The Chemistry of CO_2

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Outline

- Introduction
- Physical Properties
- Uses
- Production, Recovery, Purification
- Chemical Properties

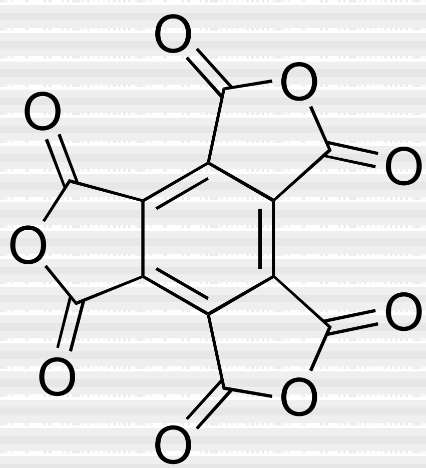
Oxides of Carbon

- Stable Oxides of Carbon
  - CO
  - CO_2
  - C_3O_2
  - $C_{12}O_9$

C≡O

O=C=O

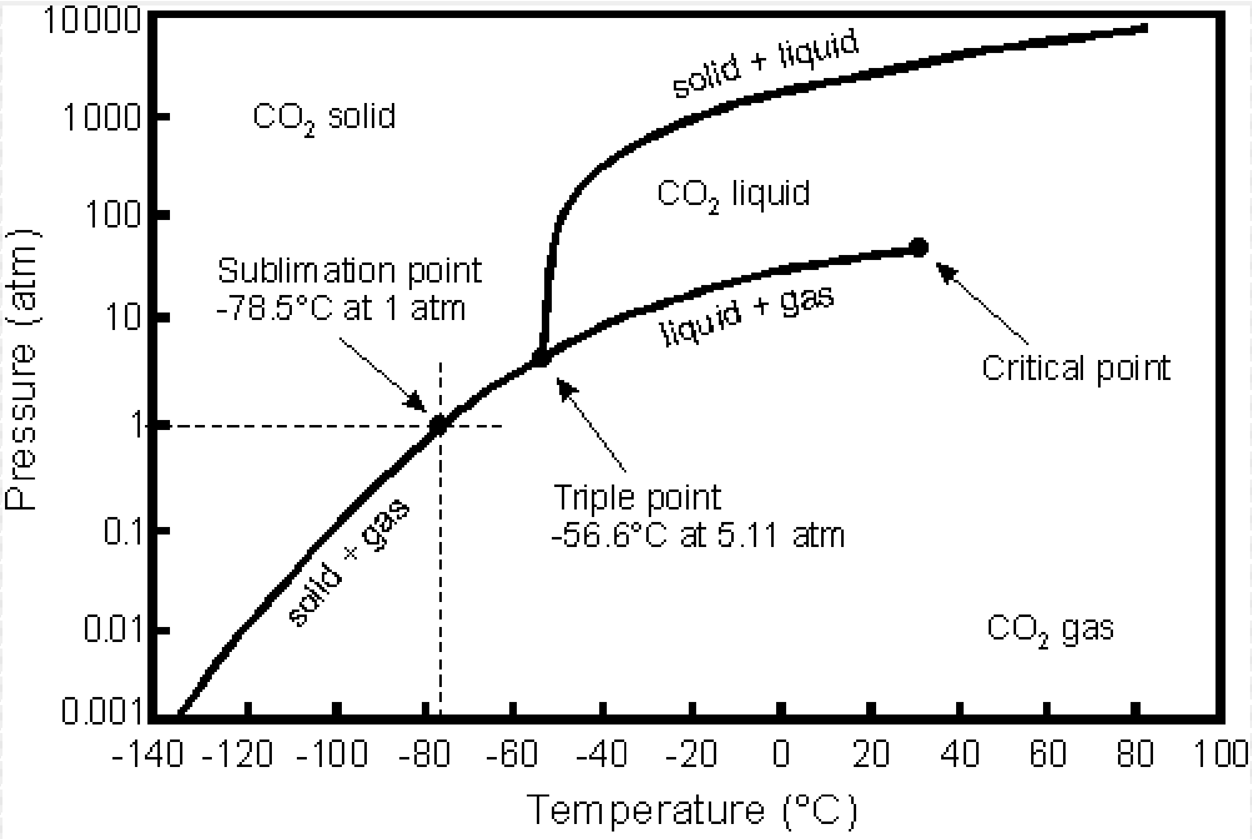
O=C=C=C=O



Selected Physical Properties of CO_2

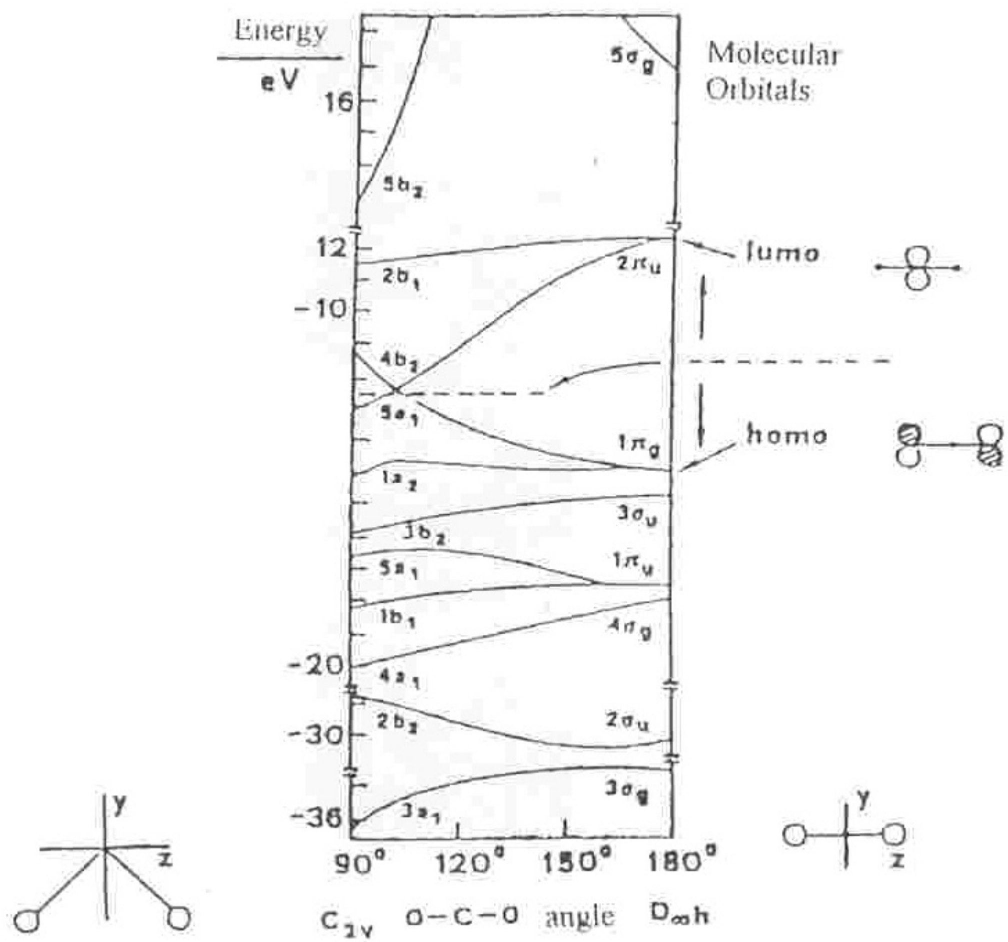
Colorless, Odorless Gas Molecular Weight	 44.01g/mol
Mp Bp @1atm	-56.6 °C (5.2 atm) -78.5 °C (subl)
Critical T Critical P	31°C 72.85 atm (1070.67 psi)
Density of Gas @1atm and 21.1 ^{0}C Relative density of gas @1atm and 21.1^{o}C (Air=1)	1.823 Kg/m^3 1.52
Solubility in water at 25^{o}C Henry's Law constant	1950 ppm (wt) 392 x 10^{-4} mol/L atm
ΔG^o_f (CO_2(g)) ΔH^o_f (CO_2(g)) ΔS^o_f (CO_2(g)) Dissociation Energy (C-O)	-394.4 kJ/mol -393.5 kJ/mol 3.02 J/mol K 531.4 kJ/mol
IR (gas) UV (gas)	2349 cm^{-1} (Asym C=O), 1285-1388 cm^{-1} (Sym C=O; Raman), 667 cm^{-1} (Bending) 1700 - 3000 Å

Phase Diagram



Pressure-Temperature phase diagram for CO_2.

Walsh Diagram



Industrial Uses of CO_2

Uses Based on Physical Properties (major)

- Refrigeration
- Cleaning fluid
- Air conditioning
- Solvent for
  - Reactions
  - Extractions
  - Nanopartical production
  - Food and Agro-chemical Applications
    - Fumigant
    - Additive to beverages
  - Inert atmosphere

Uses Based on Chemical Properties

- Production of Urea
- Production of Salicylic acid
- Inorganic carbonates and pigments
- Production of Propylene carbonate
- Neutralization of caustic waste water

Production Sources

- Ammonia/Hydrogen plants
  - $CH_4 + 2\ H_2O \rightarrow CO_2 + 4\ H_2$
- Flue gases from combustion
- Fermentation
  - $C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$
- Lime-kiln operations
  - $CaCO_3 \rightarrow CaO + CO_2$
- Sodium phosphate manufacture
  - $3\ Na_2CO_3 + 2\ H_3PO_4 \rightarrow 2\ Na_3PO_4 + 3\ CO_2 + 3\ H_2O$
- Natural CO_2 gas wells

Recovery by Reversible Absorption

- Sodium or Potassium Carbonate Process
  - $K_2CO_3(aq) + H_2O(l) + CO_2(g) \underset{\text{HOT}}{\overset{\text{COOL}}{\rightleftharpoons}} KHCO_3(aq)$
- Girbotol Amine Process
  - $2\ HOCH_2CH_2NH_2(aq) + H_2O(l) + CO_2(g) \underset{\text{100 - 150 °C}}{\overset{\text{25 - 65 °C}}{\rightleftharpoons}} (HOCH_2CH_2NH_3)_2CO_3(aq)$

Purification

- Permanganate Process
  - $3\ H_2S + 2KMnO_4 + 2\ CO_2 \rightarrow$
    $3\ S + 2\ MnO_2 + 2\ KHCO_3 + 2\ H_2O$
- Dichromate Process
  - $3\ H_2S + K_2Cr_2O_7 + H_2O + 2\ CO_2 \rightarrow$
    $3\ S + 2\ Cr(OH)_3 + 2\ KHCO_3$

Chemical Properties

- General Reactivity
- Aqueous chemistry
- Reactions of Industrial Importance
- Biological Reactions
- Organic Reactions
- Coordination Chemistry
- Reactions incorporating CO_2 without Reduction
- Reactions with Reduction

General Reactivity

- "Not very reactive at ordinary temperature"; "nonreactive"; "stable"; "inert"
- Many reactions of CO_2 are thermodynamically favorable, but kinetically slow
- Ex: $M_2SiO_4 + 2\ CO_2 \rightarrow 2\ MCO_3 + SiO_2$

Aqueous Chemistry

- Species involved: CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, OH^-, $[H_2CO_3^*] = [CO_2(aq)] + [H_2CO_3]$
- Equilibrium concentrations described completely by system of 5 equations
  - $CO_2 + H_2O \rightleftharpoons H_2CO_3$ $\quad K_1 = 1.67 \times 10^{-3}$
  - $H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$ $\quad K_2 = 4.47 \times 10^{-7}$
  - $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $\quad K_a = 2.68 \times 10^{-4}$
  - $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $\quad K_3 = 4.68 \times 10^{-11}$
  - $H_2O \rightleftharpoons H^+ + OH^-$ $\quad K_w = 1.0 \times 10^{-14}$
  - $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$
- Carbonates insoluble
  - $K_{sp}(CaCO_3) = 2.8 \times 10^{-9}$; $K_{sp}(MgCO_3) = 3.5 \times 10^{-8}$

Slow Kinetics for Reactions of CO_2

- At pH < 8
  - $CO_2 + H_2O \rightleftharpoons H_2CO_3$ (slow)
  - $H_2CO_3 + OH^- \rightleftharpoons HCO_3^-$ (fast)
- At pH > 10
  - $CO_2 + OH^- \rightleftharpoons HCO_3^-$ (slow)
  - $HCO_3^- + OH^- \rightleftharpoons CO_3^{2-}$ (fast)
- At pH 8-10 both sets of equilibria are important.

Important Reactions of CO_2, CO and O_2

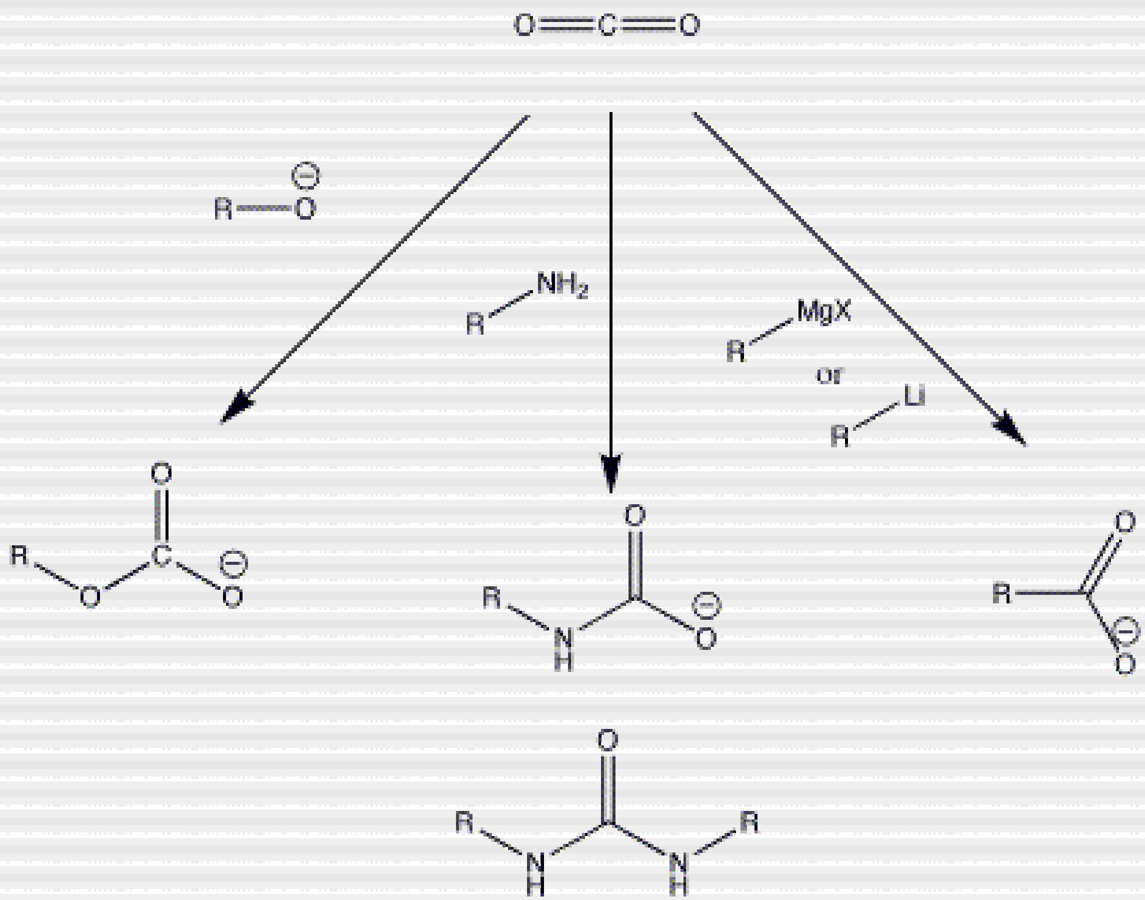
At high temperature

- $2\ C + O_2 \rightarrow 2\ CO$ $\Delta H^o = -221.0$ kJ/mol
- $C + O_2 \rightarrow CO_2$ $\Delta H^o = -393.5$ kJ/mol
- $C + H_2O \rightarrow CO + H_2$ $\Delta H^o = +131.3$ kJ/mol
- $2\ CO \rightleftharpoons C + CO_2$ $\Delta H^o = -172.5$ kJ/mol
- $CO_2 \rightleftharpoons CO + 1/2\ O_2$

Also

- $CO_2 + H_2 \rightarrow CO + H_2O$ (reverse of water-gas shift rxn)
- $CO_2 + 2\ NH_3 \rightarrow NH_4O_2CNH_2 \rightarrow NH_2CONH_2 + H_2O$

Basic Organic Reactions



Coordination Chemistry

- CO_2 is a poor ligand
- A number of complexes and bonding modes known
- Important for activation of CO_2 in reduction reactions

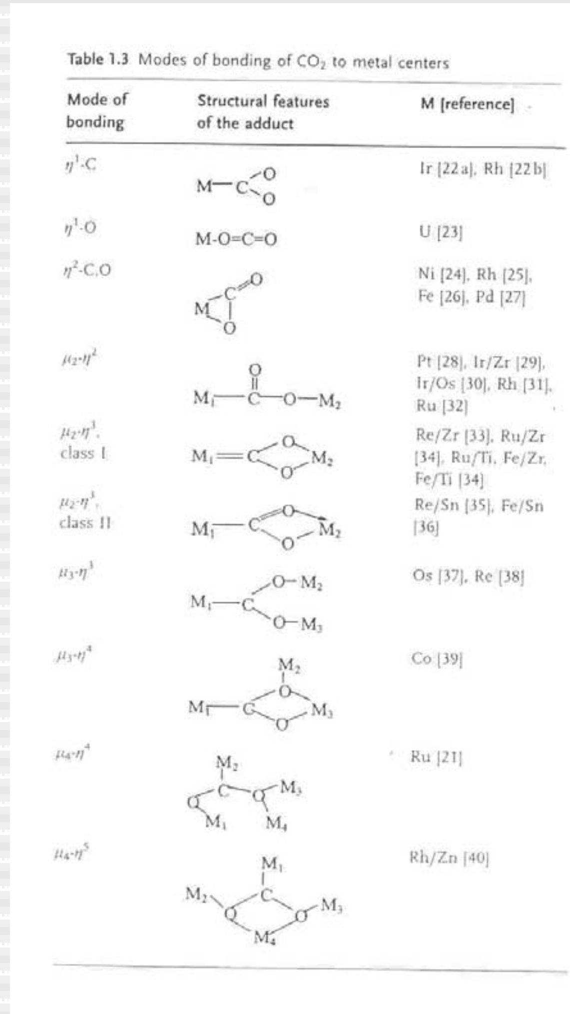


Table 1.3 Modes of bonding of CO_2 to metal centers

Mode of bonding	Structural features of the adduct	M [reference]
η^1-C		Ir [22a], Rh [22b]
η^1-O	M-O=C=O	U [23]
η^2-C,O		Ni [24], Rh [25], Fe [26], Pd [27]
μ_2-η^2		Pt [28], Ir/Zr [29], Ir/Os [30], Rh [31], Ru [32]
μ_2-η^3, class I		Re/Zr [33], Ru/Zr [34], Ru/Ti, Fe/Zr, Fe/Ti [34]
μ_2-η^3, class II		Re/Sn [35], Fe/Sn [36]
μ_3-η^3		Os [37], Re [38]
μ_3-η^4		Co [39]
μ_4-η^4		Ru [21]
μ_4-η^5		Rh/Zn [40]

Reactions of “M-CO_2”

- With Protons or other electrophile
  - “M-CO_2” + $2H^+$ + $2e^-$ $\rightarrow$ “M-CO” + H_2O
  - “M-CO_2” + R^+ $\rightarrow$ M-C(O)OR
- Hydride insertion
  - “M-H” + CO_2 $\rightarrow$ “M-O_2CH”
- With External Phosphine
  - “M-CO_2” + PR_3 $\rightarrow$ “M-CO” + O=PR_3
- With Coordinated Isonitrile
  - “M(CNR)(CO_2)” $\rightarrow$ RNCO + “M-CO”

Biological Reactions

- Ubiquitous in Nature
- Animal metabolism
  - $C_6H_6O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$ + energy
- Photosynthesis is reverse of above reaction
- Numerous enzymes catalyze reactions of CO_2
  - Carbonic anhydrase (Zn^{2+}) - $H_2CO_3 \rightarrow CO_2$
  - RuBisCO (Mg^{2+}) - carboxylation of ribose
  - Carbon monoxide dehydrogenase (Ni,Fe) - $CO_2 \rightarrow CO$

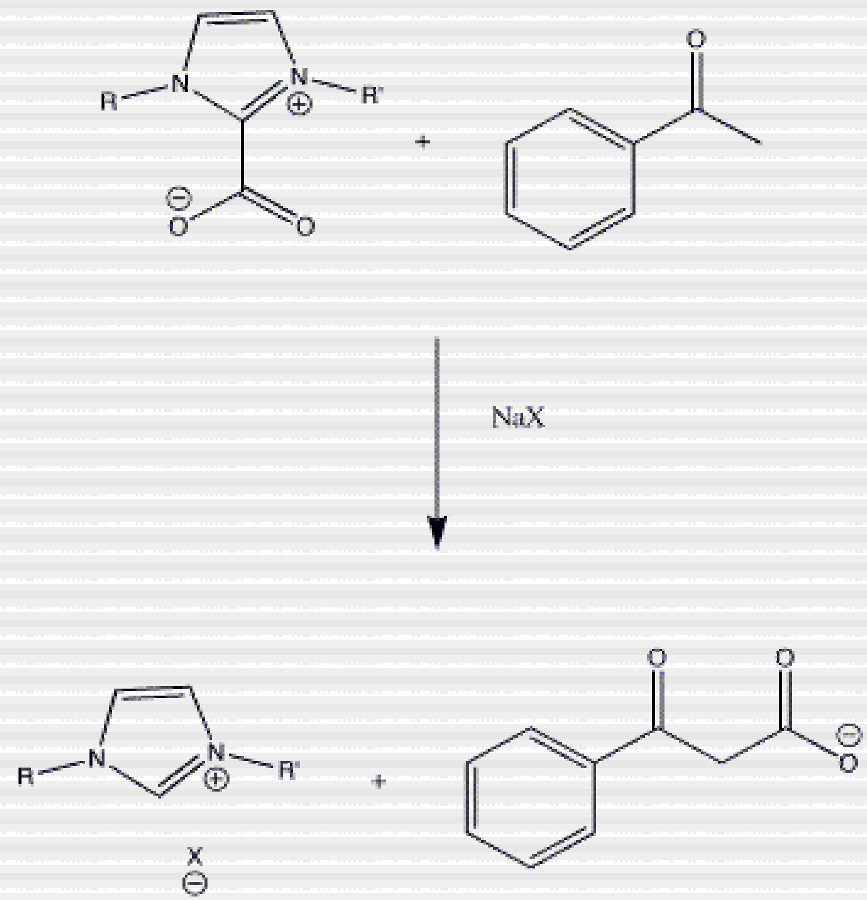
Use of CO_2 as C_1 Feedstock

- "Conversion" reactions (CO_2 not reduced)
- Carboxylates, lactones RCOOR'
- Carbamates, RR'NCOOR"
- Ureas, RR'NCONRR'
- Isocyanates, RNCO
- Carbonates, ROC(O)OR'

- Reduction of CO_2
- Formates, $HCOO^-$
- Oxalates, $^-O_2C\text{-}CO_2^-$
- Formaldehyde, H_2CO
- Carbon Monoxide, CO
- Methanol, CH_3OH
- Methane, CH_4

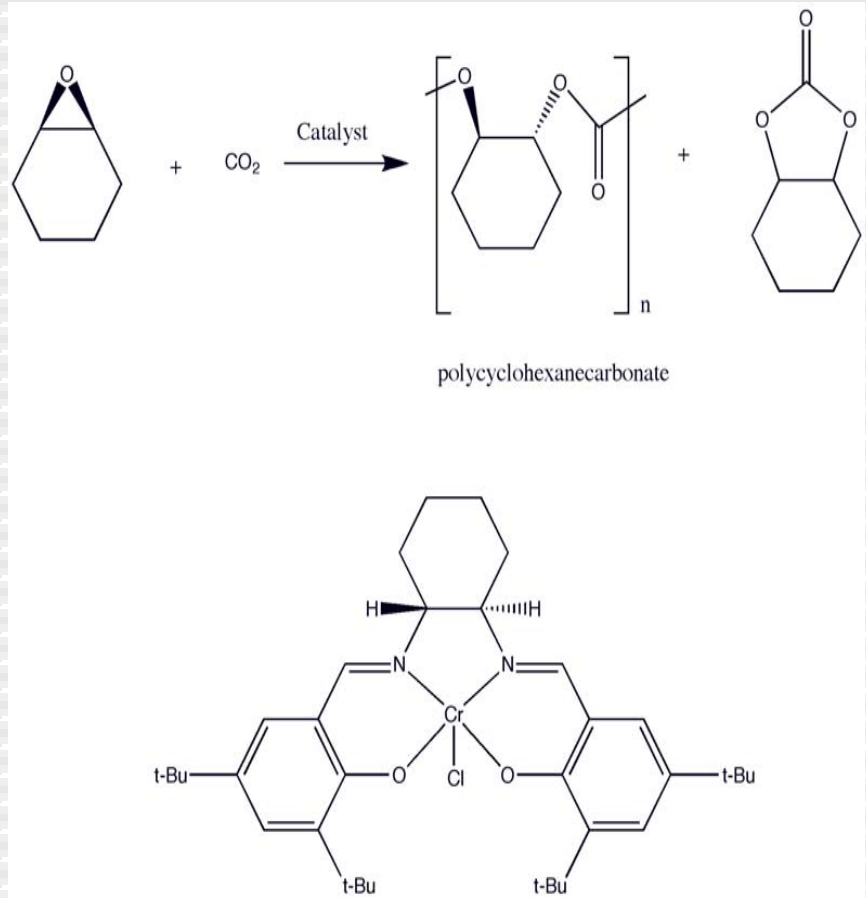
Carboxylation Reactions

- C-C bond formation
- Direct carbonylation in ionic liquid from imidazoliumcarbonate
- N-C, O-C bond formation also known

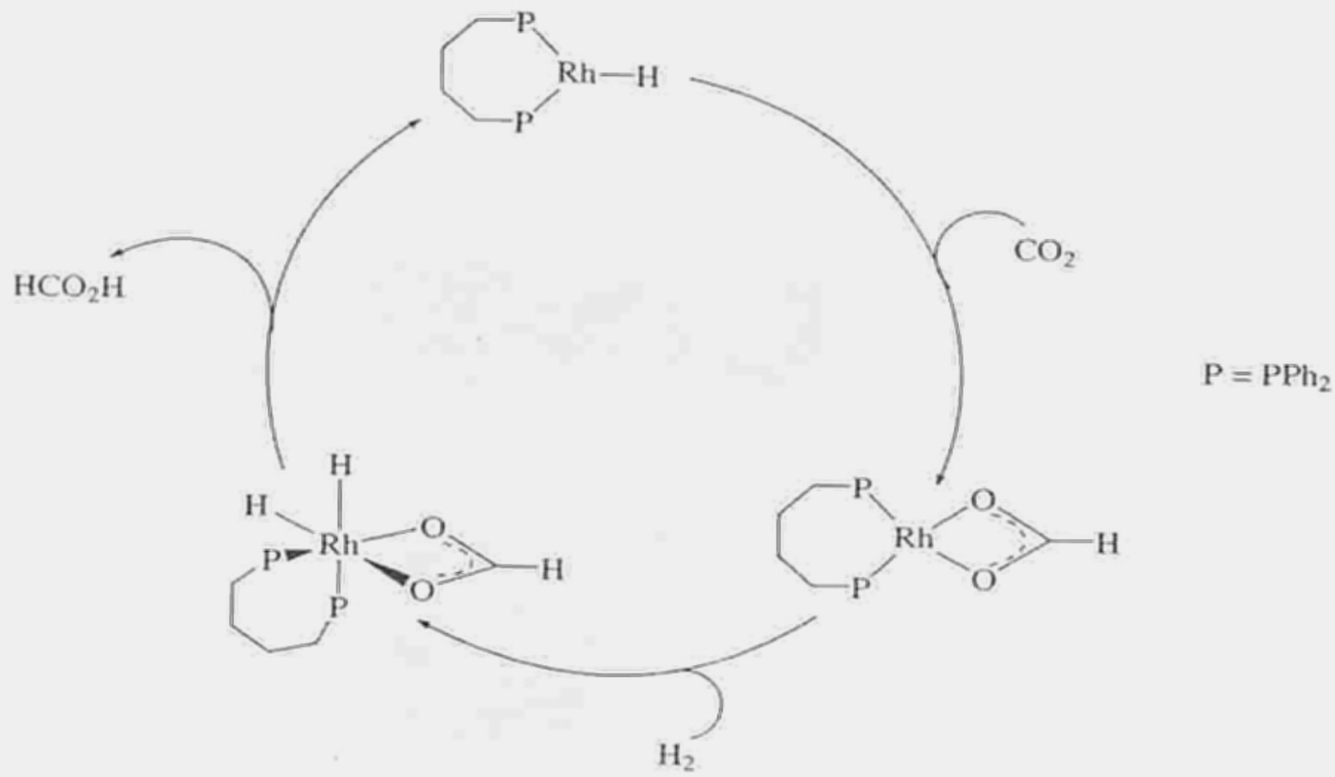


Plastics from CO_2

- Metal Salen complexes as catalysts
- Production of Polycarbonates from Epoxides and CO_2



CO_2 Hydrogenation to form Formic Acid



Production of Methanol

- $CO + 2 H_2 \rightarrow CH_3OH$
- $CO_2 + 3 H_2 \rightarrow CH_3OH$
  - Cu-Zn-O catalyst, 250 - 300ºC, 5-10 MPa
  - Up to 30% CO_2 added to syngas feedstock significantly improves yield
- $CO_2 + H_2O \rightarrow CH_3OH$
  - Cascade of enzymes
  - $CO_2 \rightarrow HCOO^-$ (formate dehydrogenase)
  - $HCOO^- \rightarrow CH_2O$ (formaldehyde dehydrogenase)
  - $CH_2O \rightarrow CH_3OH$ (methanol dehydrogenase)

Photoelectrochemical Reduction

- In anhydrous,aprotic solvent, reduction potential of CO_2 to $CO_2^{\bullet -}$ is -2.2V vs NHE!
- Large kinetic overvoltage
- Yield of photochemical conversion is low
- Proton assisted multielectron reductions more favorable
  - $CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$ -0.61V
  - $CO_2 + 6\,H^+ + 6e^- \rightarrow CH_3OH + H_2O$ -0.38V

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