Chapter 2

Properties and Fundamentals

Importance of Organic Compounds

- Volatile compounds contribute to the formation of ozone and photochemical oxidants
- Compounds can have toxic effects on plants and animals

Topics Covered

- Review of organic chemistry
- Formation of ozone and photochemical smog
- Properties of organic vapors

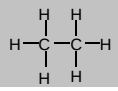
Review of Organic Chemistry

- Chemistry of the compounds of carbon
- Number of organic compounds exceeds 8 million
- Number of inorganic compounds is about 300,000

Characteristics of the Carbon Atom

- Atomic number = 6
- Atomic weight = 12
- Total electrons = 6
- Valence electrons = 4
- Forms covalent bonds
  - Single
  - Double
  - Triple

Molecular, Structural and Semi-Structural Formulas

Molecular Formula	*Structural Formula*	*Semi-structural Formula*
C_2H_6		$CH_3—CH_3$

Hydrocarbons

Compounds formed only from carbon and hydrogen

- Alkanes
- Alkenes
- Alkynes
- Cyclic compounds

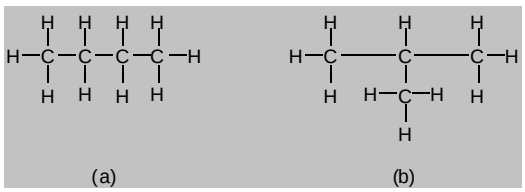
Alkanes

Carbon atoms linked only by single bonds

General formula: C_nH_{2n+2}

Methane (CH_4)
Ethane (C_2H_6)
Propane (C_3H_8)
Butane (C_4H_{10})
Pentane (C_5H_{12})

Isomers of Butane



(a) n-butane (b) i-butane

Isomers

Compounds with the same molecular formulas, but with different structures

- All alkanes with four or more carbon atoms exist as isomers
- Alkanes with five or more carbon atoms exist as more than two isomers

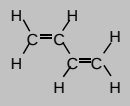
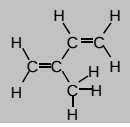
Alkenes

Hydrocarbons that contain one double bond

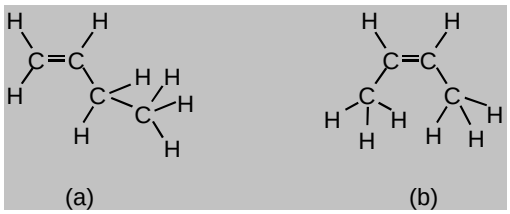
General formula: C_nH_{2n}

Ethylene (C_2H_4)
Propylene (C_3H_6)
Butylene (C_4H_8)
Pentylene (C_5H_{10})

Diolefin Compounds

Molecular Formula	*Name*	*Structural Formula*	*Semi-structural Formula*
C_4H_6	butadiene		$CH_2{=}CH{-}CH{=}CH_2$
C_5H_8	2-methyl butadiene		$CH_2{=}C(CH_3){-}CH{=}CH_2$

Butylene Isomers



Alkynes

Hydrocarbons that contain one triple bond

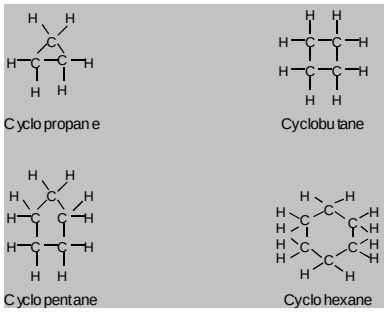
General formula: C_nH_{2n-2}

Ethyne (C_2H_2)
Propyne (C_3H_4)
Butyne (C_4H_6)
Pentyne (C_5H_8)

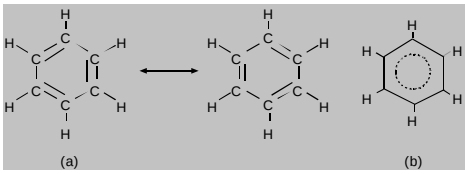
Cyclic Compounds

- Cycloparaffins
- Aromatic hydrocarbons

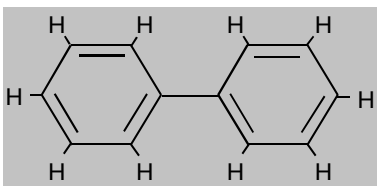
Examples of Cycloparaffin Compounds



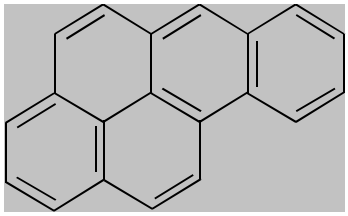
Benzene Structure



Biphenyl



Benzo (α) pyrene



Nomenclature

1 carbon	meth-	CH_4	methane
2 carbons	eth-	C_2H_6	ethane
3 carbons	prop-	C_3H_8	propane
4 carbons	but-	C_4H_{10}	butane
5 carbons	pent-	C_5H_{12}	pentane
6 carbons	hex-	C_6H_{14}	hexane
7 carbons	hep-	C_7H_{16}	heptane
8 carbons	oct-	C_8H_{18}	octane

Functional Groups

Alcohols	-OH
Amines	$-NH_2$
Mercaptans	-SH
Chlorides	-Cl

Location of Substitution

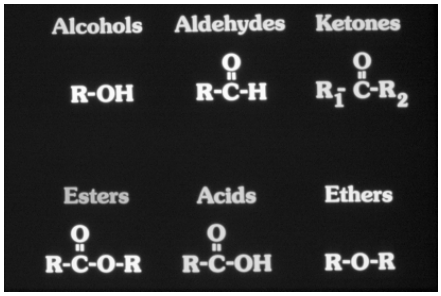
1,1,1-trichloroethane

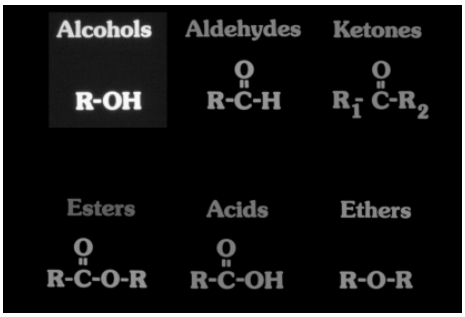
2-propylamine

1,1,2,2-tetrachloroethylene

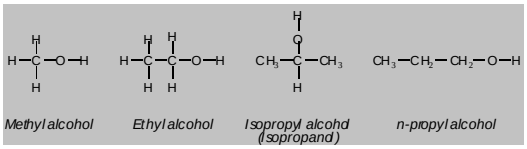
Perchloroethylene

Functional Groups Containing Oxygen

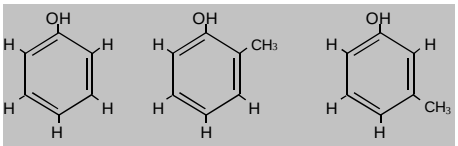




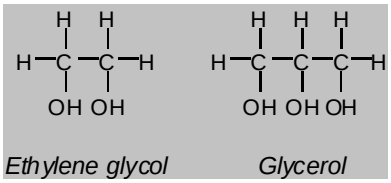
Common Alcohols

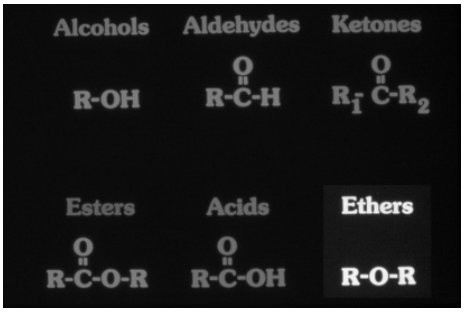


Phenols



Polyhydric Alcohols

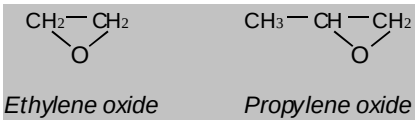




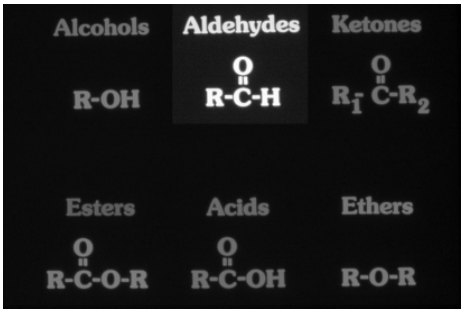
Ether Compounds

- Diethyl ether
  CH_3CH_2-O-CH_2CH_3
- Methyl ethyl ether
  CH_3-O-CH_2CH_3

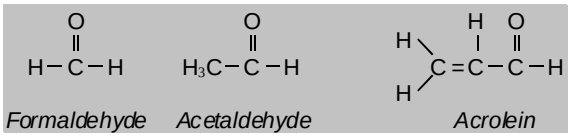
Cyclic Ethers

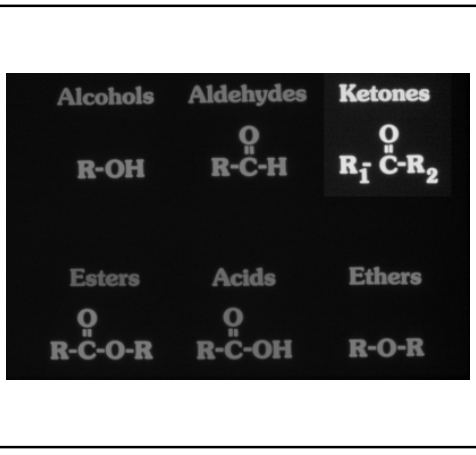


Ethylene oxide *Propylene oxide*


Alcohols
R-OH
Aldehydes
R-C-H
Ketones
R-C-R
Esters
R-C-O-R
Acids
R-C-OH
Ethers
R-O-R

Aldehydes


Formaldehyde
Acetaldehyde
Acrolein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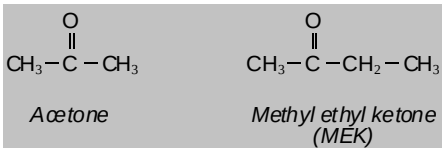
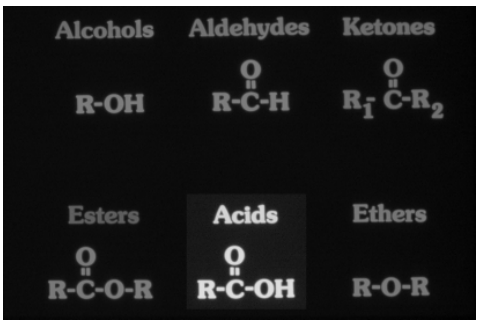
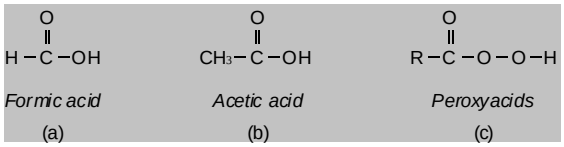
R-O-R

Ketones

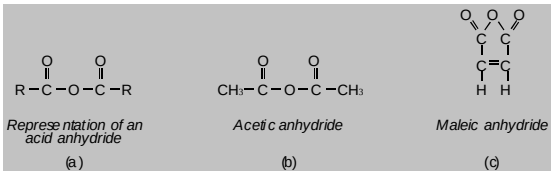


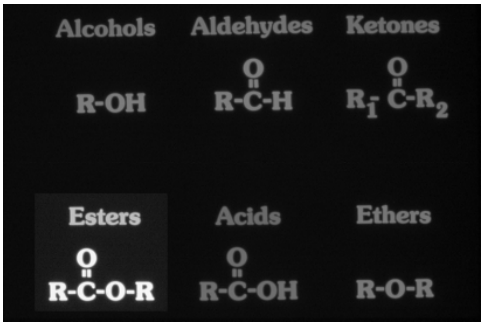


Acids

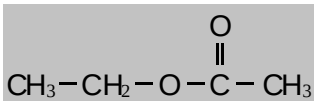


Acid Anhydrides





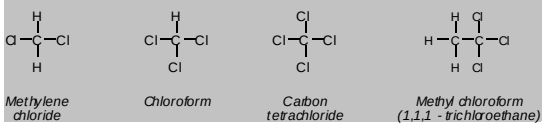
Ethyl Acetate



Organic Compounds Containing Halides

Organic Chlorides

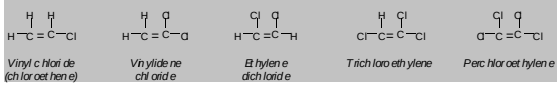
Chlorides of methane and ethane



Methylene chloride | *Chloroform* | *Carbon tetrachloride* | *Methyl chloroform (1,1,1 - trichloroethane)*

Organic Chlorides
(continued)

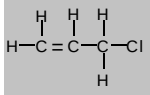
Chlorides of ethylene



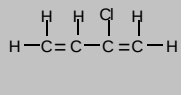
Vinyl chloride (chloroethene) | *Vinylidene chloride* | *Ethylene dichloride* | *Trichloroethylene* | *Perchloroethylene*

Organic Chlorides
(continued)

Other double-bonded chlorides



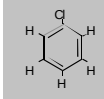
Allyl chloride



Chloroprene

Organic Chlorides
(continued)

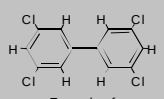
Chlorides of benzene



Chlorobenzene

Benzylchloride

p-dichlorobenzene



Example of a polychlorinated biphenyl (PCB)

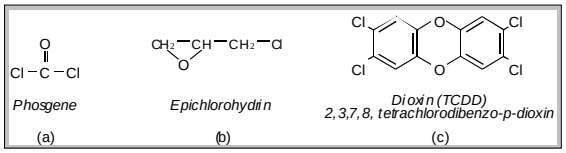
Chlorofluorocarbons

Trichlorofluoromethane (Freon 11)

Dichlorodifluoromethane (Freon 12)

Trichlorotrifluoroethane (Freon 13)

Compounds Containing Both Oxygen and Chlorine

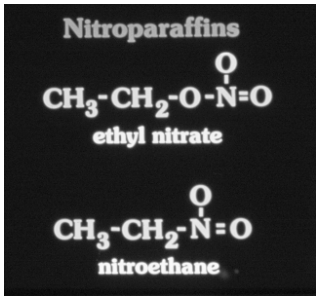


Phosgene (a)

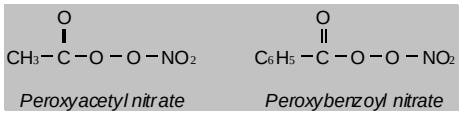
Epichlorohydrin (b)

Dioxin (TCDD)
2,3,7,8, tetrachlorodibenzo-p-dioxin (c)

Organic Compounds Containing Nitrogen



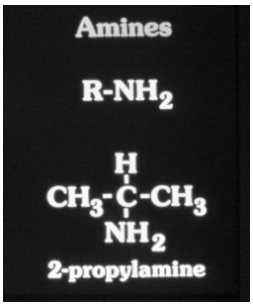
PAN and PBN Compounds



Peroxyacetyl nitrate

Peroxybenzoyl nitrate

Organic Compounds Containing Nitrogen



Amine Compounds

- Primary amine: RNH_2
  CH_3NH_2
- Secondary amine: R_2NH
  $CH_3NHC_2H_5$
- Tertiary amine: R_3N
  $(C_2H_5)_3N$

Organic Compounds Containing Sulfur

- Methyl mercaptan

  CH_3SH
- Dimethyl sulfide

  CH_3SCH_3

Formation of Ozone and Photochemical Smog

Photochemical Reactions

$$A \xrightarrow{h\nu} A^*$$

$$A^* \rightarrow B + C + ...$$

Wavelengths of interest are 280 nm to 730 nm

Variables Affecting Intensity

- Latitude
- Time of day
- Time of year
- Presence of clouds or aerosols

Summer maximum = 2 x 10^{16} photons $cm^{-2}sec^{-1}$
for 4-6 hours
Winter values = 0.7-1.5 x 10^{16} photons $cm^{-2}sec^{-1}$
for 2-4 hours

Energy Absorbing Molecules

- NO_2
- O_3
- H_2O_2
- HNO_2
- Aldehydes
- Ketones

Basic Photochemical Cycle

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 \xrightarrow{M} O_3$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

Role of VOCs

$$O_3 \xrightarrow{h\nu} O^* + O_2$$

$$O^* + H_2O \rightarrow 2OH\cdot$$

Understanding $OH\cdot$ reactions is key

Reactions of Formaldehyde

Photolysis:

$$HCHO \xrightarrow{h\nu} H\cdot + HCO\cdot$$

Reaction with OH:

$$HCHO + OH\cdot \rightarrow HCO\cdot + H_2O$$

Reactions of Formaldehyde (cont'd)

$$H\cdot + O_2 \xrightarrow{M} HO_2\cdot$$

$$HCO\cdot + O_2 \rightarrow HO_2\cdot + CO$$

Reactions of Formaldehyde (cont'd)

$$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$$

$$OH\cdot + NO_2 \rightarrow HNO_3$$

Reactions of Acetaldehyde

Photolysis:

$$CH_3CHO \xrightarrow{h\nu} CH_3\cdot + HCO\cdot$$

Reaction with OH:

$$CH_3CHO + OH\cdot \rightarrow CH_3CO\cdot + H_2O$$

Reactions of Acetaldehyde (cont'd)

$$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$$

$$CH_3O_2\cdot + NO \rightarrow NO_2 + CH_3O\cdot$$

$$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot$$

Reactions of Acetaldehyde (cont'd)

$$CH_3CO\cdot + O_2 \rightarrow CH_3COO_2\cdot$$

$$CH_3COO_2\cdot + NO \rightarrow NO_2 + CH_3COO\cdot$$

$$CH_3COO\cdot + O_2 \rightarrow CH_3O_2\cdot + CO_2$$

$$CH_3COO_2\cdot + NO_2 \rightarrow CH_3COO_2NO_2$$

Summary

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 \xrightarrow{M} O_3$$

$$O_3 \xrightarrow{h\nu} O^* + O_2$$

$$O^* + H_2O \rightarrow 2OH\cdot$$

Photolysis of Aldehydes

$$RCHO \xrightarrow{h\nu} R\cdot + HCO\cdot$$

$$HCO\cdot + O_2 \rightarrow HO_2\cdot + CO$$

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

Reaction of OH with Aldehydes

$$RCHO + OH\cdot \rightarrow RCO\cdot + H_2O$$

$$RCO\cdot + O_2 \rightarrow RCOO_2\cdot$$

$$RCOO_2\cdot + NO \rightarrow NO_2 + RCOO\cdot$$

$$RCOO\cdot \rightarrow R\cdot + CO_2$$

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

Reaction of OH with Hydrocarbons

$$RH + OH\cdot \rightarrow R\cdot + H_2O$$

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot$$

$$RO_2\cdot + NO \rightarrow RONO_2$$

$$RO\cdot + O_2 \rightarrow HO_2\cdot + RCHO$$

$$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$$

Properties of Organic Vapors

- Gas and vapor definitions
- Molecular weight and the mole
- Equation of state
- Vapor pressure
- Partial pressure and partial volume
- Concentration expressions
- Explosive limits

Gas and Vapor Definitions

- A gaseous material below its critical temperature is a vapor. Compressing a vapor at constant temperature will cause it to condense.
- A gaseous material above its critical temperature is a gas. Compressing a gas at constant temperature will not cause it to condense.

Molecular Weight

Molecular weight is the sum of the atomic weights of all atoms in a molecule

$$MW_{mixture} = \sum_{i=1}^{n} \chi_i MW_i$$

χ_i = mole fraction of component I

MW_i = molecular weight of component i

The Mole

A mole is a mass of material that contains a certain number of molecules. It is numerically equal to the molecular weight.

The gram-mole is the mass of material that contains Avogadro's number of molecules.

Equation of State

The ideal gas law:

$$PV = nRT$$

P = absolute pressure
V = gas volume
n = number of moles
R = constant
T = absolute temperature

Values for R

10.73 psia-ft^3/lb-mole-°R

0.73 atm-ft^3/lb-mole-°R

82.06 atm-cm^3/g-mole-K

8.31 x 10^3 kPa-m^3/kg-mole-K

Volume Correction

$$\frac{PV}{T} = nR = \text{CONSTANT (if n = CONSTANT)}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_1 = V_2\left(\frac{P_2}{P_1}\right)\left(\frac{T_1}{T_2}\right)$$

Molar Volume

$$\frac{V}{n} = \frac{RT}{P}$$

At 68°F and 1 atm:

$$\frac{V}{n} = \frac{RT}{P} = \frac{\left(0.73\frac{\text{atm}-\text{ft}^3}{\text{lb}-\text{mole}\cdot{}^\circ\text{R}}\right)(528{}^\circ\text{R})}{1\,\text{atm}} = 385.4\,\frac{\text{ft}^3}{\text{lb}-\text{mole}}$$

Gas Density

$$PV = \left(\frac{m}{MW}\right)RT$$

$$\rho = \frac{m}{V} = \frac{P \cdot MW}{RT}$$

Vapor Pressure

Antoine equation:

$$\ln(p^*) = A - \frac{B}{T + C}$$

p* = vapor pressure

T = temperature

A,B,C = constants

Partial Pressure

Dalton stated that the total pressure of a gas mixture is the sum of the individual pressures of each component

$$\frac{p_i}{P_T} = \frac{n_i}{n_T}$$

Partial Volume

Amagat stated that the total volume of a gas mixture is the sum of the individual volumes of each component

$$\frac{\nu_i}{V_T} = \frac{n_i}{n_T}$$

$$\frac{p_i}{P_T} = \frac{n_i}{n_T} = \frac{\nu_i}{V_T}$$

Concentration Expressions

- Partial pressure
- Parts per million by volume (ppmv)

$$ppmv_i = \left(\frac{\nu_i}{V_T}\right) x10^6$$

- Mass per unit volume

Conversion Equation

$$1\text{ppmv} = \frac{1\text{ft}^3\text{ VOC}}{10^6\text{ft}^3}\left(\frac{1}{V_{molar}}\frac{\text{lb}-\text{mole VOC}}{\text{ft}^3\text{VOC}}\right)\left(MW_{VOC}\frac{\text{lb VOC}}{\text{lb}-\text{mole VOC}}\right)$$

$$1\text{ppmv} = \frac{MW_{VOC}}{V_{molar}\text{x }10^6}\frac{\text{lb VOC}}{\text{ft}^3}$$

Explosive Limits

- LEL is the concentration of VOC below which combustion will not be self-sustaining
- UEL is the concentration of VOC that produces a non-burning mixture because of the lack of oxygen

Explosive Limits of Selected VOCs

	Explosive Limit (Volume %)	
Substance	Lower	Upper
Methane	5.00	15.00
n-Hexane	1.18	7.40
Ethylene	2.75	28.60
Toluene	1.27	6.75
Xylene	1.00	6.00
Methanol	6.72	36.50
Ethanol	3.28	18.95
Gasoline	1.40	7.60