimerization, 162
Al₂O₃-modified ceria, 197
Amine-catalyzed mechanism, 103
Ammonium carbamates, 74
Amphoteric oxide, 9
Amphoteric reactivity, 11–12
Anionic clusters, 2
Antibonding, 4, 9
Antisymmetric stretching, 21
Antropogenic emissions, 1
Applications of CO₂ hydrates, 390–398
Ar matrix, 8
Aromatic amines, 74
Atomic orbitals (AOs), 3

B

Back-biting and elimination of cyclic carbonate, 223
Bacteria and methanogenic *Archaea*, 351
Band gap, 338
Bent equilibrium structures, 7

Bent excited valence state, 8
Bimetallic Al–O–Al catalysts, 219
Bimolecular decay of CO₂⁻, 18
Bio-carboxylation of epoxides, 353–357
Biological CO₂ fixation, 348
Bn₂NC(O)OH, 75
Bonding character, 5
Bonding combinations, 3

C

Calorimetric method, 388
Calvin–Benson–Bassham-cycle, 349
Carbamic acid, 75
Carbon capture and sequestration (CCS), 392
Carbon dioxide chemical utilization (CCU), 1
Carbon dioxide radical anion, CO₂⁻, 12–19
Carbon dioxide radical cation, CO₂⁺, 19–20
α-Carbonia, 12
Carbonic anhydrase (CA), 91
Carbon monoxide dehydrogenase (CODH), 358–359
Carbon-recycling, 340
Carboxylation of alkynes, 156–163
Carboxylation of allenes, 164–169
Carboxylation of conjugated dienes, 169–176
Carboxylation of cyclic ethers, 216–223
Carboxylation of diols and polyols, 210–212
Carboxylation of epoxides, 217
Carboxylation of isoprene, 172
Carboxylation of methylenecyclopropane, 118
Carboxylation of N-tosylaziridines, 121
Carboxylation of olefins, 147–156
Carboxylation of quadricyclane, 117

- Carboxylation of styrenes, 155
 Carboxylation reactions, 353–358
 Carboxylative cyclization of enynes, 156
 Catalytic systems for CO₂ hydrogenation, 280–285
 Catalytic systems for CO₂-OCM, 239–241
 Catalytic systems for CO₂-ODE to styrene, 256–258
 Catalytic systems for CO₂-ODH of alkanes, 244–248
 Catalytic systems for the DRM process, 267–271
 CCS. *See* Carbon capture and sequestration (CCS)
 CCU. *See* Carbon dioxide chemical utilization (CCU)
 C-cycle, 1
 C-electrophile, 10–11
 C-footprint, 187
 Chemical water traps, 200
 Chemico-physical techniques, 187
 Chemiluminescence, 7
 Chemoautotrophic organisms, 348
 Chlorine hydrates, 374
 Climate change, 1
¹³C-NMR, 26
 CO(¹Σ), 24
 CO₂-binding constants, 324
 CoCl(NO)₂[PhP(OCH₂CH₂)₂N-CO₂H], 75
 CODH. *See* Carbon monoxide dehydrogenase (CODH)
 C-O distance, 2
 CO₂ economy, 340
 Coefficient of performance (COP), 397
 Co-encapsulated enzymes, 365
 C-O equilibrium distances, 7
 CO₂ as Lewis acid, 9
 CO₂ hydrates, 375
 CO₂ hydrates in refrigeration processes, 396–398
 CO₂ hydrates on other planets, 376
 CO₂ hydrogenation to methanol and DME, 278–280
 CO₂ insertion into activated C–H bonds, 129
 CO₂ insertion into C–C bonds, 117–120
 CO₂ insertion into C–N bonds, 120–127
 CO₂ insertion into M–C bonds, 95–96
 CO₂ insertion into M–N bonds, 102–115
 CO₂ insertion into M–OH bonds, 91–94
 CO₂ insertion into M–OR bonds, 97–98
 CO₂ insertion into M–P bonds, 115–117
 CO₂ insertion into M-phosphido bond, 116
 CO₂ insertion into the N–Si bond, 114
 Co(*n*-Pr-salen)(CO₂)K(THF), 39
 Collisions of alkali-metal atoms, 13
 Collisions of electrons, 13
 Compressional velocity, 384
 Computational studies, 96
 Conformational isomers, 326
 Conversion of CO₂ and H₂ into HCO₂H, 88
 Conversion of CO₂ into methanol, 364
 Cooligomerization of butadiene with CO₂, 173
 Co-operative effect, 329
 Co-ordination of CO₂, 36
 CO₂ photodissociation, 23
 Copolymerization of aziridines, 224
 CO₂[−] radical anion, 2
 CO₂[−] radicals, 14
 CO₂ (dry) reforming of methane, 265–277
 Corrins, 335
 Corroles, 335
 Coupling of two reactions, 187
 Coupling terminal alkynes with CO₂, 158
 C-protonation, 12
 Crossover zone, 26
 Crown-ether, 81
 Crystalline “super-hard” phase, 11
 Crystallization kinetics of hydrate, 390
 Crystal structures, 376
 Cubic structure I (sI), 376
 Cubic structure II (sII), 376
 C_{2v}, 3
 Cyclic carbamate, 126
 Cycloaddition of allene with CO₂, 168
 Cycloaddition of CO₂ to aziridines, 120
 Cycloaddition of CO₂ with aziridines, 123
- D**
 Decay of the CO₂[−] radical, 14
 Degenerate π-orbitals, 5
 Dehydrogenation of hydrocarbons (DH), 237
 DFT calculations, 153, 191, 324
 D_{∞h}, 3
 ΔH° and ΔG° for the synthesis of organic carbonates, 186
 Dialkylcarbonates, 191
 Dicarboxylate, 147
 1,4-Dicarboxylation of 1,3 dienes, 170
 Dicyclohexylcarbodiimide, 200
 Diethylcarbonate (DEC), 183
 Diffusion electrodes, 315
 Dihydroxo-carbene, 328
 3,4-Dihydroxybenzoate, 354
 Dimeric alkylzinc amides, 109

Dimethyl-carbonate (DMC), 183
Dimethylether, 237
4,6-Dimethyl-2-pyrone, 167
Direct carboxylation of alcohols, 185
Discovery of CO₂ hydrates, 375
Dissociation of CO₂ hydrate, 391–392
Dissociative ionization, 20
DME, 279–280
Donor, 9
Doubly degenerate, 3
Dual-face electrode, 340

E

Efficiency of PV, 333
Elastic properties of hydrates, 384
Electric quadrupole, 2
Electrocatalysis, 320, 347
Electrochemical reductive conversion of CO₂, 365
Electrode deterioration, 320
Electron delocalization, 12
Electronically excited oxygen atoms, 23
Electronic ground state, 2
Electron scattering, 13
Electron-transfer processes, 321
Electrophilic attack on coordinated CO₂, 61
Electroreduction of CO₂, 312
End-on (η^1 -OCO) coordination, 10
End-on protonation, 10
Energy profiles, 194
Energy thresholds, 17, 23
Enolate moiety, 350
Enthalpy effect, 186
Enthalpy of reaction, 186
Entropic effect, 186
Enzymatic approach to convert CO₂, 347
Enzymatic reduction of CO₂, 366
Enzyme-catalyzed processes, 347
Excitation energy, 7
Excited electronic configuration, 6

F

fac-(bpy)(CO)₃Re(OCHO), 87
Faradic efficiency, 335
Fermi level pinning, 338
Fluorescence, 7
Fluxional behavior, 54
Fluxionality, CO₂ Molecule, 51–54

Formaldehyde dehydrogenase (F_{ald}DH) enzyme, 358
Formate dehydrogenases (F_{ate}DH), 358
Formation of metallacycles, 146
Formation of polyurethanes, 223–225
Fourier transform IR (FTIR) studies, 36
Free Gibbs energy of formation, 312
Frost diagram, 312
Frustrated Lewis pairs, 40

G

Gas hydrates, 374
Glycerol carbonate, 211
Green sulfur photosynthetic bacterium, 350
Guest (entrapped gas molecules), 374

H

H-bonded pyridinium-to-pyridine dimers, 330
 η^1 -C coordination, 41
 η^2 -C,O coordination, 39
 η^1 (C)-CO₂ Ru(diphos)₂(CO)₂, 90
Head-to-head recombination, 18
Head-to-tail homocoupling, 144
Head-to-tail recombination, 18
Hemicarbonate, 190
Heterogeneous catalysis, 194–199, 347
Heterogeneous nucleation, 391
Heterogenized catalysts, 188
Hexagonal structure H (sH), 376
Hexakaidecahedron (5¹²6⁴), 378
Highest occupied molecular orbital (HOMO), 8
Highest unoccupied molecular orbital (HUMO), 35
Highly excited vibrational states, 8
High resolution absorption spectrum, 8
High temperature catalyzed reactions, 237
 η^1 -O-coordinated CO₂, 43
Homogeneous nucleation, 391
Host (water molecules), 374
Hybrid bioinspired systems, 366
Hybrid system, 334
Hydration–dehydration of CO₂, 91
Hydration number of sI hydrates, 381, 382
 β -Hydride elimination from a metalla-lactone complex, 154
Hydrides, 71
Hydrocarboxylation of allenes, 165
Hydrocarboxylation of styrenes, 155

- Hydrogenation of CO₂, 277–294
 Hydrogenation of CO₂ to formic acid, 63
 Hydrogenation of HCO₃⁻(aq), 88
 Hydrogen carbonate, 315
 Hydroxycarbonyl cation HOCO⁺, 9
 4-Hydroxy-3-methylbenzoate, 354
 Hydroxymethylene, 329
 3-Hydroxypropionate/4-hydroxybutyrate pathway, 351
 Hyperfine coupling coefficients, 13
 Hyperfine interaction, 26
- I**
- Icosahedron (5¹²6⁸), 378
 Incorporation of CO₂ into the cyclopropane, 119
 Increase of the catalyst activity, 195
 Indole-3-carboxylase, 356
 Infrared data of transition metal complexes, 47–49
 Insertion into amides of non-metallic elements, 112–115
 Insertion into C–H bonds, 129–130
 Insertion into main group and post-transition metal amides, 110–112
 Insertion into M–H bonds, 85–91
 Insertion into M–M bonds, 127–128
 Insertion into M–O₂ bonds, 98–102
 Insertion into Si–H bonds, 128–129
 Insertion into the P–N bond, 113
 Insertion into transition metal amides, 102–108
 Insertion of CO₂ in the Zn–N bond, 110
 Insertion of CO₂ into a Ru–H bond, 62
 Insertion of CO₂ into the Si–N bond, 112–113
 “2+2” Interaction, 86
 Interaction of CO₂ with C–C multiple bonds, 143–176
 Interstellar lines, 9
 Intramolecular transfer, 191
 Inverse isotope dependence, 86
 Ionic hydrides, 71
 Ionic metal hydroxides, 72
 [(IPr)Ni]₂(μ-CO)(μ-η², η²-CO₂), 43
 Ir(CO₂)(Cl)(dmpe)₂, 41
 Irregular dodecahedron (4³5⁶6³), 378
 IR spectra of CO₂-TM complexes, 47
 IR spectroscopy, 20–22
 Isobaric condition, 387
 Isochoric P–T Cycle, 387–388
 Isocitrate dehydrogenase, 350
 Isothermal condition, 387
 Isotope-labelled CO₂, 36
- Isotopic labelled CO₂, 47
 Isotopologues, 26
 Isourea protonation, 203
- K**
- α-Ketoglutarate, ferredoxin oxidoreductase, 350
 Kinetic modeling for the DRM process, 276–277
 Kinetics and reaction mechanism for CO₂ exchange, 110
 Kinetics studies, 76
 Kolbe–Schmitt reaction, 353
 Kolbe–Schmitt synthesis, 129
- L**
- Latent heat of evaporation, 396
 Lewis base, 9
 Li⁺CO₂⁻(C_s), 16
 Li⁺CO₂⁻(C_{2v}), 16
 L-Lactic acid, 355
 Lowering of the selectivity, 195
 Lowest excited states, 6
 Lowest excited triplet state, 8
 Lowest unoccupied molecular orbital (LUMO), 8, 35
 Low-temperature solid-inert-gas matrices, 55–57
- M**
- Macrocyclic N-ligands, 315
 Matrix isolation, 15, 55
 Maximum density of CO₂ hydrates, 385
 M⁺CO₂⁻(C_{2v}), 16
 M–C(O)OH, 89, 91
 Mechanical properties of CO₂ hydrates, 384
 Mechanical strength of pure gas hydrates, 384
 Mechanism of conversion of Ti–CO₂ into O=Ti (CO), 56
 Mechanism of the coupling reaction of CO₂, 148
 Mechanism the formation of the metal carbamate, 103
 Mechanistic studies, 117
 Metal–amido bond, 102, 103
 Metallocarboxylic species, 89
 Metalla dihydroxycarbene, 91
 Metalla-lactone structure, 151
 Metal organic frameworks (MOF), 46
 Metastable sII CO₂ hydrate phase, 381

- Methyl acrylate, 151
 Methyl-Co-species, 350–351
 Microscopic perspective, 376
 Miniaturization, 340
 Mixed oxides, 197
 $M[N(\text{SiMe}_3)_2]_2$, 114
 $M^+(\text{CO}_2)_n$ adducts, 57
 $M\text{-OCHO}$, 85
 Mo-CODH enzymes, 358
 Modes of bonding of CO_2 , 35
 Modes of bonding of the formate ion, 87
 Molecular-level gas storage, 374
 Molecular orbital (MO), 3
 Multielectron process, 312
 Multinuclear complexes, 43–46
 Multiple ionization, 20
 Multireference configuration, 7
- N**
- NADH-dependent FDH, 363
 NADH-independent FDH enzymes, 363
 Natural photosynthesis, 321
 $\text{Nb}(\text{OR})_4(\text{OCO}_2)\text{R}$, 189–190
 $n\text{-Bu}_2\text{Sn}(\text{OR})_2$, 188
 n -Dibutyldialkoxostannanes, 188
 Neutral clusters, 2
 New concept photobioreactors, 340
 $(\text{PC}_{y3})_2\text{Ni}(\text{CO}_2)$, 37
 Ni-carbonyl-species, 351
 Nickelacycle carboxylate, 149
 Nickelacyclopentadiene, 162
 $\text{Ni}(\text{cyclam})\text{Cl}_2$, 40
 Ni-CODH/ACS (acetyl CoA synthetase), 358
 Ni-CODH enzymes, 358
 $\text{Ni-C}(\text{O})\text{OH}$, 89
 NMR data, transition metal complexes, 49–51
 Nodal planes, 4
 Non-stoichiometric clathrate solid, 374
 Normal and abnormal insertion, 85
 Normal vibration modes, 21
 N-substituted phenylaziridines, 126
 Natural population analysis (NPA), 12
 Nucleation, 390
- O**
- $\text{O}(^1\text{D})$, 24
 $\text{O}(^3\text{P})$, 24
 OCM. *See* Oxidative coupling of methane (OCM)
 OCO bond angle, 3, 36
 2-OH-benzoic acid, 353
 4-OH-benzoic acid, 353
 One-electron transfer, 312, 324
 One-electron transfer to CO_2 , 321–322
 One-step pathway for CO_2 -ODE, 259
 O-nucleophile, 9–10
 O-protonation, 12
 Organic carbonates, 183–185
 Organic promoters, 201–208
 Overpotential, 323
 Overvoltage, 320
 Oxazolidinones, 212, 224
 Oxidation state of Ni, 37
 Oxidative carbonylation of methanol, 184
 Oxidative carboxylation of olefins, 213–216
 Oxidative coupling of methane (OCM), 237, 239–243
 Oxidative coupling with CO_2 , 144
 Oxidative dehydrogenation of alkanes, 243–254
 Oxidative dehydrogenation of ethylbenzene, 254–265
 Oxygen anion mobility, 239
 Oxygen containing fuels, 237
- P**
- $\text{Pd-C}(\text{CO})\text{OH}_2$, 328
 Pentagonal dodecahedron (5^{12}), 377, 378
 Peroxocarbonates, 98
 Pervaporation membrane, 201
 Phase equilibria of CO_2 , 374
 Phase equilibrium of CO_2 hydrates, 376, 386–389
 $[(\text{PhCH}_2)_2\text{NCO}_2\text{H}]_2$, 104
 Phenolic acid decarboxylases, 357
 Phosphite dehydrogenase (PTDH), 365
 Phosphocarbamates, 112
 Photoautotrophic organisms, 348
 Photocatalysis, 347
 Photocatalytic C–H activation, 130
 Photocatalytic reduction, 366
 Photochemical (PC), 321
 Photoelectrochemical (PEC), 321
 Photoreduction processes, 17
 Photosynthesis, 1
 Phthalocyanines, 335
 Physical properties of CO_2 hydrates, 382–386
 $(\text{C}_3\text{H}_5\text{N}_2)_3(\text{C}_3\text{H}_4\text{N}_2)[\text{PMo}_{11}\text{CoO}_{38}(\text{CO}_2)]_4\text{H}_2\text{O}$, 46
 Point group $\text{D}_{\infty h}$, 2
 Polyaniline, 339
 Polycarbonates, 221–223
 Polydentate P-ligand, 328
 Polyhedral cavities, 374

- Pressure–temperature phase diagram of CO₂ +H₂O, 389
- Production of acetic acid, 361–362
- Proteobacteria, 350
- Proton affinity, 9
- PTDH. *See* Phosphite dehydrogenase (PTDH)
- P-type semiconductors, 239
- Pulsed ESR, 17
- PV, 321
- PV-generated H₂, 333
- Pyridine as an organic catalyst, 330
- Pyridine-N-carboxylic acid, 330
- Pyrone, 161
- Pyrole-2-carboxylate decarboxylase enzyme, 355–356
- Pyruvate decarboxylase, 354
- Pyruvate, ferredoxin oxidoreductase, 350
- Q**
- Quantum efficiency, 334
- R**
- Rate constants, 72, 324
- Rate determining step, 77
- Rate of carbamate formation, 77
- γ-Rays, 13
- Reaction mechanism for CO₂ hydrogenation, 285–294
- Reaction mechanism for CO₂-OCM, 241–243
- Reaction mechanism for CO₂-ODE to styrene, 258–265
- Reaction mechanism for CO₂-ODH of alkanes, 248–254
- Reaction mechanism for DME synthesis, 293–294
- Reaction mechanism for methanol synthesis, 287–293
- Reaction mechanism for RWGS, 285–287
- Reaction mechanism for the carboxylation of epoxides, 219
- Reaction mechanism for the DRM process, 271–276
- Reaction of alcohols with urea, 185
- Reaction of co-ordinated CO₂ with electrophiles, 59–63
- Reaction of CO₂ with amines, 74–82
- Reaction of CO₂ with carbanions, 73–74
- Reaction of CO₂ with hydroxyl and alkoxyl species, 72–73
- Reaction of CO₂ with R₃Si–H, 128
- Reaction of CO₂ with the hydride ion, 71–72
- Reaction of ionic hydrides with CO₂, 71
- Reactions of co-ordinated CO₂, 58–59
- Reactions of co-ordinated CO₂ with nucleophiles, 63–64
- Reduce emission, 1
- Reduction of CO₂ to carbon monoxide/formate, 362–364
- Reduction reactions, 358–366
- Reductive acetyl-CoA (Wood–Ljungdahl) pathway, 350–351
- Reductive TCA, 350–351
- Reforming of methane (MDR), 237
- Refrigeration systems, 376
- Regeneration of the cofactor NADH, 366
- Regularity of the alternate insertion, 222
- Replacement of CH₄ by CO₂, 395–396
- Reverse water gas shift reaction (RWGS), 278
- Reversible binding, 324
- Reversible interconversion, 191
- Rh(diars)₂(Cl)(CO)₂, 41
- (diphos)Rh(O₂C–C₆H₅), 95
- Rh-catalyzed cooligomerization of butadiene, 175
- Ring-opening carboxylative polymerization, 216
- Ring opening of epoxides, 217
- Ring opening of vinylaziridines, 127
- Ring stress energy, 216
- Rotational structure, 8
- Ru(bpy)₂(CO)(COOH)²⁺, 90
- [Ru(diphos)₂(COOH)]⁺, 90
- RubisCO, 349
- RuCl₂(1,3,5-triaz-7-phosphaadamantane), 89
- RuCO₂H, 327
- RuC(O)OH₂, 327
- RWGS. *See* Reverse water gas shift reaction (RWGS)
- S**
- Secondary refrigerant, 397
- Second-order reaction, 72
- Semiconducting materials, 366
- Sequential “one-electron plus one-proton”, 326–332
- Single-metal catalysts, 194–195
- Single-step, third-order reaction, 78
- Singlet ground state (¹Σ_g⁺), 24
- Sn-tethered complexes, 194
- Solar driven cyclic interconversion, 59
- Solar-driven water splitting, 340
- Solar energy, 321

Solid–liquid junction, 339
Solid matrix, 13
Solubility of CO₂, 315
Solubility of CO₂ in organic solvents, 319
Solubility of CO₂ (g) in water, 319
Sonic and seismic velocity, 384
Space issue, 340
Spherical-like cages, 374
Spontaneous release of formic acid, 89
Structure of gas hydrates, 376–382
Substituted allenes, 164
Sustainability, 187
Symmetric stretching mode, 21
Synthesis of oxalates, 322

T

(^{Ad}ArO)₃tacnU(η¹-OCO), 43
Tetraikadecahedron (5¹²6²), 378
Theoretical calculations, 36
Thermal conductivity of gas hydrates, 385
Thermal expansion, 385
Thermal properties of CO₂ hydrates, 384–386
Thermodynamic and kinetic issues, 185–187
Thermodynamic barriers, 185
Thermodynamic data, 88
Thermodynamic models, 374
Thermodynamic potential, 320
Time-dependent kinetic behavior, 374
Time-to-market, 340
TOF, 327
Trans-esterification, 184
Transfer of “1e⁻” to CO₂, 311
Transition state, 86, 98
Transition states, 62
trans-Mo(CO)₂HN
(CH₂CH₂PMe₂)₂(PMe₃), 38
trans-Ru(dmpe)₂(O₂C-CH₃)₂, 96
trans-Ru(dmpe)₂(H)CH₃, 95
trans-Ru(dmpe)₂(O₂C-CH₃)CH₃, 96
Triplet-singlet transition, 8
Triplet state ³B₂, 26

Two-electron transfer, 324
Two-step pathway, EB dehydrogenation,
262, 263

U

Unfavorable thermodynamics, 186
Unimolecular transition structure, 154
Unoccupied molecular orbitals, 4
Unpaired electron spin density, 17
Unperturbed electronic structure of CO₂⁻, 16
Unsaturated carboxylic acid, 164
Upper (bound) singlet state ¹B₂, 25
Urea as an active form of CO₂, 208–210
UV spectrum, 22–26

V

Variable temperature NMR spectroscopy, 26
Vibrational structure, 5
5-Vinylloxazolidinones, 127
VT-multinuclear NMR, 51

W

Walsh diagram, 7, 35
Water removal, 200–201
Water trapping, 187
W-shape, 16

X

XANES, 324
X-ray diffraction (XRD) structure of solid
complexes, 36

Z

Zwitterion mechanism, 78