CHEMISTRY refresher

Llanie Nobile

Topics

Petroleum

- Physical and chemical properties
  - Like dissolves like
  - Volatility
  - Polarity
  - Density
- Compare fresh vs. weathered
  - Reaction (how and why)
- Bioremediation
  - Oxidation and reduction

Chlorinated Solvents

- Nomenclature
- Physical and chemical properties
- Chemical reaction, mechanism
  - How and why

Topics

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Chlorinated Solvents

- Nomenclature
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  - How and why

Gasoline

Table 7. Major organic compounds in a typical gasoline blend.[1]

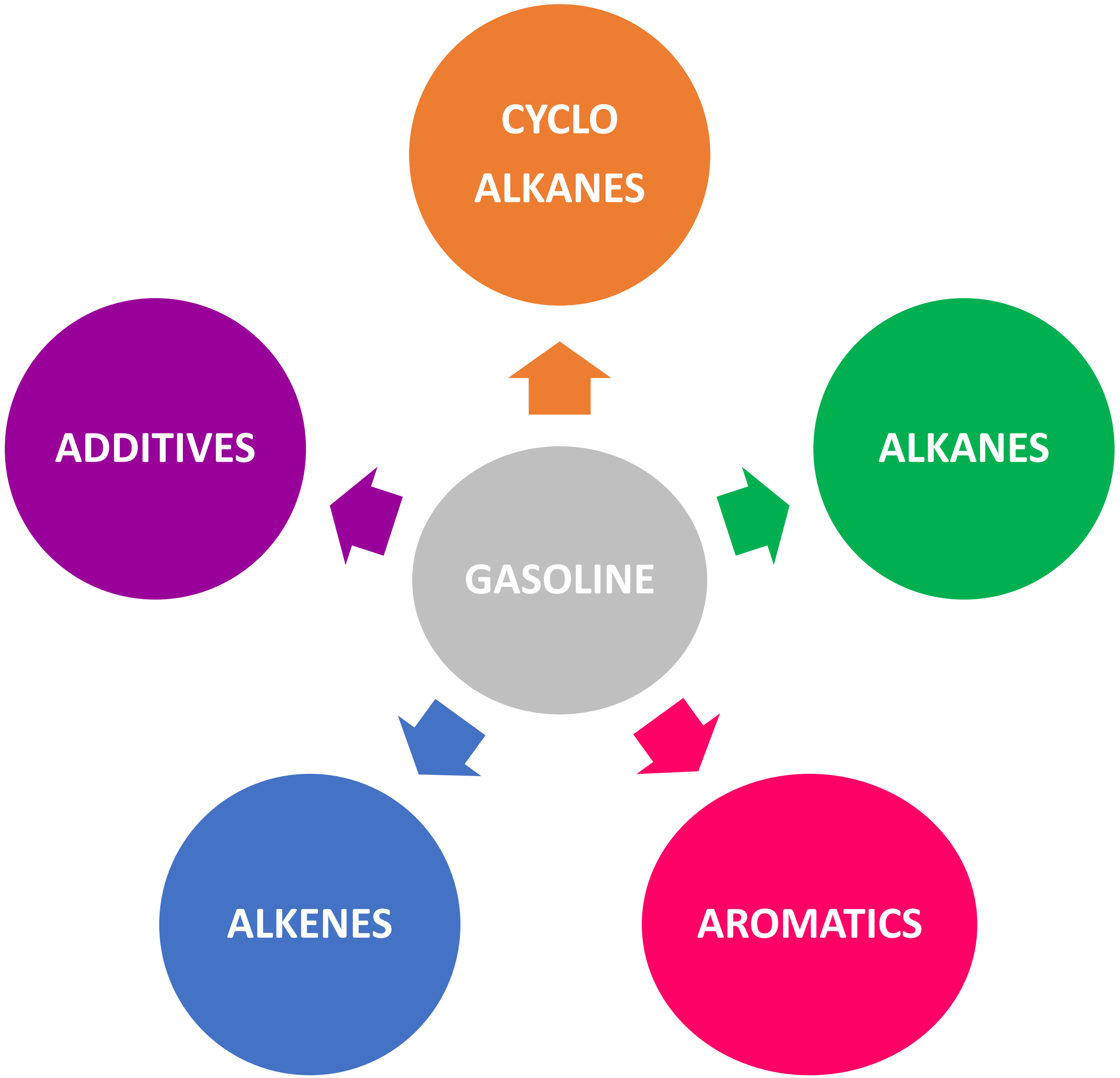
[n, C_5-C_{13} carbon chain; MTBE, methyl *tert*-butyl ether; TBA, *tert*-butyl alcohol]

Major compounds	Percent composition by weight
n-alkanes	17.3
Branched alkanes	32.0
Cycloalkanes	5.0
Olefins	1.8
Aromatic hydrocarbons	30.5
Benzene	3.2
Toluene	4.8
Ethylbenzene	1.4
Xylenes	6.6
Other benzenes	11.8
Other aromatics	2.7

Other possible additives

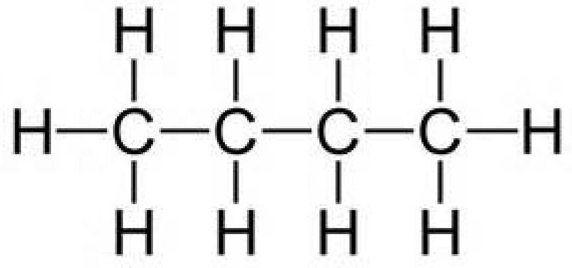
Octane enhancers: MTBE, TBA, ethanol
Antioxidants: N, N'-dialkylphenylenediamines, di- and tri-alkylphenols, butylated methyl, ethyl and dimethyl phenols
Metal deactivators: various N, N'-disalicylidene compounds
Ignition controllers: tri-o-cresylphosphate (TOCP)
Detergents/dispersants: alkylamine phosphates, poly-isobutene amines, long-chain alkyl phenols, alcohols, carboxylic acids, and amines
Corrosion inhibitors: phosphoric acids, sulfonic acids, carboxylic acids

[1]Harper and Liccione, 1995

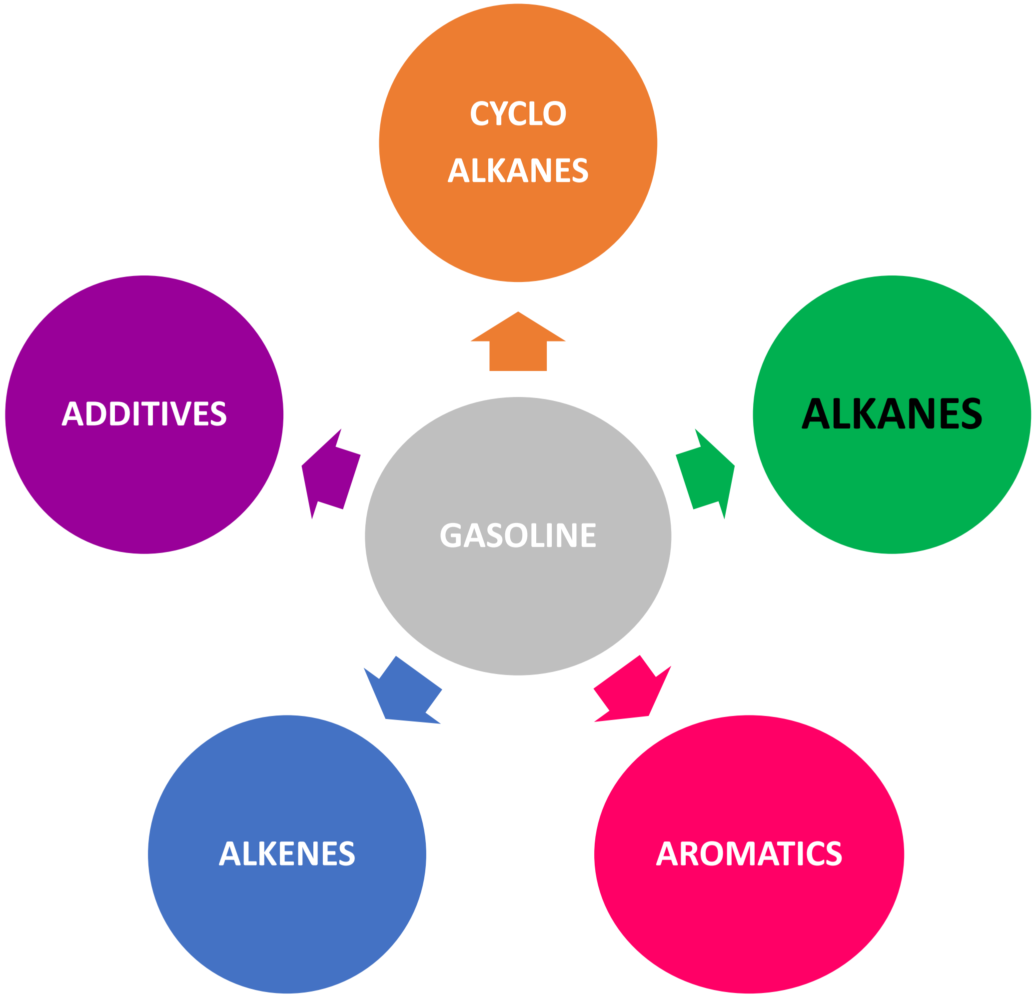


Gasoline

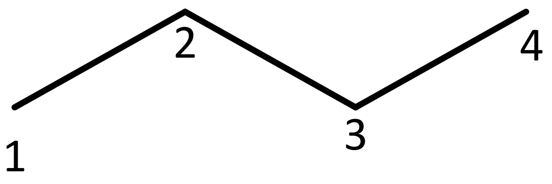
C_4H_{10} $CH_3CH_2CH_2CH_3$



Alkanes C_nH_{2n+2}



Prefix	Number of Carbon Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10



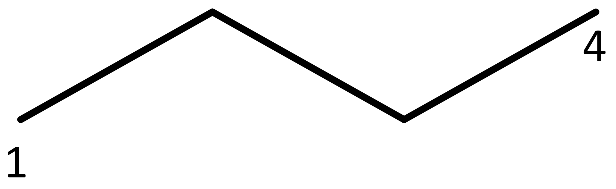
Butane

or

n-butane

Gasoline

Alkanes C_nH_{2n+2}



C_4H_{10} Butane

Prefix	Number of Carbon Atoms
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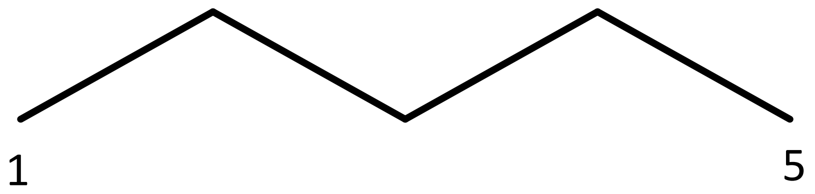
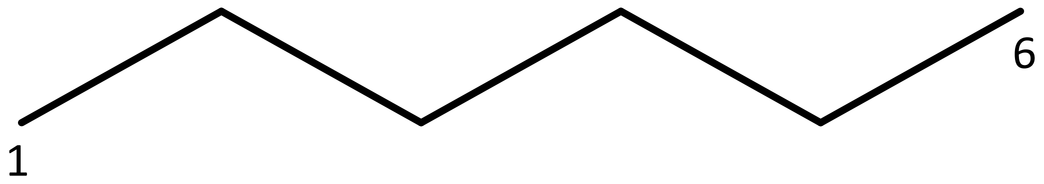
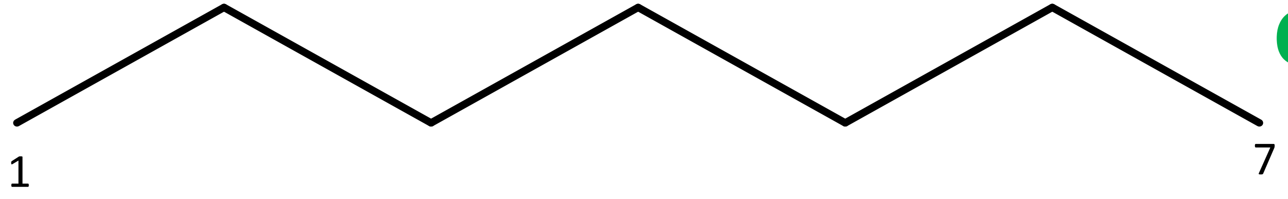


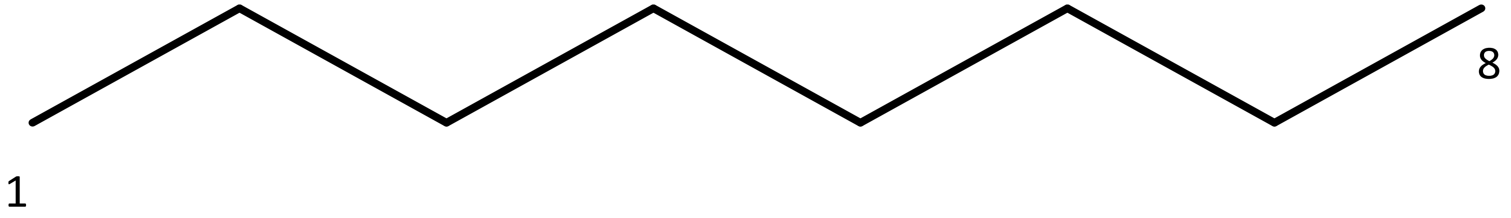
C_5H_{12} Pentane



C_6H_{14} Hexane



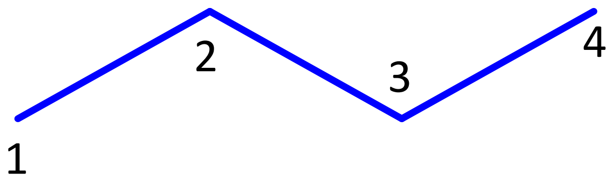
C_7H_{16} Heptane



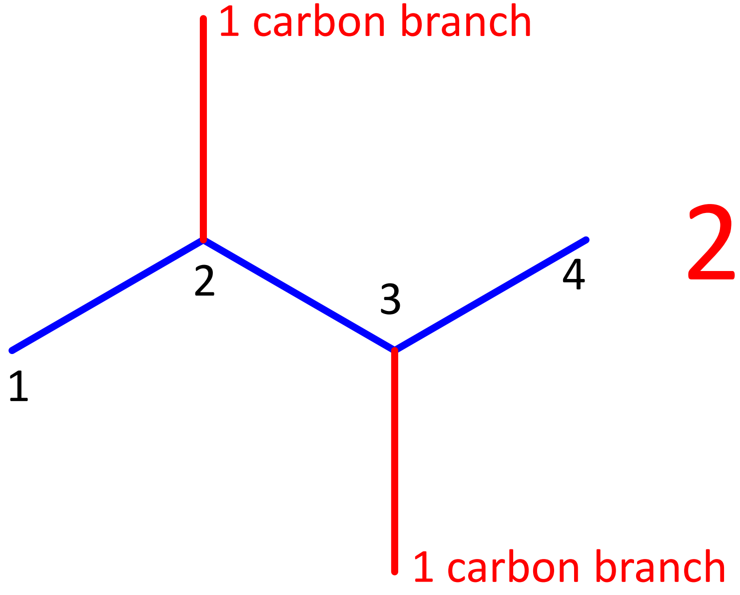
C_8H_{18} Octane

Gasoline

Branched Alkanes C_nH_{2n+2}



n-butane



2,3-dimethylbutane

branches

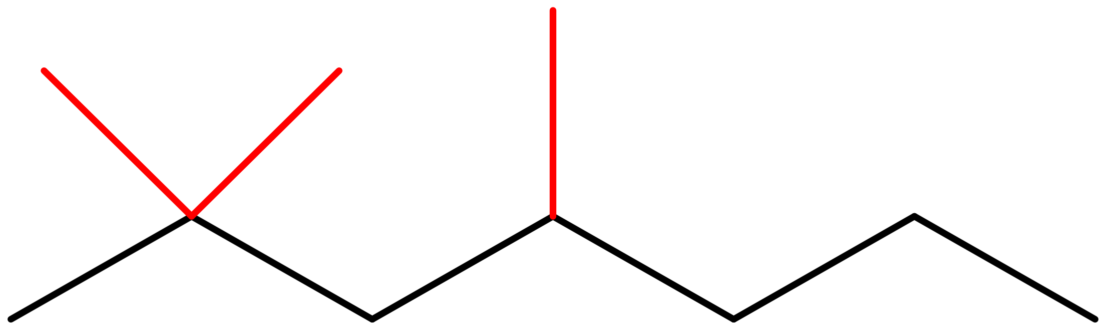
parent chain

Prefix	Number of Carbon Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Branches

Number	Prefix
1	mono-
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

Branched Alkanes C_nH_{2n+2}



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Branches

Number	Prefix
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2	di-
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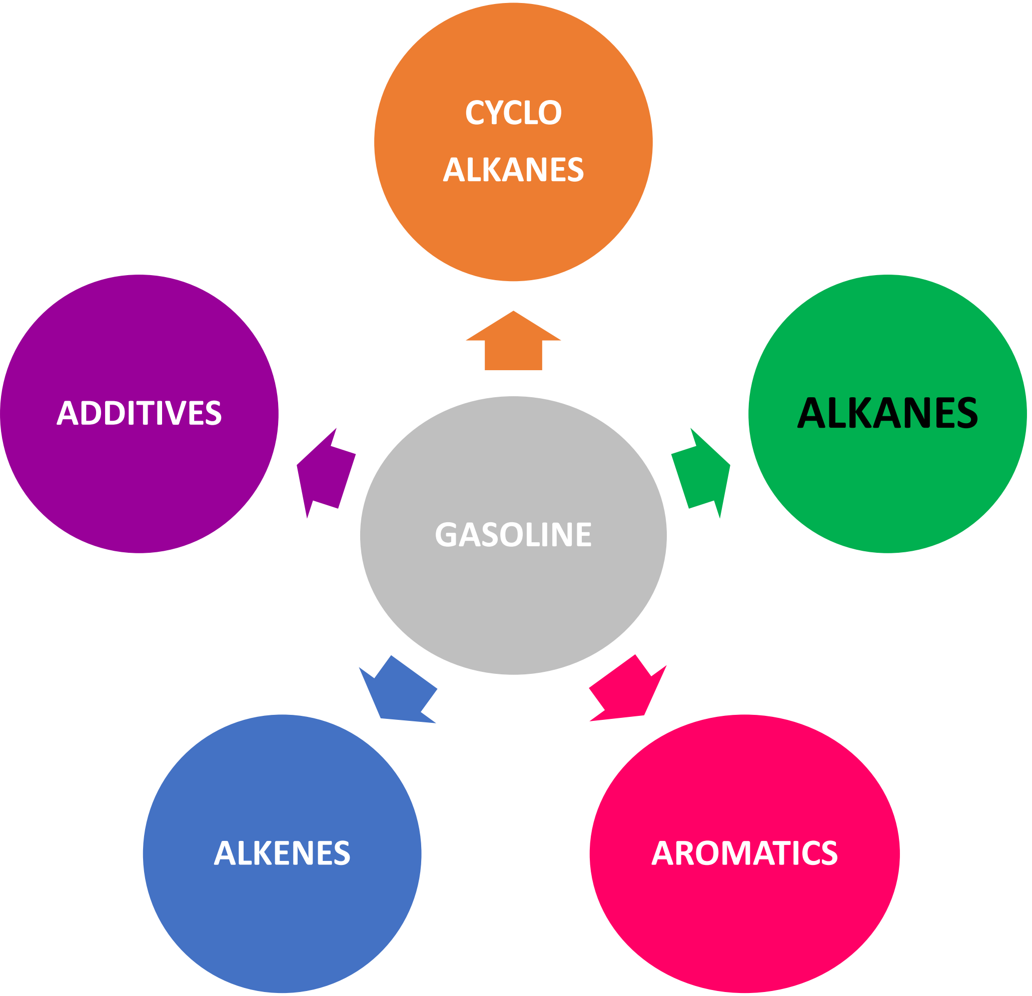
10	deca-

Alkanes



- Aliphatic (linear and/or branched) C_3-C_{13} are the most common
- C_3-C_8 have high vapor pressures (rapidly evaporate)
- C_3-C_8 are volatile by photochemical oxidation
  - Molecular oxygen (O_2) needs to be present
  - $CH_3CH_2CH_3 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
    ΔH = -2220kJ (negative value means release of E)
  - Why does this oxidation happen?
    - products are favored because they are more stable, lower in energy

Gasoline

Alkanes – Fresh vs. Weathered

TABLE 2

Composition (Mass Fractions) of Fresh and Weathered Gasolines

Compound Name	Mw (g)	Fresh Gasoline	Weathered Gasoline	Approximate Composition
propane	44.1	0.0001	0.0000	0
isobutane	58.1	0.0122	0.0000	0
n-butane	58.1	0.0629	0.0000	0
trans-2-butene	56.1	0.0007	0.0000	0
cis-2-butene	56.1	0.0000	0.0000	0
3-methyl-1-butene	70.1	0.0006	0.0000	0
isopentane	72.2	0.1049	0.0069	0.0177
1-pentene	70.1	0.0000	0.0005	0
2-methyl-1-butene	70.1	0.0000	0.0008	0
2-methyl-1,3-butadiene	68.1	0.0000	0.0000	0
n-pentane	72.2	0.0586	0.0095	0
trans-2-pentene	70.1	0.0000	0.0017	0
2-methyl-2-butene	70.1	0.0044	0.0021	0
2-methyl-1,2-butadiene	68.1	0.0000	0.0010	0
3,3-dimethyl-1-butene	84.2	0.0049	0.0000	0
cyclopentane	70.1	0.0000	0.0046	0.0738
3-methyl-1-pentene	84.2	0.0000	0.0000	0
2,3-dimethylbutane	86.2	0.0730	0.0044	0
2-methylpentane	86.2	0.0273	0.0207	0
3-methylpentane	86.2	0.0000	0.0186	0

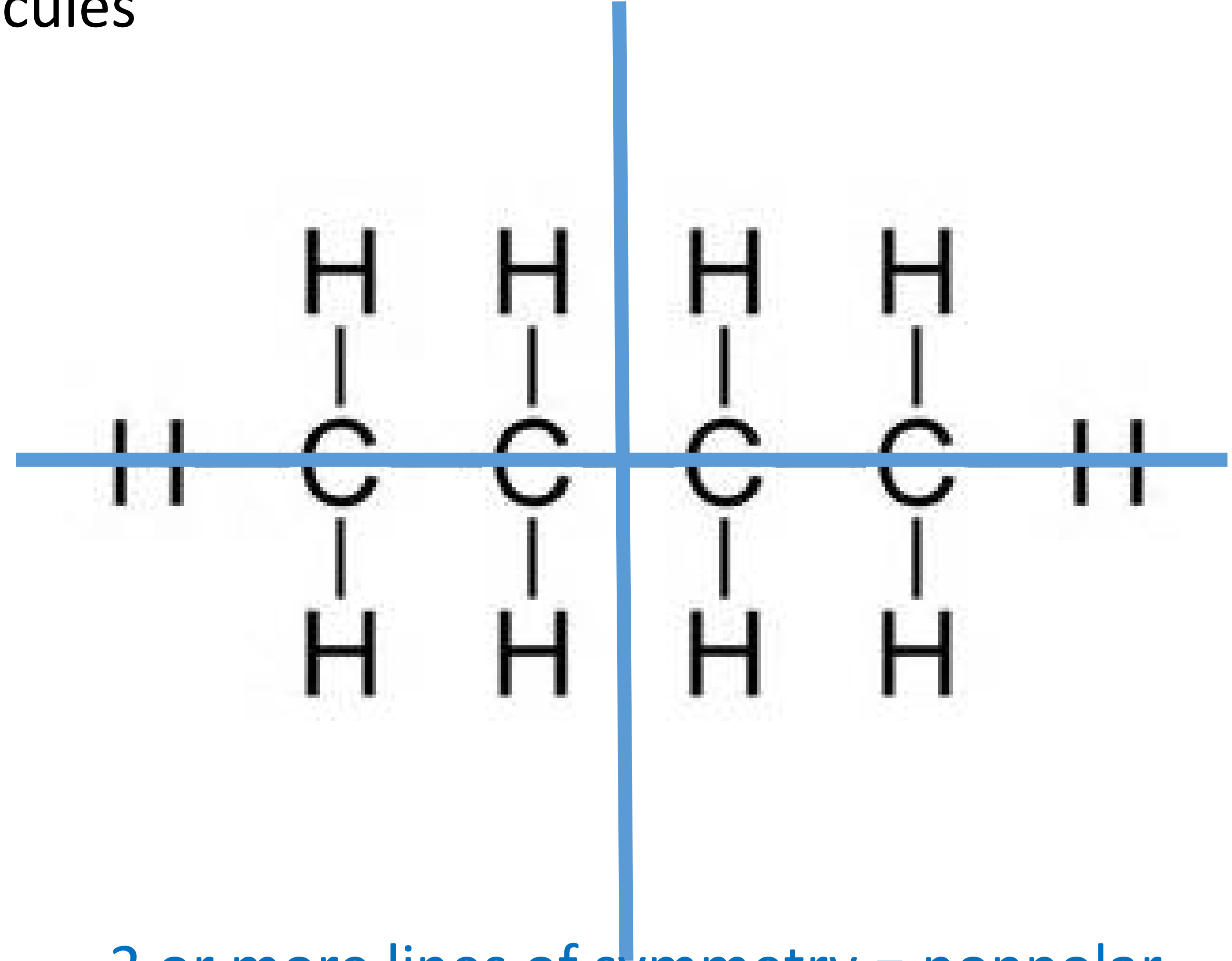
$CH_3CH_2CH_3 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad \Delta H = -2220kJ$

P.C.Johnson, C.C.Stanley, M.W. Kemblowksi, D.L.Byers, and J.D. Colthart
A Practical Approach to the Design, Operation, and Monitoring of In Situ Soil Venting Systems
Spring 1990 GWMR, pp. 159-178

Gasoline

Alkanes

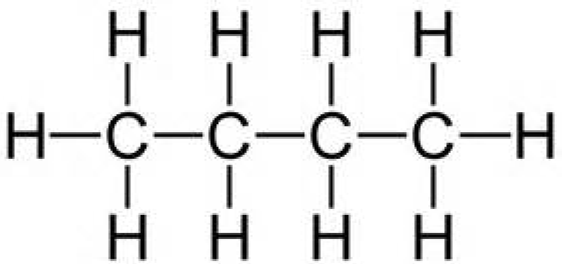
- Nonpolar molecules

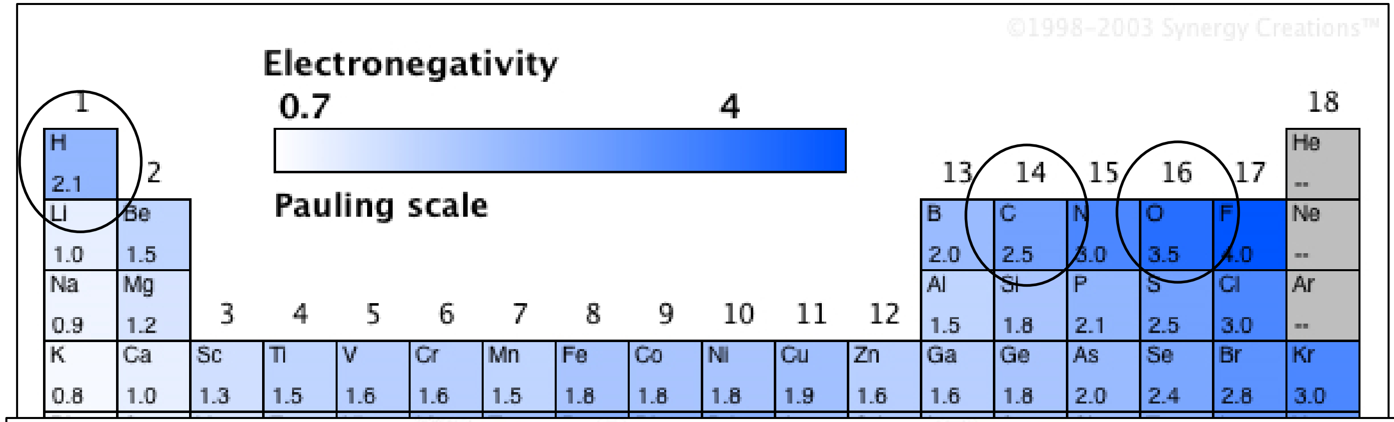


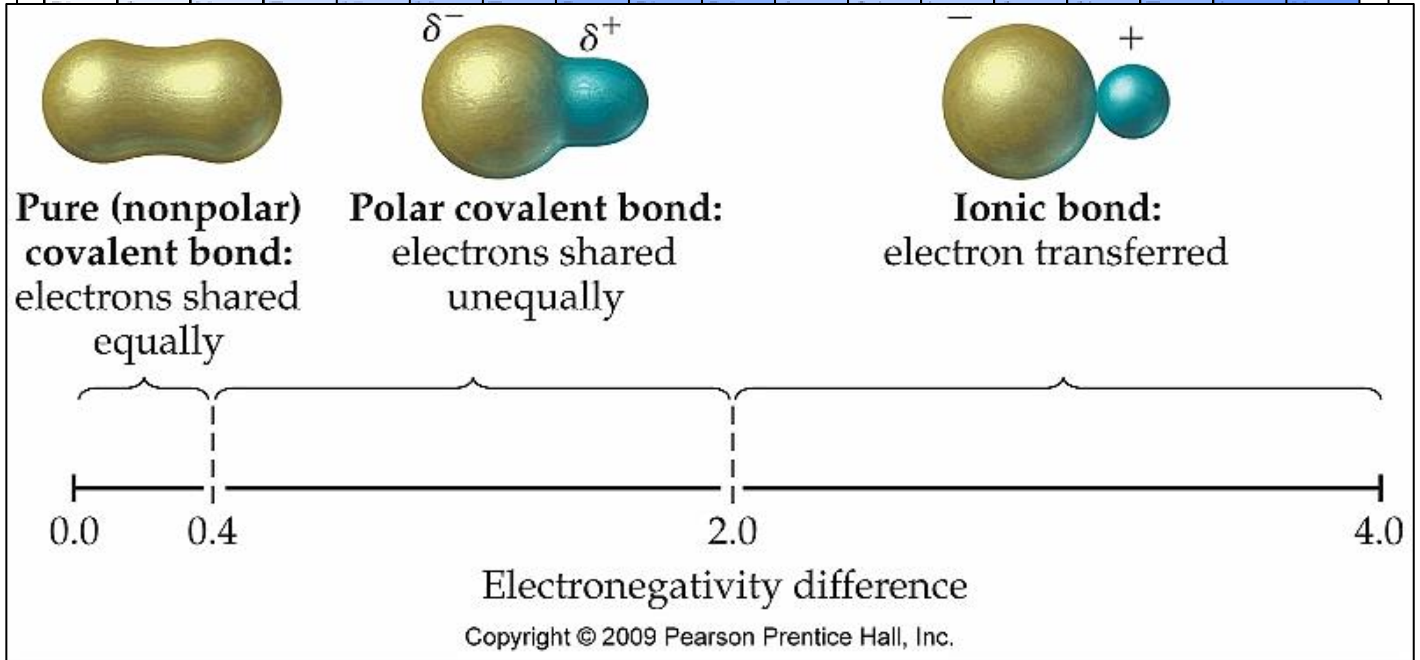
2 or more lines of symmetry = nonpolar

Alkanes

- Nonpolar molecules





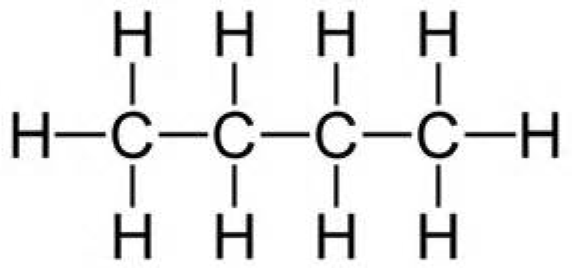


- Polar molecule

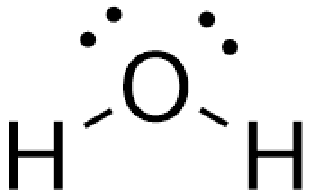
Gasoline

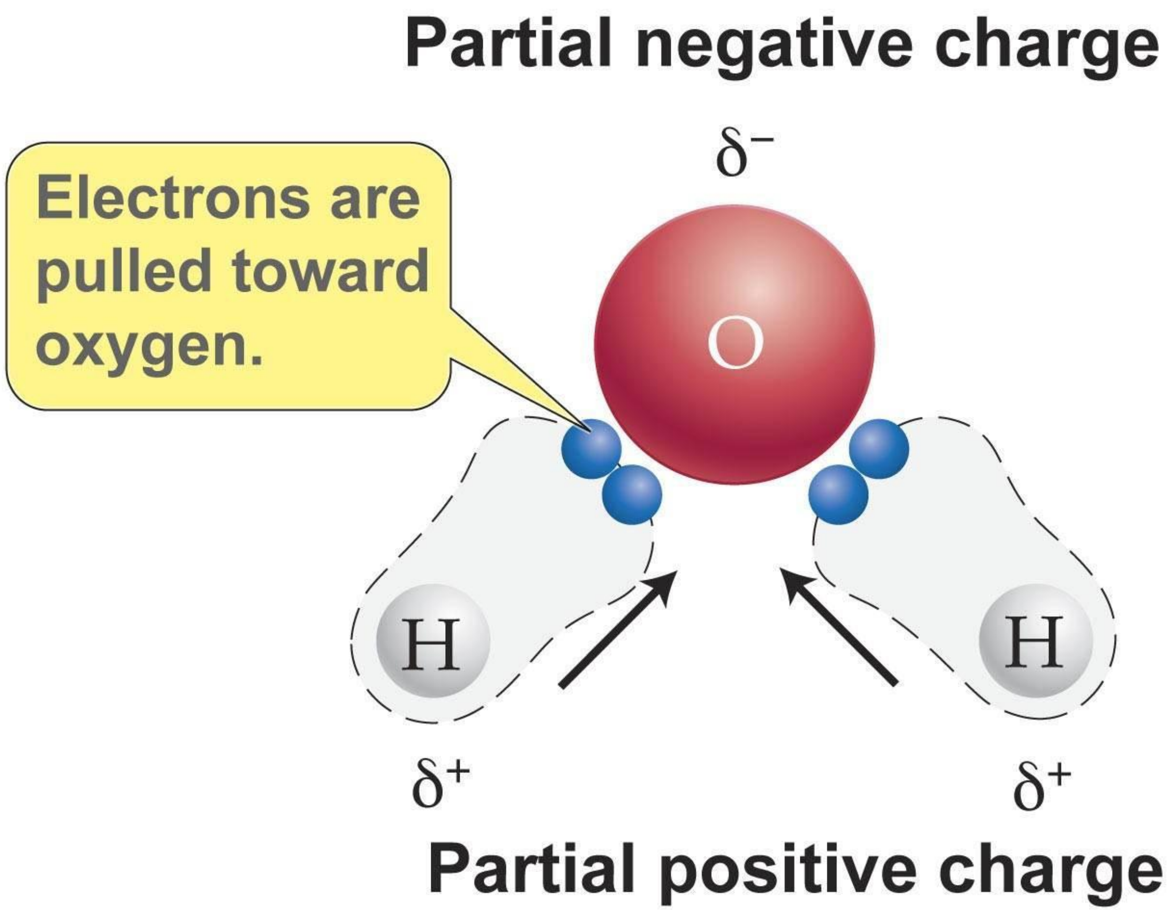
Alkanes

- Nonpolar molecules



- Polar molecule





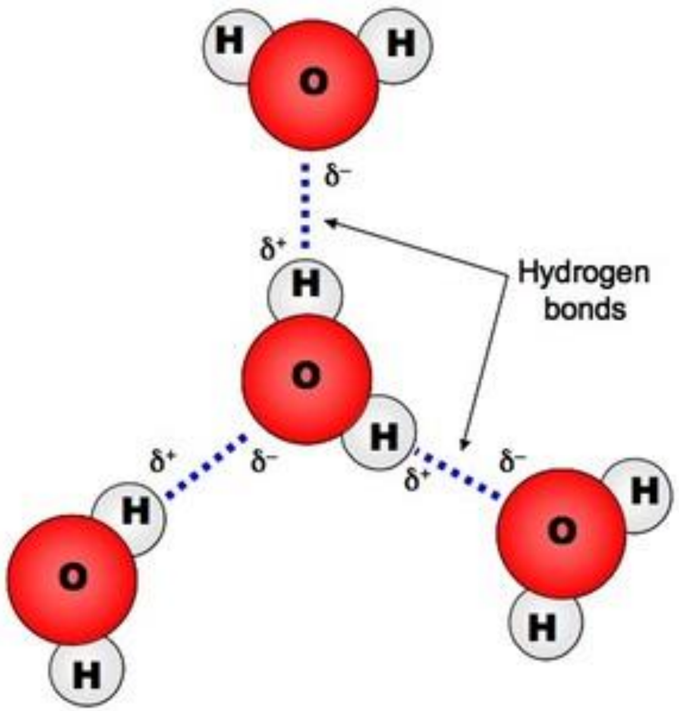
Alkanes

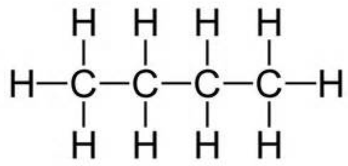
- C_3-C_8 have <u>low water solubility</u> due to being nonpolar molecules

"Like dissolves like"

Solvent	Solute	Is Solution Likely?
Polar	Polar	Yes
Polar H_2O	Nonpolar **Alkanes**	No
Nonpolar	Polar	No
Nonpolar	Nonpolar	Yes

THEY WON'T MIX…. BUT WHY?

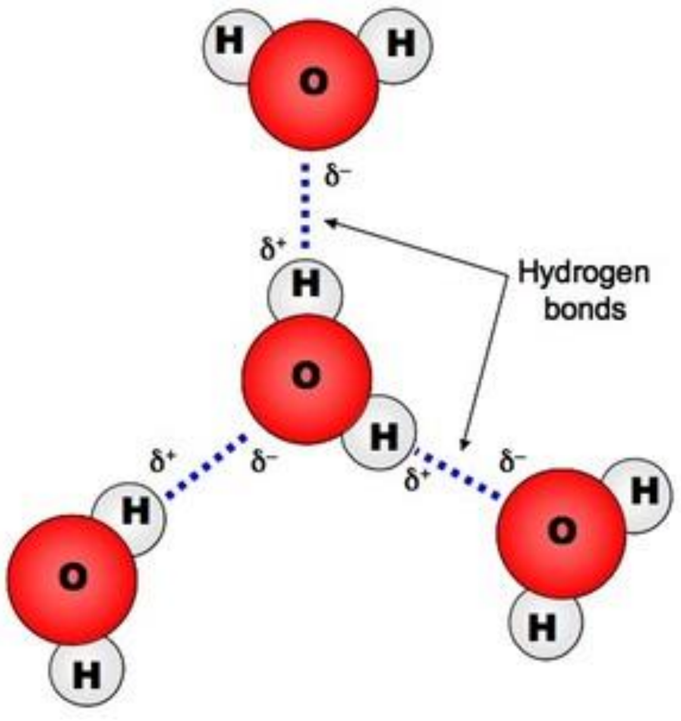


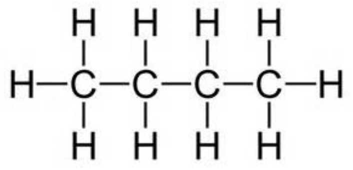


Alkanes

- C_3-C_8 have <u>low water solubility</u> due to being nonpolar molecules
- Why can't alkanes dissolve in water???

Intermolecular Forces		
Type	**Strength**	**Present in:**
London Dispersion	Weak	all molecules and atoms
Dipole-Dipole	Moderate	polar molecules
Hydrogen bonds	Strong	H-F, H-N, H-O molecules





Alkanes can't break the intermolecular forces in the water so that the alkanes can fit between the water molecules.

Alkanes

- Higher molecular weight hydrocarbons <u>absorb into the soil</u>

"Like dissolves like"

Solvent	Solute	Is Solution Likely?
Polar	Polar	Yes
Polar	Nonpolar	No
Nonpolar	Polar	No
Nonpolar **Soil**	Nonpolar **High MW alkanes**	Yes

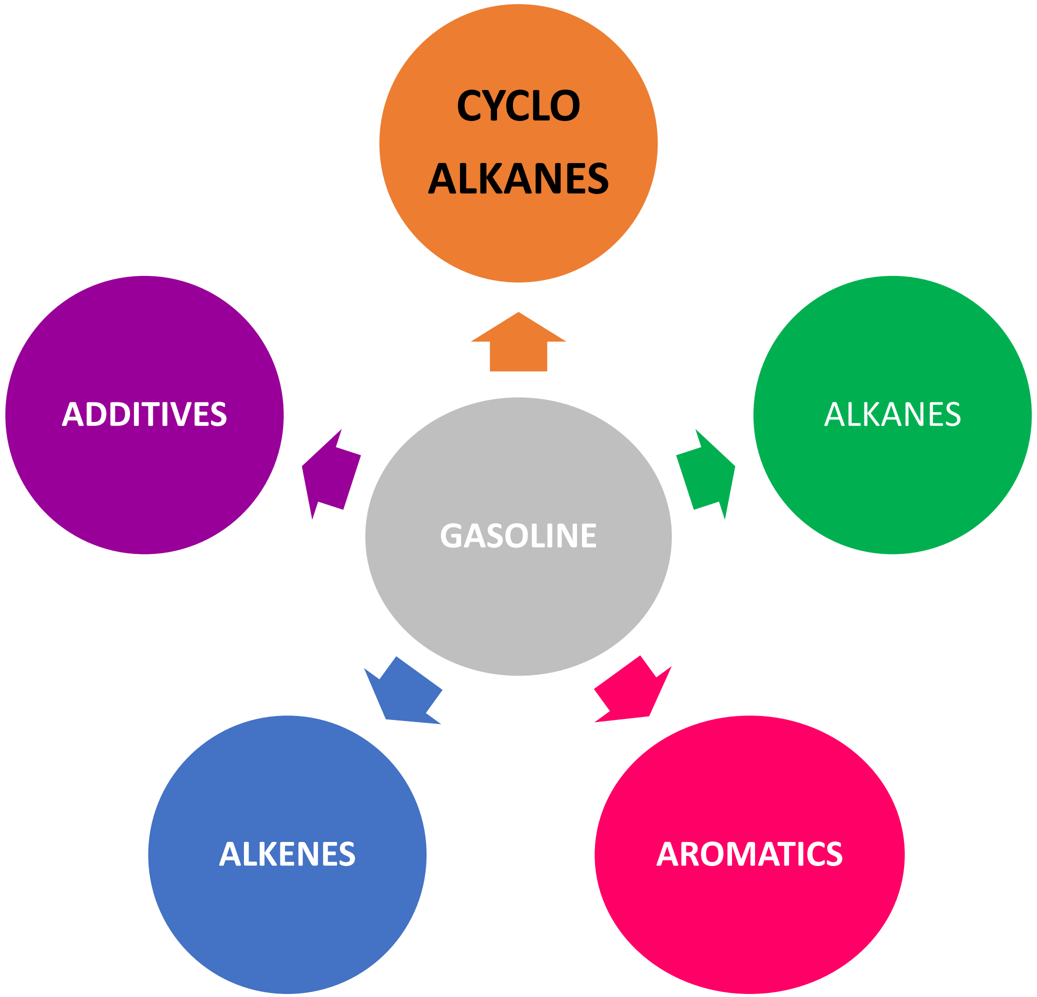
Alkanes

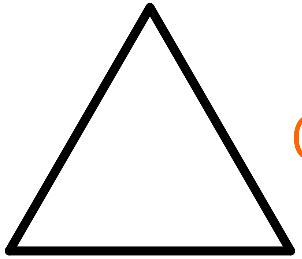
- What is present in the soil?
  - Microorganisms (bacteria, yeasts, fungi, etc.) love linear alkanes (C_{10}-C_{22})
    - Ideal pH, temperature, O_2 levels, salinity

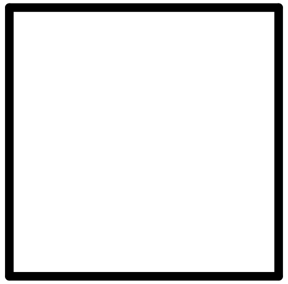
Bioremediation

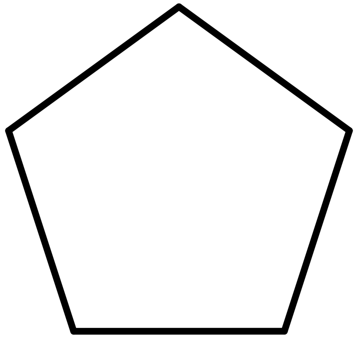
Gasoline

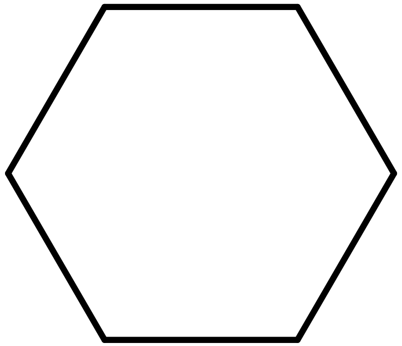
Cycloalkanes




Cyclopropane


Cyclobutane

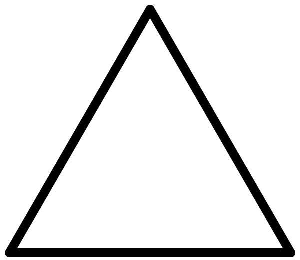

Cyclopentane

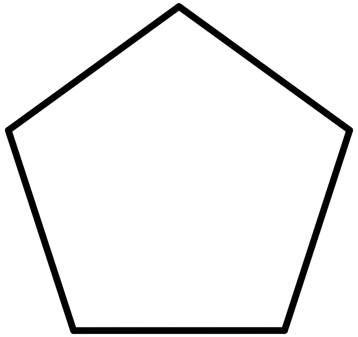

Cyclohexane

Prefix	Number of Carbon Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Cycloalkanes

- Cycloalkanes are very similar to the alkanes in reactivity, except for the very small ones - especially cyclopropane.
  - The reason has to do with the bond angles in the ring. Normally, when carbon forms four single bonds, the bond angles are about 109.5°. In cyclopropane, they are 60°.



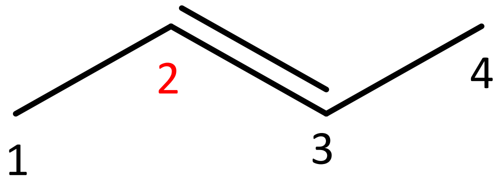


- Cycloalkanes are also nonpolar and do not have intermolecular hydrogen bonding; they are usually hydrophobic (meaning they do not dissolve in water) and are less dense than water.

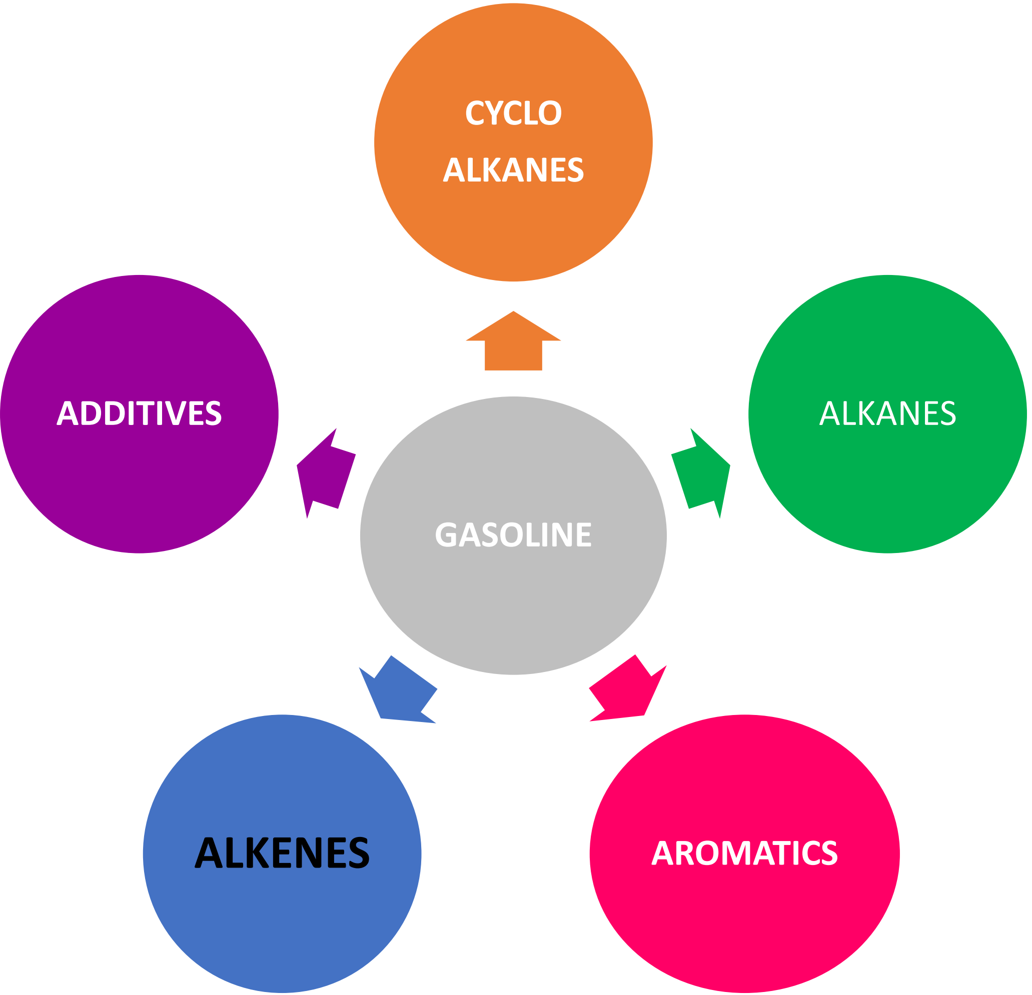
Gasoline

Alkenes C_nH_{2n}

C_4H_8 $CH_3CH{=}CHCH_3$



2-butene



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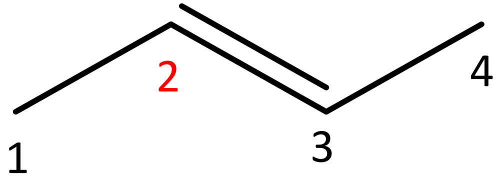
Gasoline

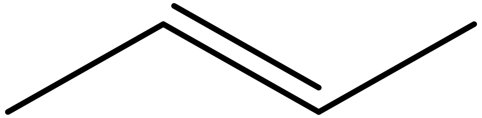
Alkenes C_nH_{2n}

C_4H_8

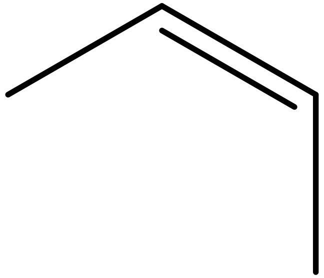
$CH_3CH=CHCH_3$



2-butene



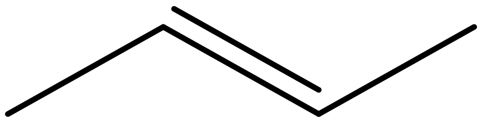
2-butene



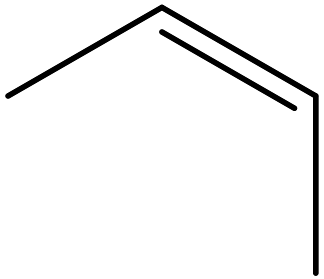
2-butene

Alkenes

- Cis vs. Trans alkenes



Trans-2-butene



Cis-2-butene

Gasoline

Alkenes C_nH_{2n}

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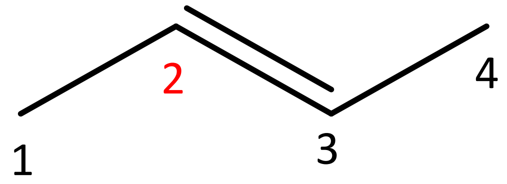
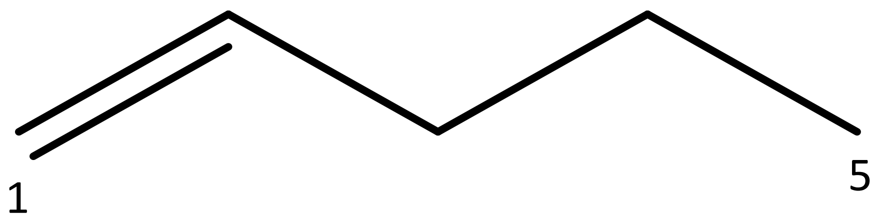
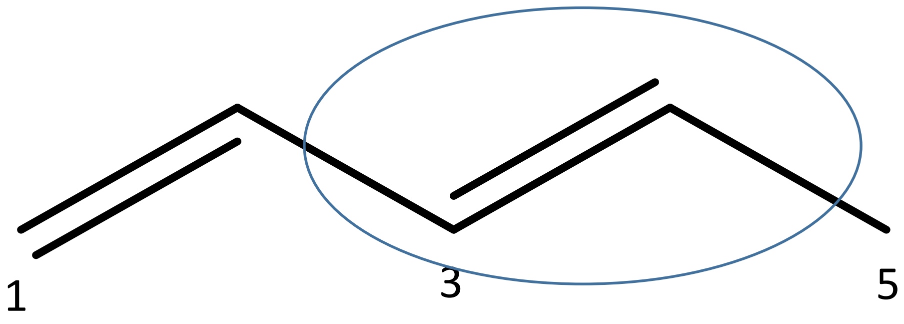


2-butene



1-pentene



1,3-pentadiene

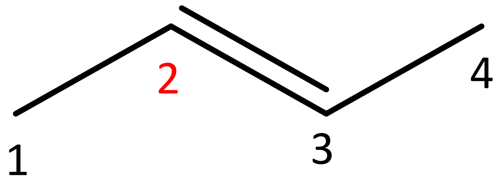
Prefix	Number of Carbon Atoms
meth-	1

Number	Prefix
1	mono-
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

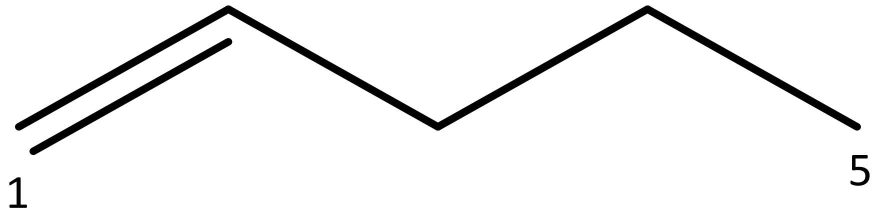
Gasoline

Alkenes C_nH_{2n}

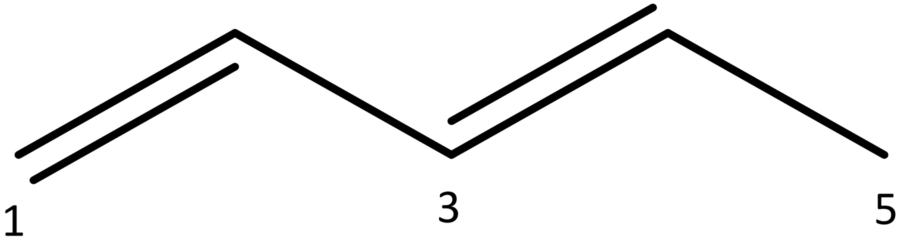
C_4H_8 $CH_3CH=CHCH_3$



2-butene

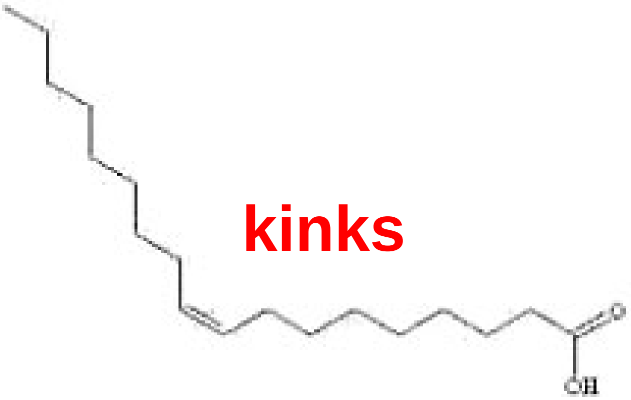


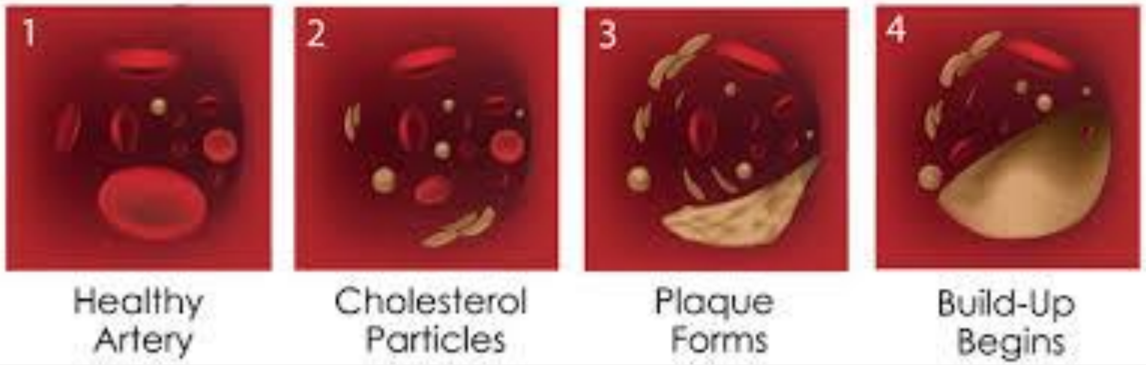
1-pentene



1-trans-3-pentadiene

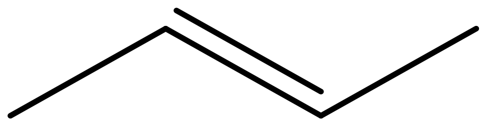
Fatty Acids

Type	Structure	Source
Saturated fatty acid		Animal fat
Unsaturated fatty acid (*cis* double bond)	 kinks	Olive oil
Unsaturated fatty acid (*trans* double bond)	stacks 	Partially hydrogenated oils



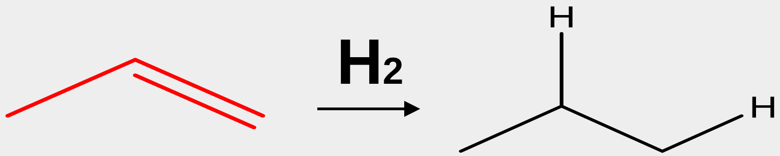
Alkenes

- Sometimes called olefins
- Most alkenes like to absorb into the soil
  - Nonpolar compounds

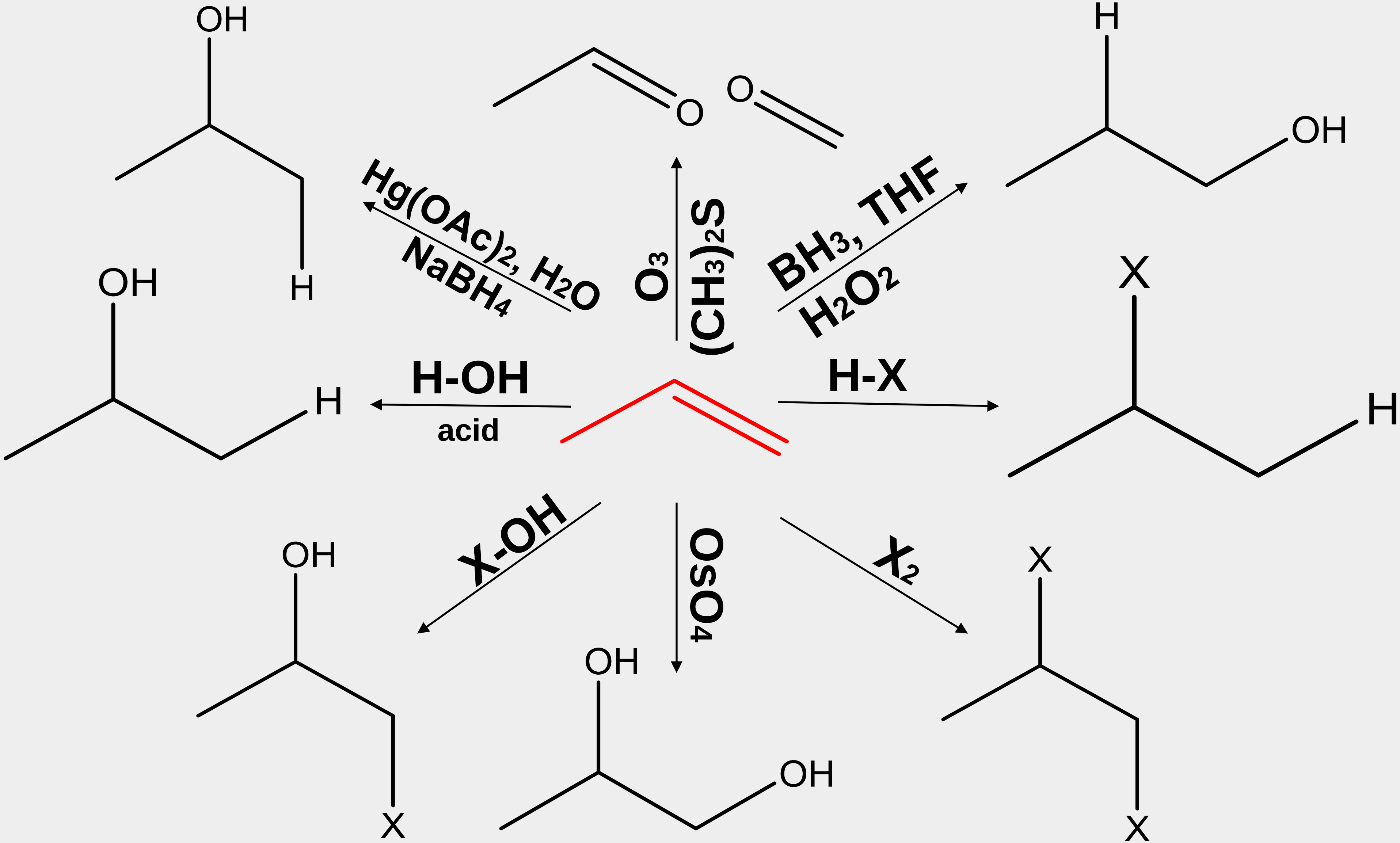


"Like dissolves like"

Solvent	Solute	Is Solution Likely?
Polar	Polar	Yes
Polar	Nonpolar	No
Nonpolar	Polar	No
Nonpolar Soil	Nonpolar alkenes	Yes

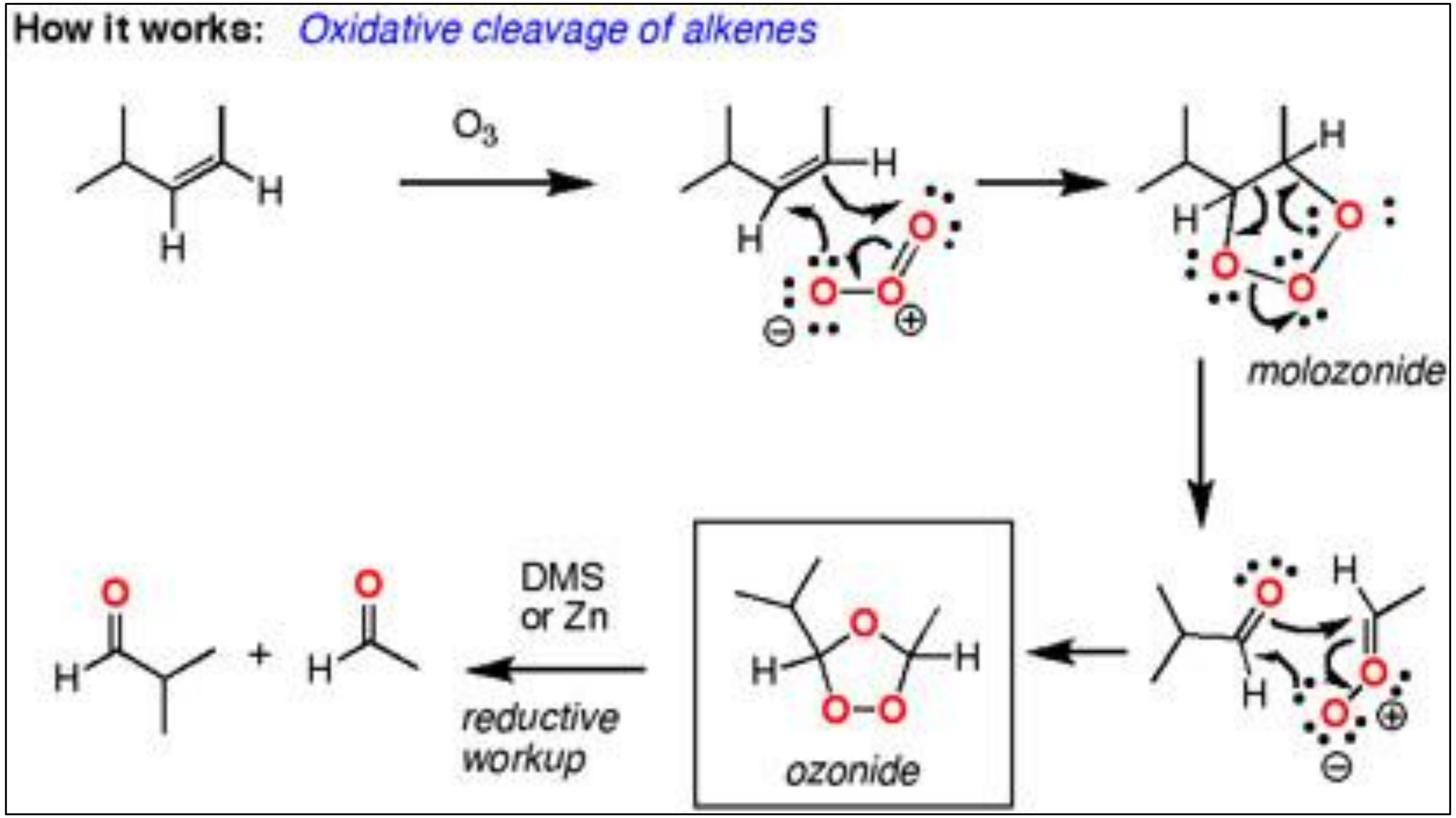


The double bond is very reactive!!!



Alkenes

- Small MW alkenes are oxidized by O_3 (ozonolysis - fast reaction)



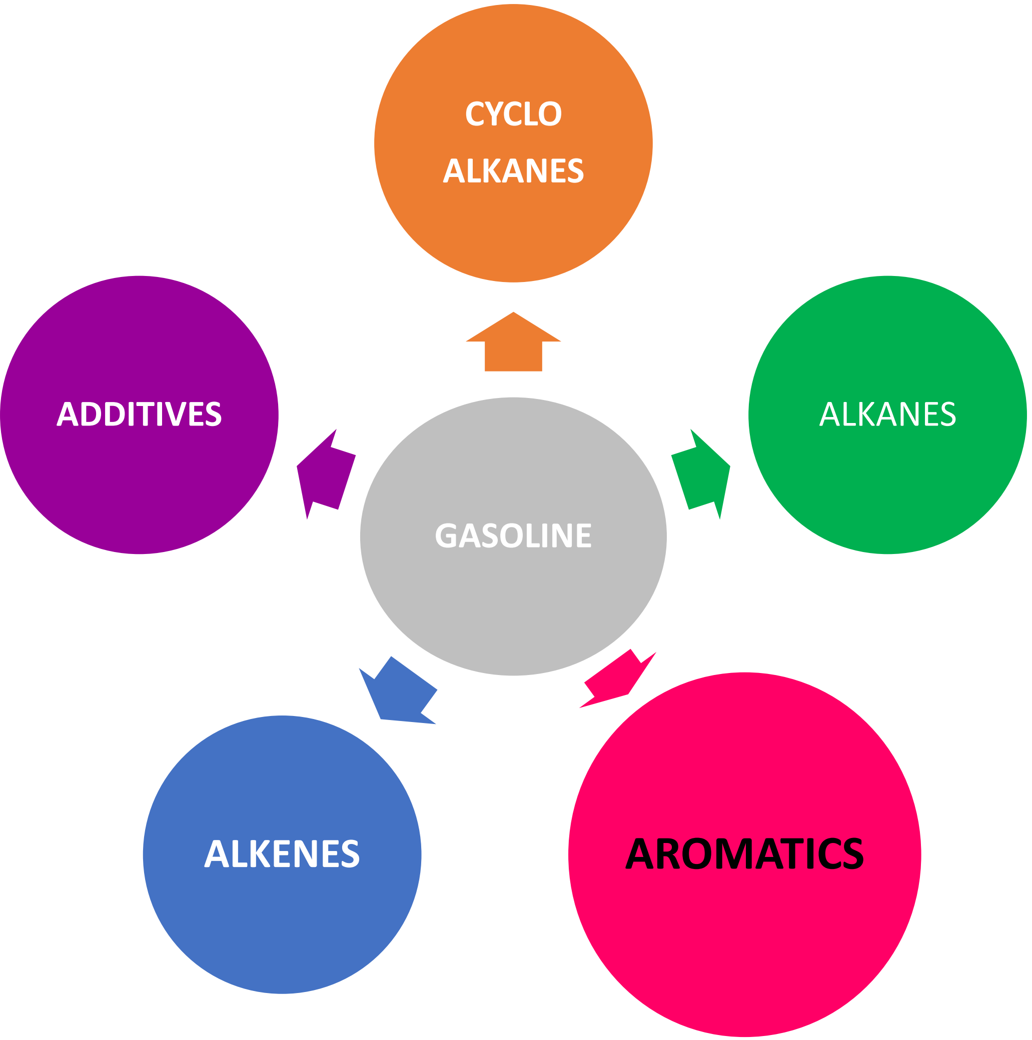
Alkenes

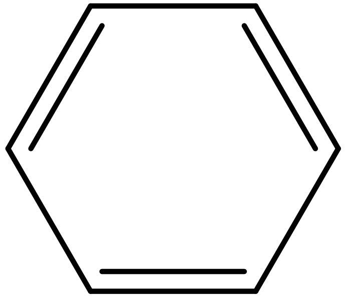
TABLE 2
Composition (Mass Fractions) of Fresh and Weathered Gasolines

Compound Name	Mw (g)	Fresh Gasoline	Weathered Gasoline	Approximate Composition
propane	44.1	0.0001	0.0000	0
isobutane	58.1	0.0122	0.0000	0
n-butane	58.1	0.0629	0.0000	0
trans-2-butene	56.1	0.0007	0.0000	0
cis-2-butene	56.1	0.0000	0.0000	0
3-methyl-1-butene	70.1	0.0006	0.0000	0
isopentane	72.2	0.1049	0.0069	0.0177
1-pentene	70.1	0.0000	0.0005	0
2-methyl-1-butene	70.1	0.0000	0.0008	0
2-methyl-1,3-butadiene	68.1	0.0000	0.0000	0
n-pentane	72.2	0.0586	0.0095	0
trans-2-pentene	70.1	0.0000	0.0017	0
2-methyl-2-butene	70.1	0.0044	0.0021	0
2-methyl-1,2-butadiene	68.1	0.0000	0.0010	0
3,3-dimethyl-1-butene	84.2	0.0049	0.0000	0
cyclopentane	70.1	0.0000	0.0046	0.0738
3-methyl-1-pentene	84.2	0.0000	0.0000	0
2,3-dimethylbutane	86.2	0.0730	0.0044	0
2-methylpentane	86.2	0.0273	0.0207	0
3-methylpentane	86.2	0.0000	0.0186	0

Gasoline

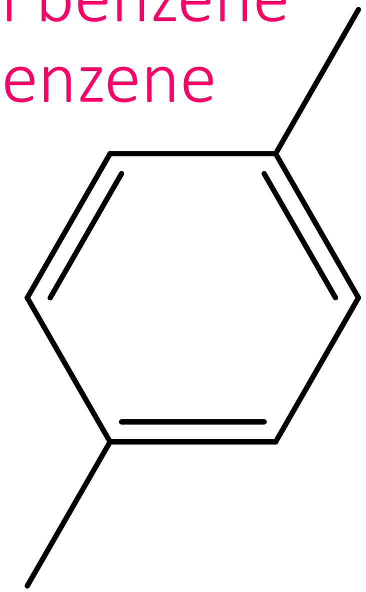
Aromatics



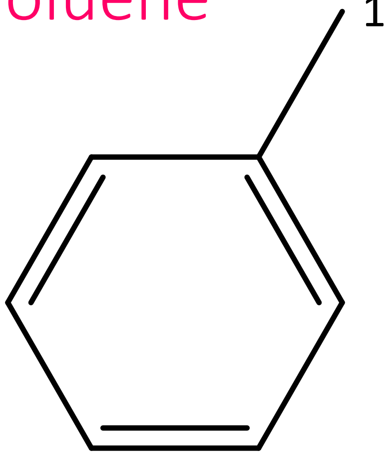


Benzene

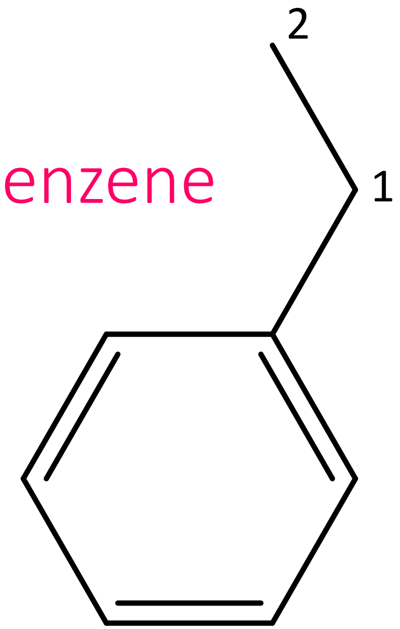
1,4-dimethyl benzene
p-dimethylbenzene
Xylene



Methyl benzene
Toluene



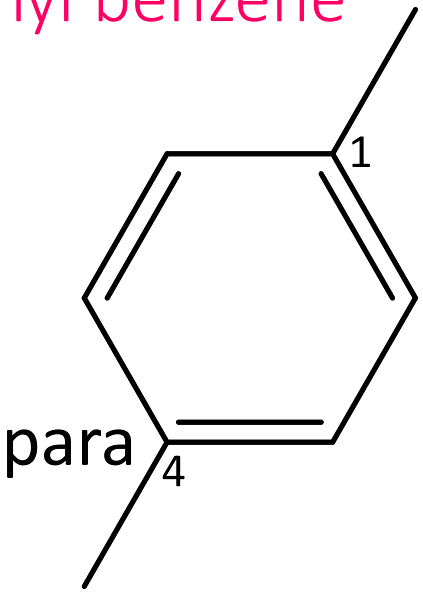
Ethyl benzene

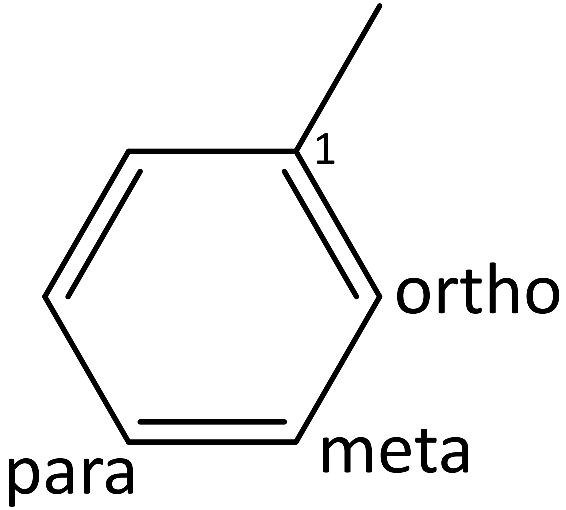


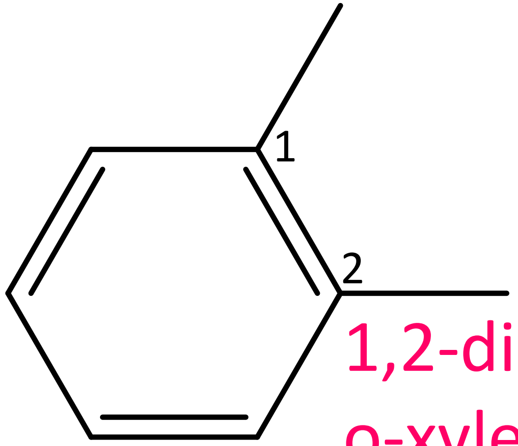
Gasoline

Aromatics

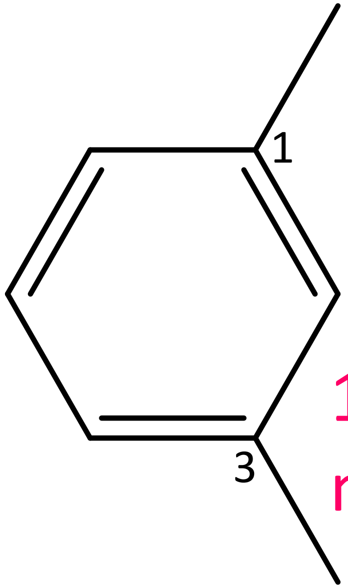
1,4-dimethyl benzene
Xylene
p-xylene







1,2-dimethylbenzene
o-xylene

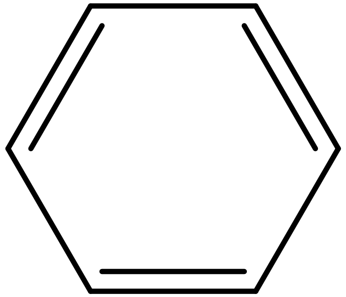


1,3-dimethylbenzene
m-xylene

Gasoline

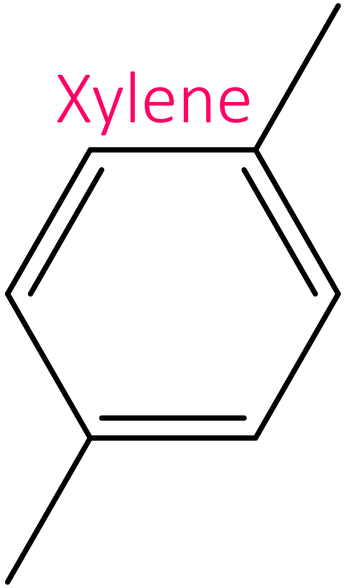
Aromatics

- Water soluble fractions (nonpolar, less dense than water = float)
- BTEX - Benzene, toluene, ethylbenzene, xylene are mostly associated with health issues

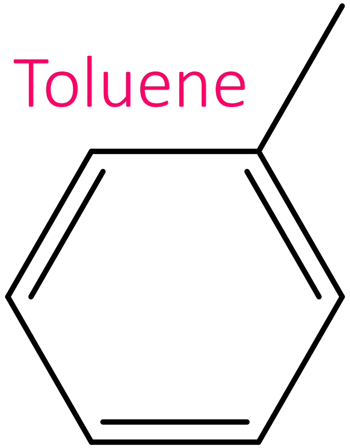


Benzene

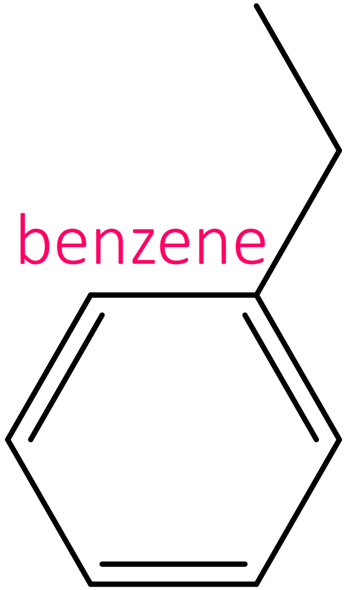
Xylene



Toluene



Ethyl benzene



Gasoline

Low water solubility: less than 10 mg/L or 10 ppm
Moderate water solubility: 10-1,000 mg/L or 10-1,000 ppm
High water solubility: more than 1,000 mg/L or 1,000 ppm

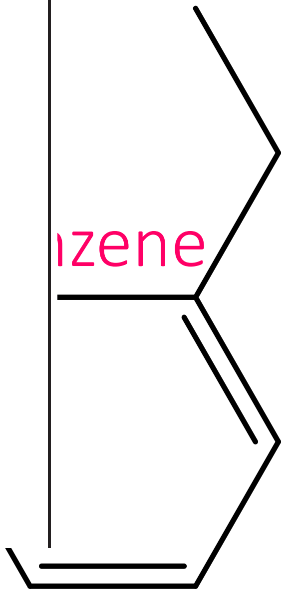
Xylene

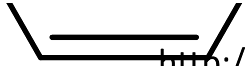
Ar

IUPAC name[1]	Common or alternative name[2]	Water solubility[3] (mg/L at 25°C)
benzene	—	1,780
1,1,1-trichloroethane	methyl chloroform	1,290
1,1,2-trichloroethene	1, 1, 2-trichloroethylene, TCE	1,280
tetrachloromethane	carbon tetrachloride	1,200
methylbenzene	toluene	531
chlorobenzene	—	495
stryrene	vinyl benzene	321
tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE	210
1,2-dimethylbenzene	*o*-xylene	207
1,4-dimethylbenzene	*p*-xylene	181
1,3-dimethylbenzene	*m*-xylene	161

- Water s (nonpol water =
- BTEX - E ethylbe mostly a issues

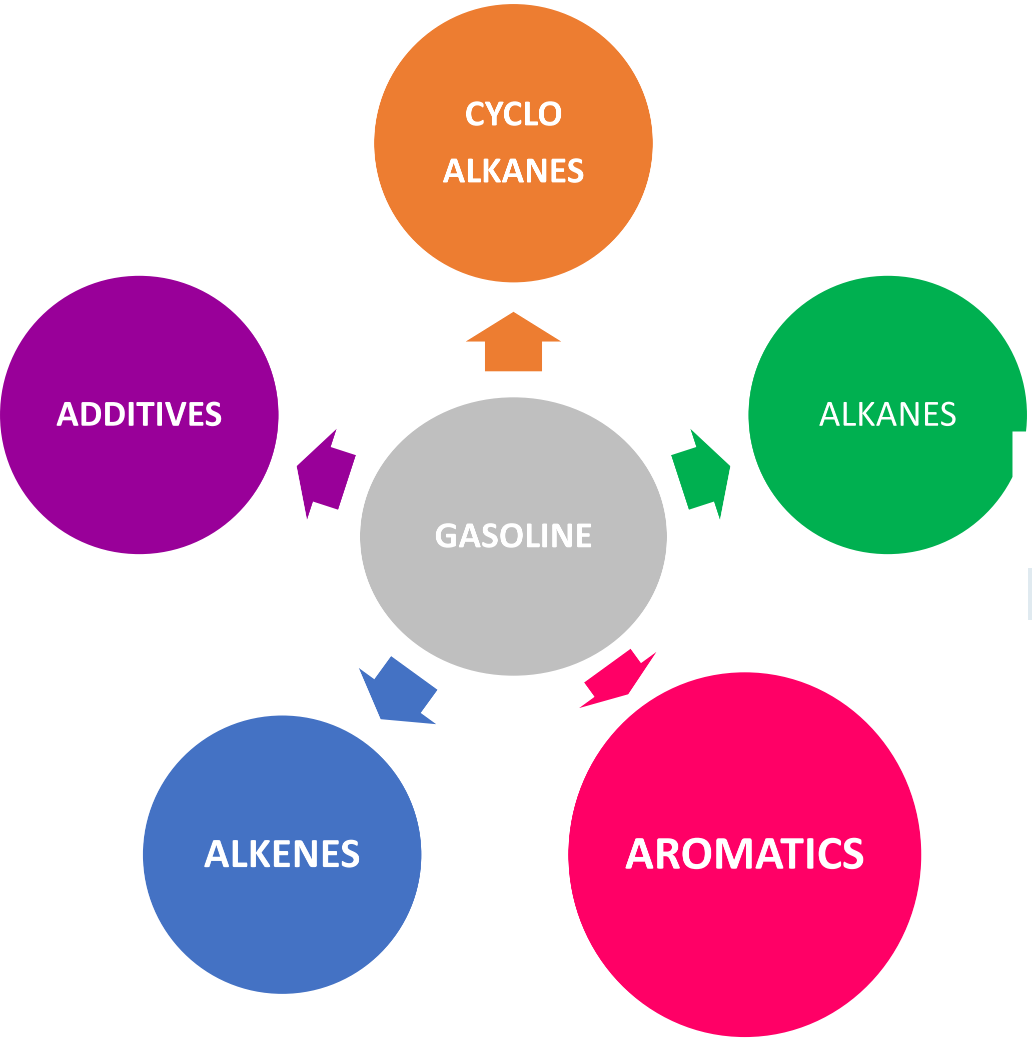
nzene

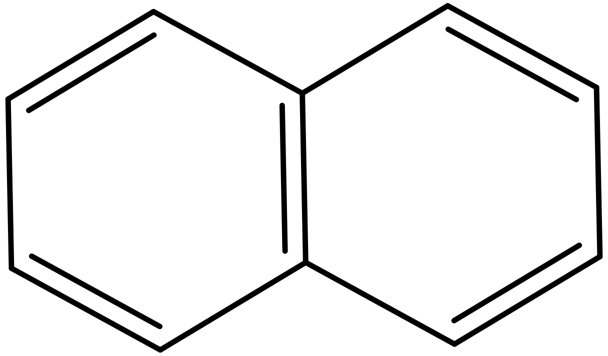




http://pubs.usgs.gov/of/2006/1338/pdf/ofr2006-1338.pdf

Polynuclear Aromatic Hydrocarbons (PAHs)





Naphthalene

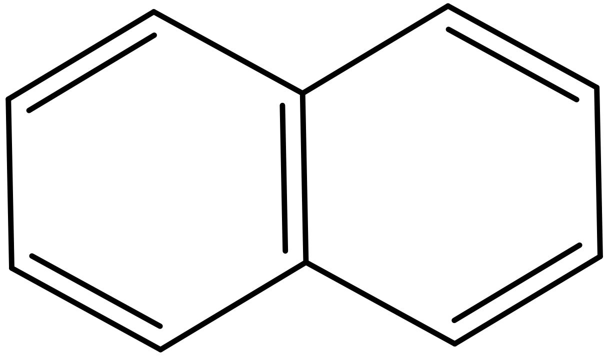
IUPAC name[1]	Common or alternative name[2]	Water solubility[3] (mg/L at 25°C)
naphthalene	naphthene	[6]31.0

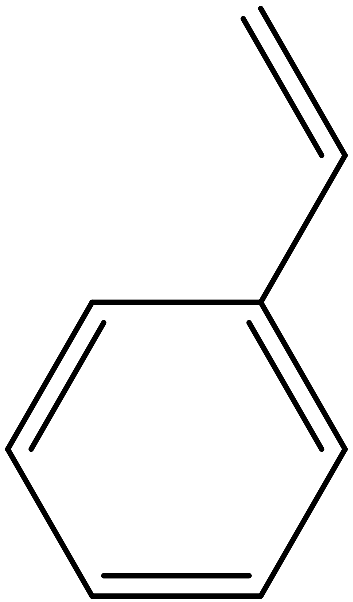
Low water solubility: less than 10 mg/L or 10 ppm
Moderate water solubility: 10-1,000 mg/L or 10-1,000 ppm
High water solubility: more than 1,000 mg/L or 1,000 ppm

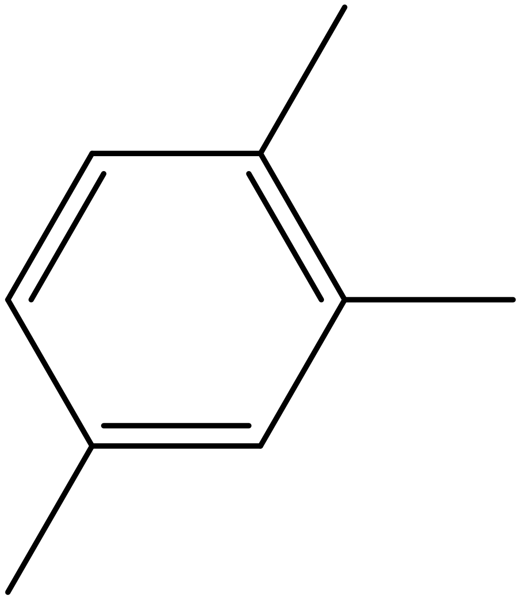
http://pubs.usgs.gov/of/2006/1338/pdf/ofr2006-1338.pdf

Aromatics

- Higher molecular weight components partition to sediments.
  - Naphthalene
  - Vinyl benzene (styrene)
  - 1,2,4-trimethylbenzene



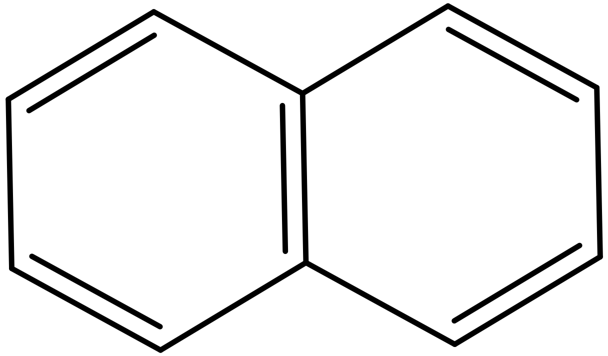




Gasoline

Aromatics

- Higher molecular weight com
  - Naphthalene
  - Vinyl benzene (styrene)
  - 1,2,4-trimethylbenzene



IUPAC name[1]	Common or alternative name[2]	Soil-sorption coefficient (Log K_{oc} in soil)
1,2,4-trimethylbenzene	pseudocumene	[3]3.34
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	[4]3.18–[3]3.42
naphthalene	naphthene	[3]2.98
1,2,4-trichlorobenzene	1,2,4-trichlorobenzol	[5]2.94
vinyl benzene	styrene	[2]2.72–2.74
1,2-dichlorobenzene	o-dichlorobenzene	[6]2.46–[5]2.51
tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE	[7]2.37
ethylbenzene	—	[5]2.22
1,1-dichloroethene	1,1-dichloroethylene, DCE	[2]2.18
1,3-dimethylbenzene	*m*-xylene	[7]2.11–2.46
1,1,1-trichloroethane	methyl chloroform	[8]2.03
1,1,2-trichloroethene	1,1,2-trichloroethylene, TCE	[7]2.00
chlorobenzene	monochlorobenzene	[5]1.91
1,1,2-trichloroethane	methyl chloroform	[7]1.78–2.03
tetrachloromethane	carbon tetrachloride	[9]1.78
methylbenzene	toluene	[7]1.75–[10]2.28
chloroethene	vinyl chloride, chloroethylene	[2]1.75
1,2-, 1,4-dimethylbenzene	*o*-xylene, *p*-xylene	[2]1.68–1.83
chloroethane	ethyl chloride	[4]1.62
cis-1,2-dichloroethene	*cis*-1,2-dichloroethylene	[2]1.56–1.69
1,2-dichloroethane	1,2-ethylidene dichloride, glycol dichloride	[6]1.52
trans-1,2-dichloroethene	*trans*-1,2-dichloroethylene	[2]1.56–1.69
1,1-dichloroethane	1,1-ethylidene dichloride	[12]1.52
benzene	—	[5]1.49–[7]1.73
methyl *tert*-butyl ether	MTBE	[11]1.09

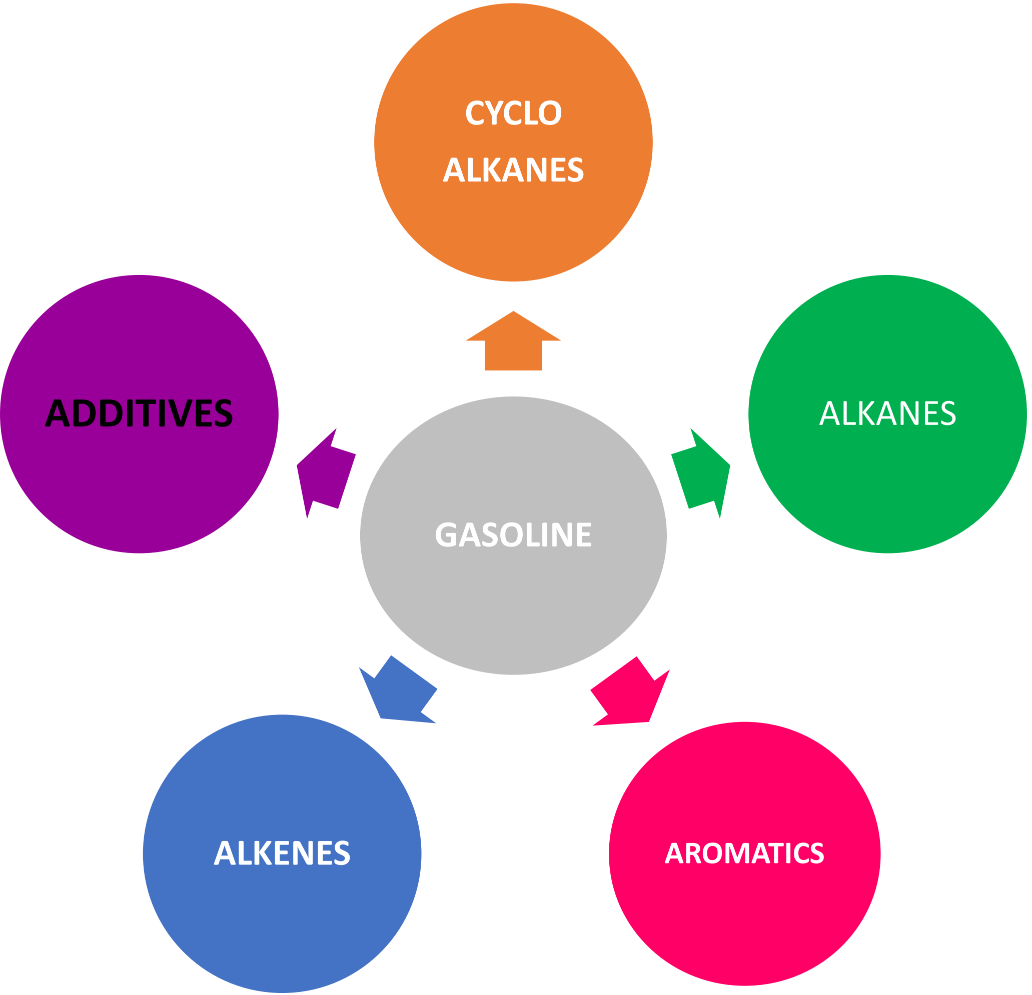
Increasing affinity for soil organic matter

http://pubs.usgs.gov/of/2006/1338/pdf/ofr2006-1338.pdf

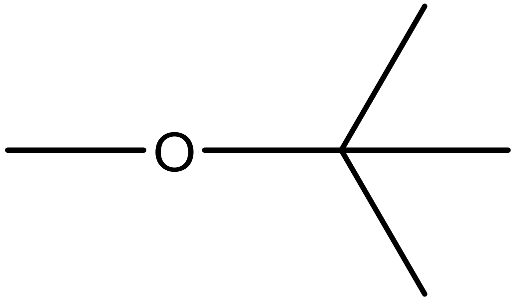
Aromatics

- Some small molecular weight compounds are oxidized by O_2 (which attacks the ring structure)
  - Oxidized slowly by O_3 (ozone)

Additives

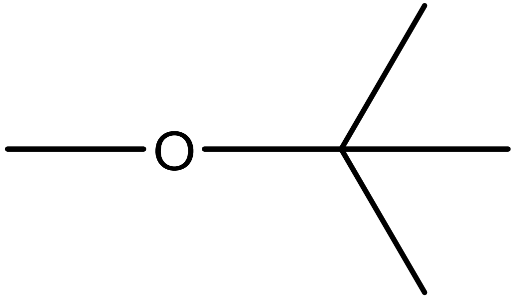


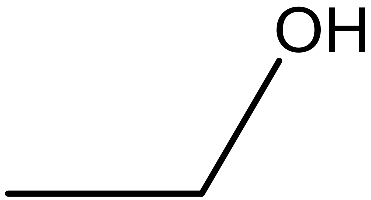
- Used to improve performance and stability of gasoline
- Typically are oxygenates - enriches gasoline with oxygen to improve combustion efficiency and reduction of CO emissions
- such as methyl tert-butyl ether (MTBE), ethanol, methanol, antirust agents, lubricants, detergents, dyes

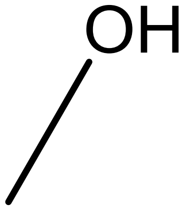


Additives

- methyl tert-butyl ether (MTBE), ethanol, methanol – water soluble because they are POLAR







IUPAC name[1]	Common or alternative name[2]	Water solubility[3] (mg/L at 25°C)
2-methoxy-2-methylpropane	methyl *tert*-butyl ether, MTBE	36,200

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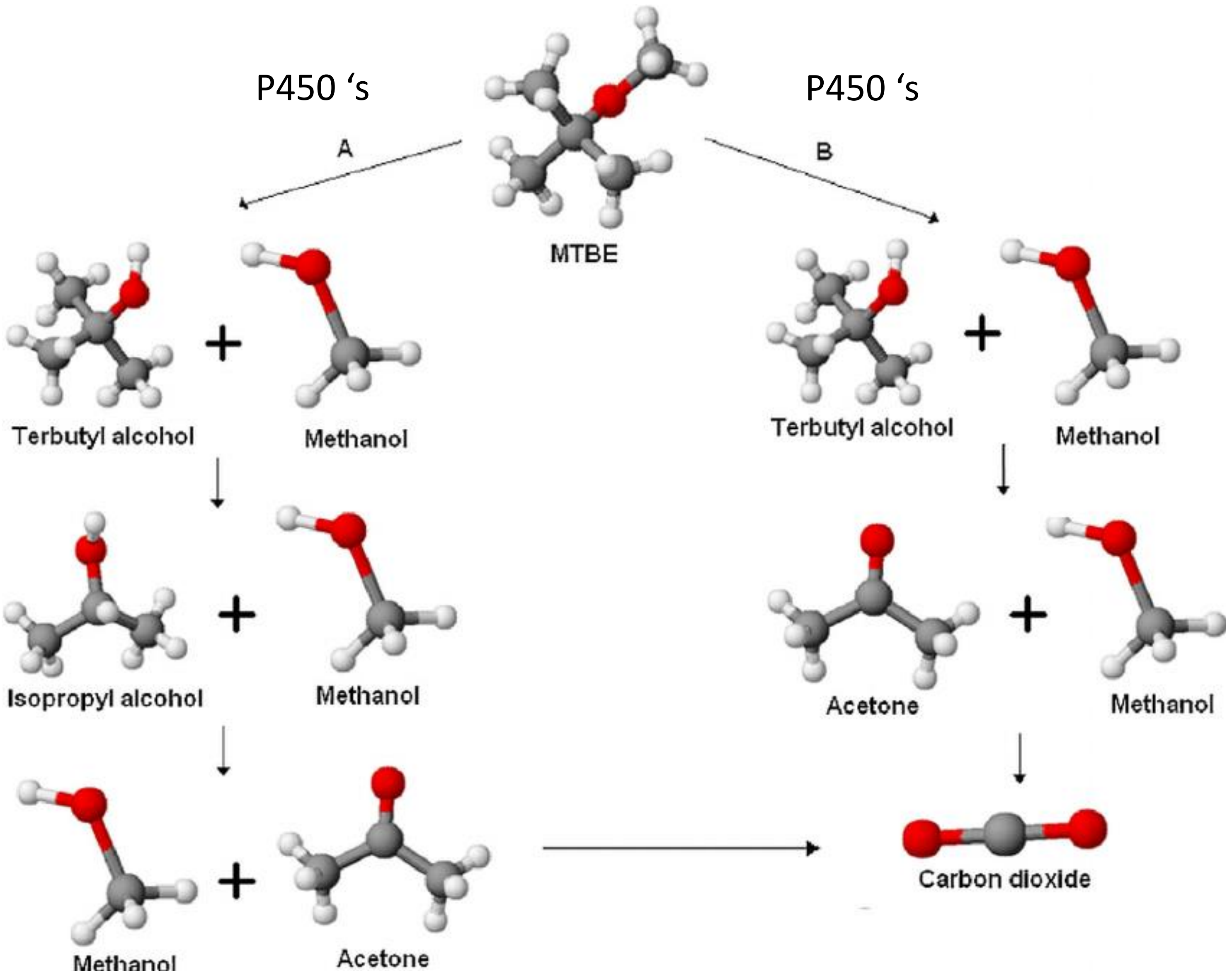
Additives


P450 's
P450 's
A
B
MTBE
Terbutyl alcohol
+
Methanol
Terbutyl alcohol
+
Methanol
Isopropyl alcohol
+
Methanol
Acetone
+
Methanol
Methanol
+
Acetone
Carbon dioxide

Summary of gasoline's fate in the environment

1. Compound's tendency to volatilize
2. Compound's tendency to dissolve in water (polarity)

float (density)

in the ground (polarity)

Table C-1. Default physicochemical constants for BTEXN an

Chemical/carbon range[1]	Molecular weight	Vapor pressure (atms)
Benzene	78	0.1
Ethylbenzene	106	0.01
Toluene	92	0.04
Xylenes, m-	106	0.01
Naphthalene	128	1.0×10^{-4}
C5–C8 Aliphatics	93	0.1
C9–C12 Aliphatics	149	8.7×10^{-4}
C13–C18 Aliphatics	170	1.4×10^{-4}
C19–C36 Aliphatics	280	1.1×10^{-6}
C9–C10 Aromatics	120	2.9×10^{-3}
C11–C22 Aromatics	150	3.2×10^{-5}

[1]Constants for BTEXN from USEPA RSL guidance (USEPA 2014a); vapor pressures from T
except C13-C18 Aliphatics (based on EC > 12-16) and C19-C36 Aliphatics (based on EC >

Summary of gasoline's fate in the environment

1. Compound's tendency to volatilize
2. Compound's tendency to dissolve in water (polarity)

Table C-1. Default physicochemical constants for BTEXN and TPH carbor

Chemical/carbon range[1]	Molecular weight	Vapor pressure (atms)	Solubility in water (mg/L)
Benzene	78	0.1	1,790
Ethylbenzene	106	0.01	169
Toluene	92	0.04	526
Xylenes, m-	106	0.01	161
Naphthalene	128	1.0×10^{-4}	31
C5–C8 Aliphatics	93	0.1	11
C9–C12 Aliphatics	149	8.7×10^{-4}	0.07
C13–C18 Aliphatics	170	1.4×10^{-4}	3.5×10^{-4}
C19–C36 Aliphatics	280	1.1×10^{-6}	1.5×10^{-6}
C9–C10 Aromatics	120	2.9×10^{-3}	51
C11–C22 Aromatics	150	3.2×10^{-5}	5.8

[1]Constants for BTEXN from USEPA RSL guidance (USEPA 2014a); vapor pressures from TOXNET (US
except C13-C18 Aliphatics (based on EC > 12-16) and C19-C36 Aliphatics (based on EC > 16-35 aliphati

density)

e ground (polarity)

Low water solubility: less than 10 mg/L or 10 ppm
Moderate water solubility: 10-1,000 mg/L or 10-1,000 ppm
High water solubility: more than 1,000 mg/L or 1,000 ppm

Summary of gasoline's fate in the environment

1. Compound's tendency to volatilize
2. Compound's tendency to dissolve in water (polarity)
3. Compound's tendency to sink or float (density)
   Floaters – aliphatics, olefins, cyclo's, aromatics
   Sinkers – PAH's
4. Compound's tendency to dissolve in the ground (polarity)

Summary of gasoline’

1. Compound’s tendency to vola
2. Compound’s tendency to diss
3. Compound’s tendency to sink
4. Compound’s tendency to diss

“Like dissolves like”

Solvent	Solute	Is Solution Likely?
Polar	Polar	Yes
Polar	Nonpolar	No
Nonpolar	Polar	No
Nonpolar	Nonpolar	Yes

IUPAC name[1]	Common or alternative name[2]	Soil-sorption coefficient (Log K_{oc} in soil)
1,2,4-trimethylbenzene	pseudocumene	[3]3.34
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	[4]3.18–[3]3.42
naphthalene	naphthene	[3]2.98
1,2,4-trichlorobenzene	1,2,4-trichlorobenzol	[5]2.94
vinyl benzene	styrene	[2]2.72–2.74
1,2-dichlorobenzene	o-dichlorobenzene	[6]2.46–[5]2.51
tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE	[7]2.37
ethylbenzene	—	[5]2.22
1,1-dichloroethene	1,1-dichloroethylene, DCE	[2]2.18
1,3-dimethylbenzene	*m*-xylene	[7]2.11–2.46
1,1,1-trichloroethane	methyl chloroform	[8]2.03
1,1,2-trichloroethene	1,1,2-trichloroethylene, TCE	[7]2.00
chlorobenzene	monochlorobenzene	[5]1.91
1,1,2-trichloroethane	methyl chloroform	[7]1.78–2.03
tetrachloromethane	carbon tetrachloride	[9]1.78
methylbenzene	toluene	[7]1.75–[10]2.28
chloroethene	vinyl chloride, chloroethylene	[2]1.75
1,2-, 1,4-dimethylbenzene	*o*-xylene, *p*-xylene	[2]1.68–1.83
chloroethane	ethyl chloride	[4]1.62
cis-1,2-dichloroethene	*cis*-1,2-dichloroethylene	[2]1.56–1.69
1,2-dichloroethane	1,2-ethylidene dichloride, glycol dichloride	[6]1.52
trans-1,2-dichloroethene	*trans*-1,2-dichloroethylene	[2]1.56–1.69
1,1-dichloroethane	1,1-ethylidene dichloride	[12]1.52
benzene	—	[5]1.49–[7]1.73
methyl *tert*-butyl ether	MTBE	[11]1.09

Increasing affinity for soil organic matter

http://pubs.usgs.gov/of/2006/1338/pdf/ofr2006-1338.pdf

?’s

Topics

Petroleum

- Physical and chemical properties
  - Like dissolves like
  - Volatility
  - Polarity
  - Density
- Compare fresh vs. weathered
  - Reaction (how and why)
- Bioremediation
  - Oxidation and reduction

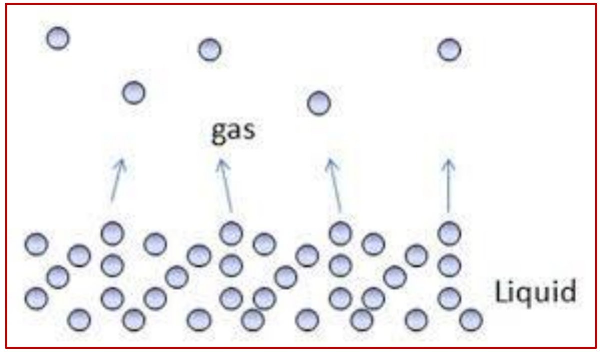
Chlorinated Solvents

- Nomenclature
- Physical and chemical properties
- Chemical reaction, mechanism
  - How and why

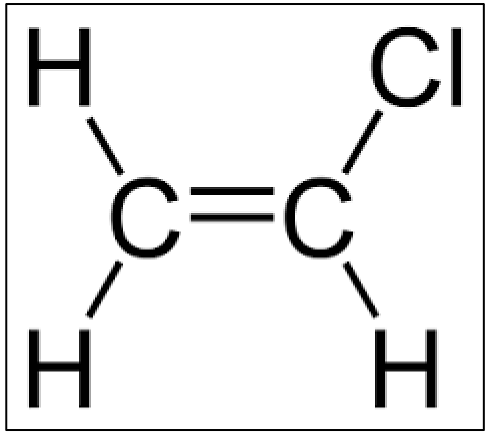
Chlorinated Volatile Organic Compounds

Contains chlorine

Easily evaporated at normal temperatures

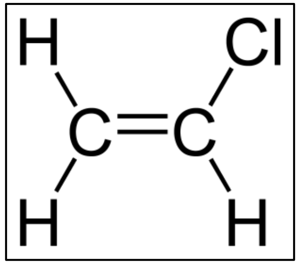


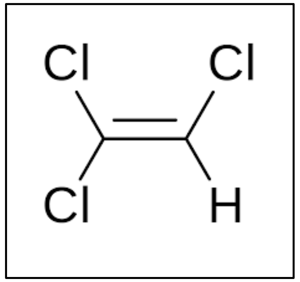
Covalent (share electrons in the bond) molecule with carbon

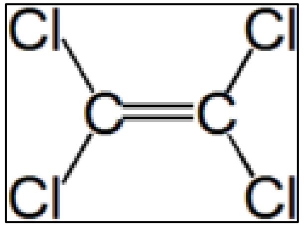


Chlorinated Solvents

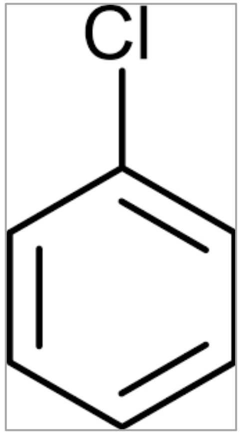
Chlorinated Aliphatics

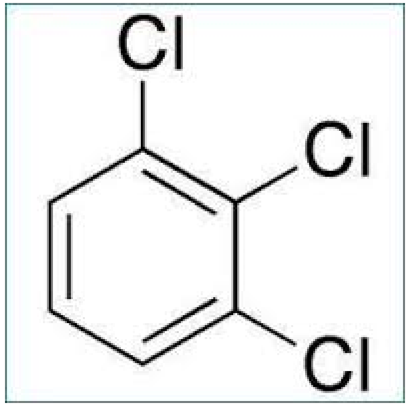






Chlorinated Aromatics



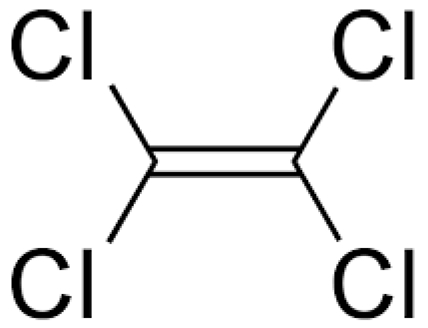


Nomenclature – IUPAC name (international union of pure and applied chemistry)

- Tetrachloroethene (perchloroethylene; PCE; PERC®; ethylene tetrachloride)
- 1,1,2-trichloroethene (1,1,2-trichloroethylene; TCE; acetylene trichloroethylene)
- Cis-1,2-dichloroethene (Cis-1,2-dichloroethylene; 1,2 DCE; Z-1,2-dichloroethene)
- Trans-1,2-dichloroethene (Trans-1,2-dichloroethylene; E-1,2-dichloroethene)
- 1,1-dichloroethene (1,1-dichloroethylene; DCE)
- Chloroethene (vinyl chloride; chloroethylene; monovinyl chloride; MVC)

Chlorinated Solvents

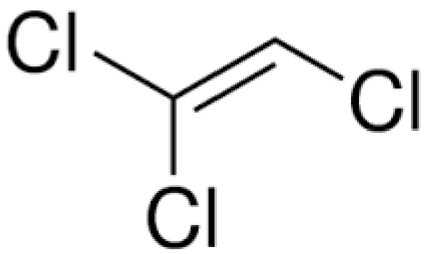
Tetrachloroethene (perchloroethylene; PCE; PERC®; ethylene tetrachloride)



- Heavily used in cleaning and degreasing products, processing, finishing of raw and finished textiles
- Polar or nonpolar?
  - Not very water soluble (nonpolar)
- Vaporize easily
- More dense than water → sink
  - Nonpolar nature means it is attracted to soil

Chlorinated Solvents

1,1,2-trichloroethene (1,1,2-trichloroethylene; TCE; acetylene trichloroethylene)

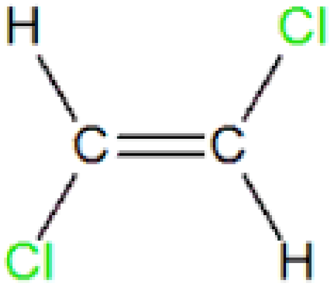


- Solvents, degreasers
- Volatile
- Polar molecule (water soluble)
- More dense than water → sink

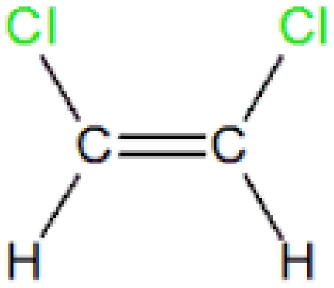
Chlorinated Solvents

Cis-1,2-dichloroethene (Cis-1,2-dichloroethylene; 1,2 DCE; Z-1,2-dichloroethene)

Trans-1,2-dichloroethene (Trans-1,2-dichloroethylene; E-1,2-dichloroethene)



trans-1,2-dichloroethene

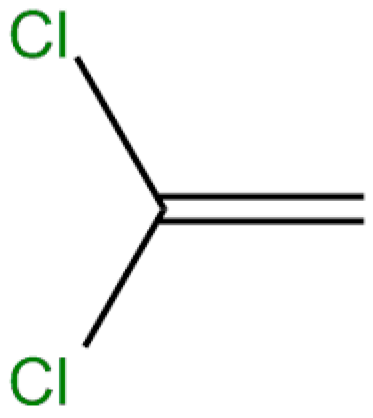


cis-1,2-dichloroethene

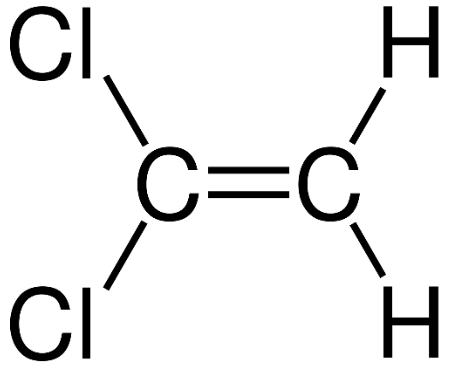
- Degradation products
- Volatile
- Polarity
  - Trans is nonpolar
  - Cis is polar
- Cis is more soluble than trans
- More dense than water → sink

Chlorinated Solvents

1,1-dichloroethene (1,1-dichloroethylene; DCE)

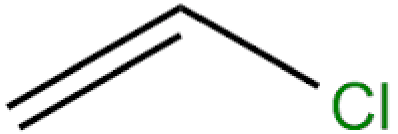


- Degradation product
- Volatile
- Polar (soluble in water)
- More dense than water → sink



Chlorinated Solvents

Chloroethene (vinyl chloride; chloroethylene; monovinyl chloride MVC)



- Degradation product
- As volatile as PERC®
- Polar (water soluble)
- More dense than water → sink

- PCE > 1,1-DCE > TCE > VC > cis (affinity for soil matter)

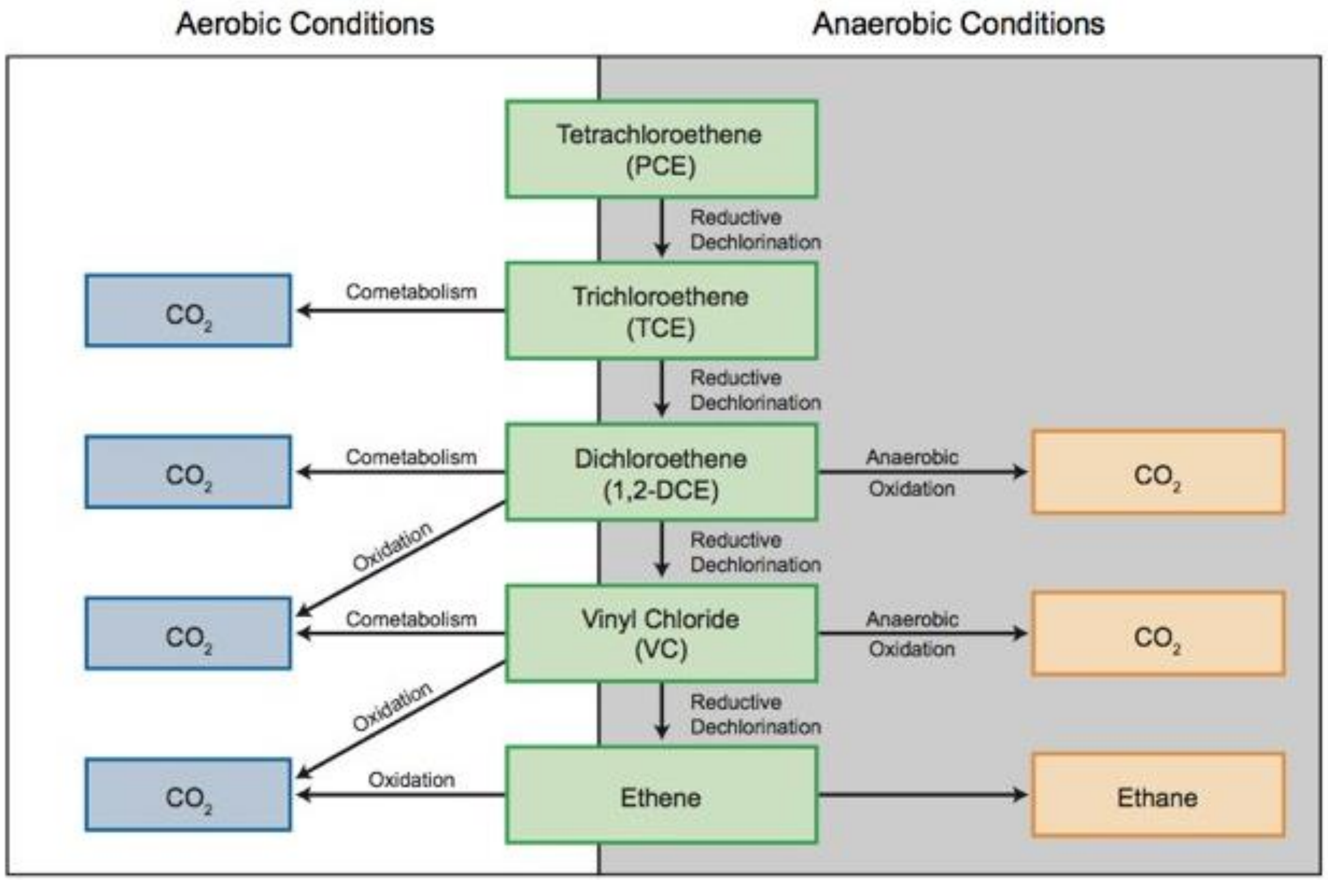
Degradation of Chlorinated VOCs

PCE → TCE → DCE → VC → Ethene → Ethane → CO_2

- Most organic compounds degrade but the speed is determined by:
  - Presence of ENERGY HUNGRY microorganisms
  - Environmental conditions (temperature, oxygen, soil composition)

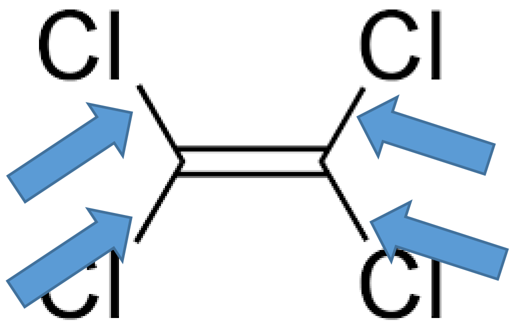
Degradation of Chlorinated VOCs

- The most common method is microbial reductive dechlorination under <u>anaerobic conditions</u> (PCE and TCE are favored)
- Biodegradation of TCE, DCE's, and VC can also proceed via oxidation pathways under <u>aerobic conditions</u>



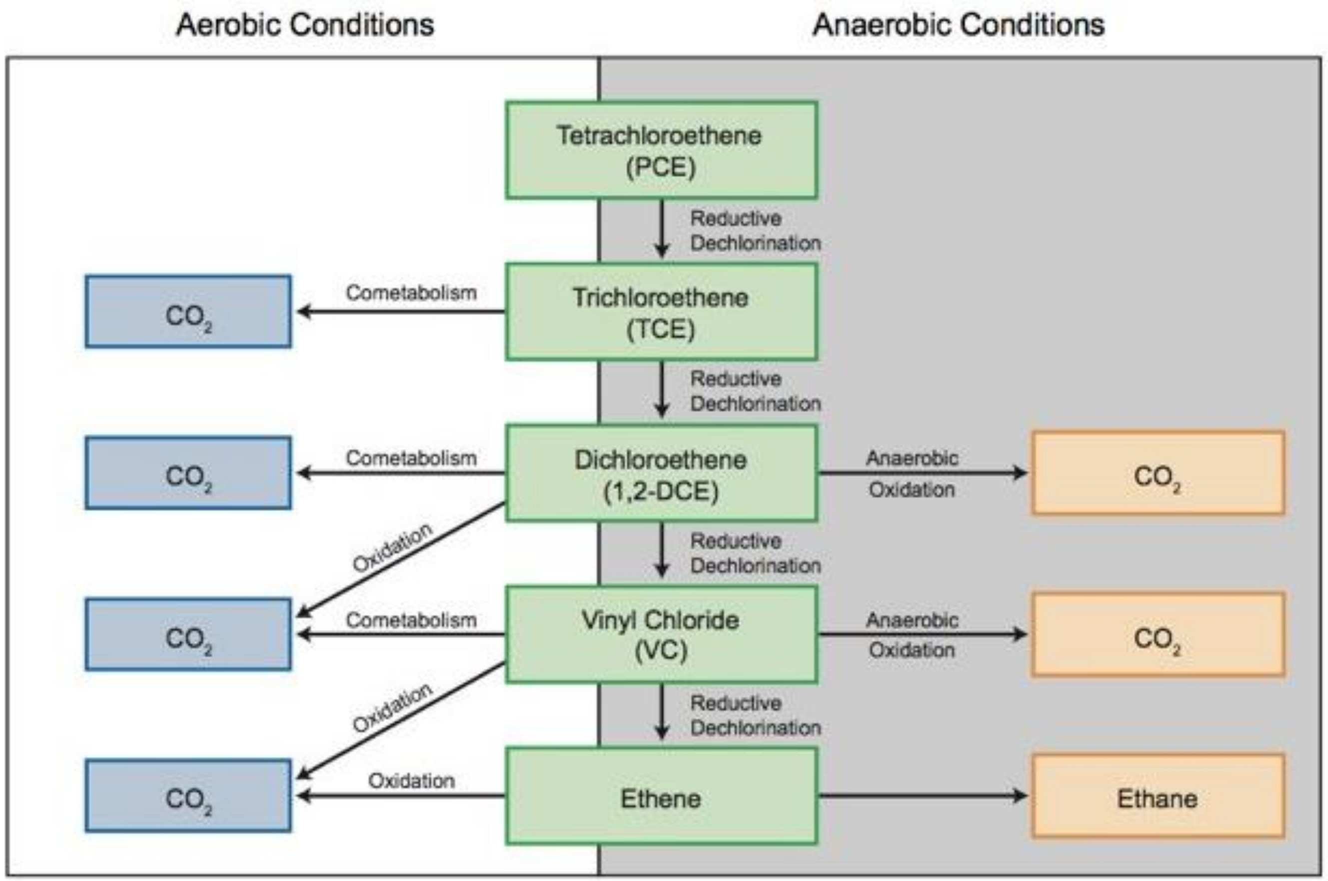
Degradation of Chlorinated VOCs

- Why do certain bacteria like PERC ®?



Four C-Cl bonds have a ton of energy stored in the bonds.

Bacteria are ENERGY HUNGRY!!!

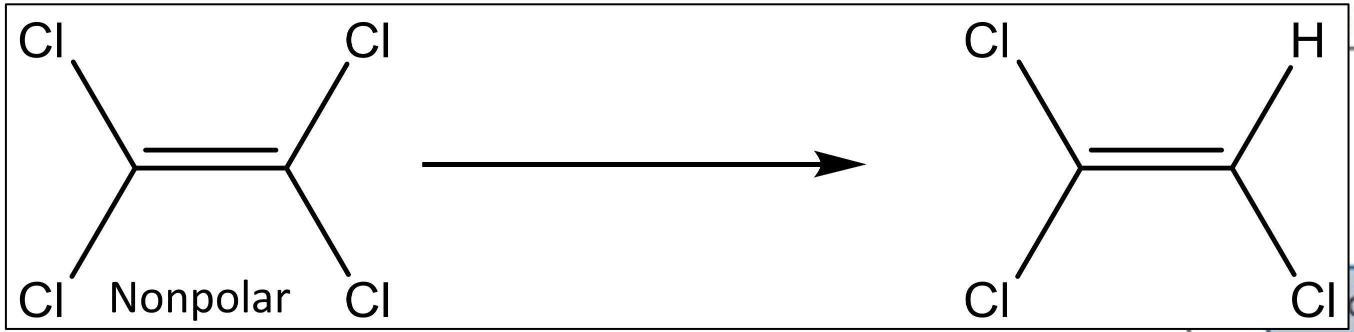


Degradation of Chlorinated VOCs

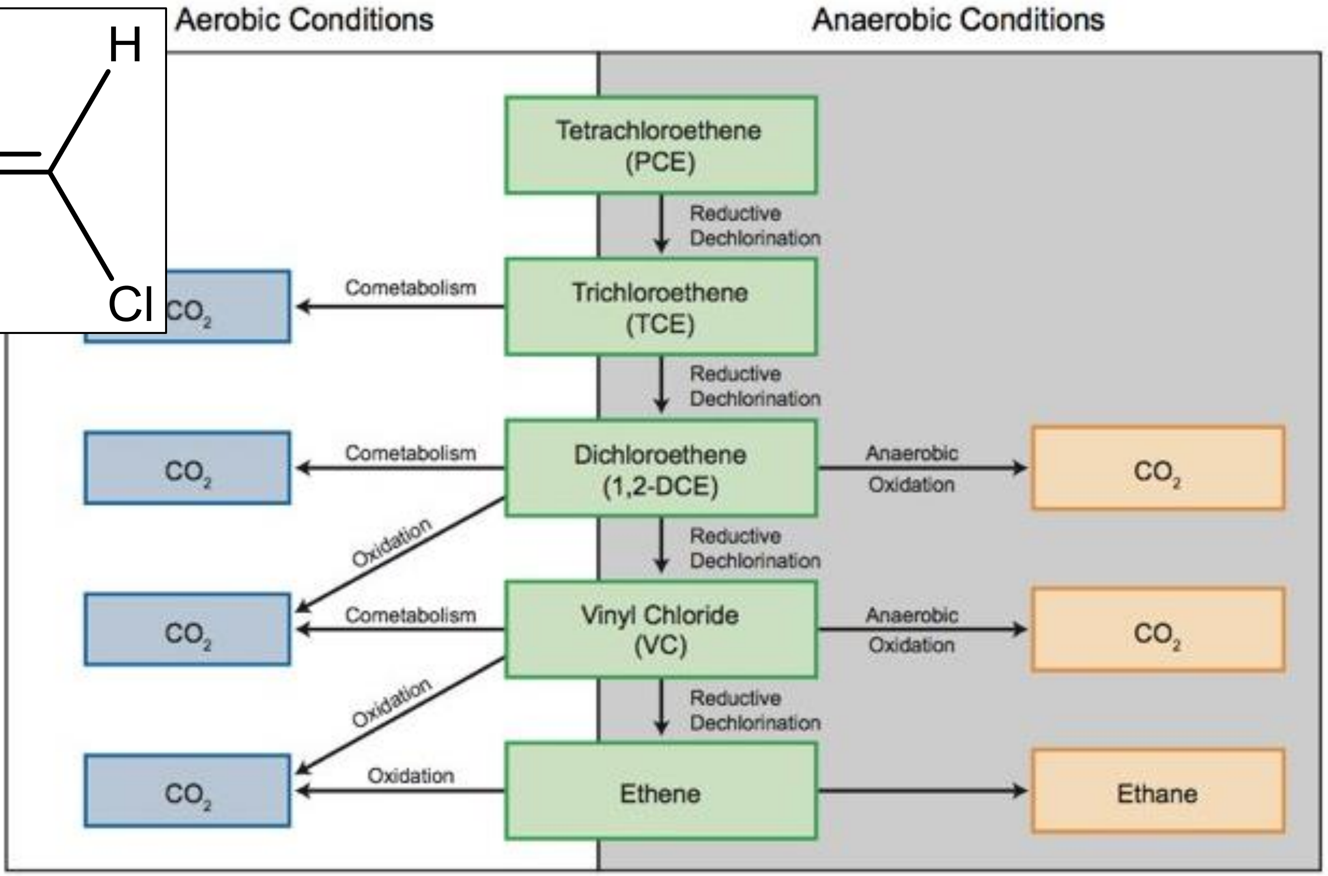
- Why is the first step <u>anaerobic</u>?

$$H_2 \longrightarrow 2H^+ + 2e^-$$

- Hydrogen gas is a byproduct of fermentation (naturally present in soil)



Nonpolar
Soil fraction



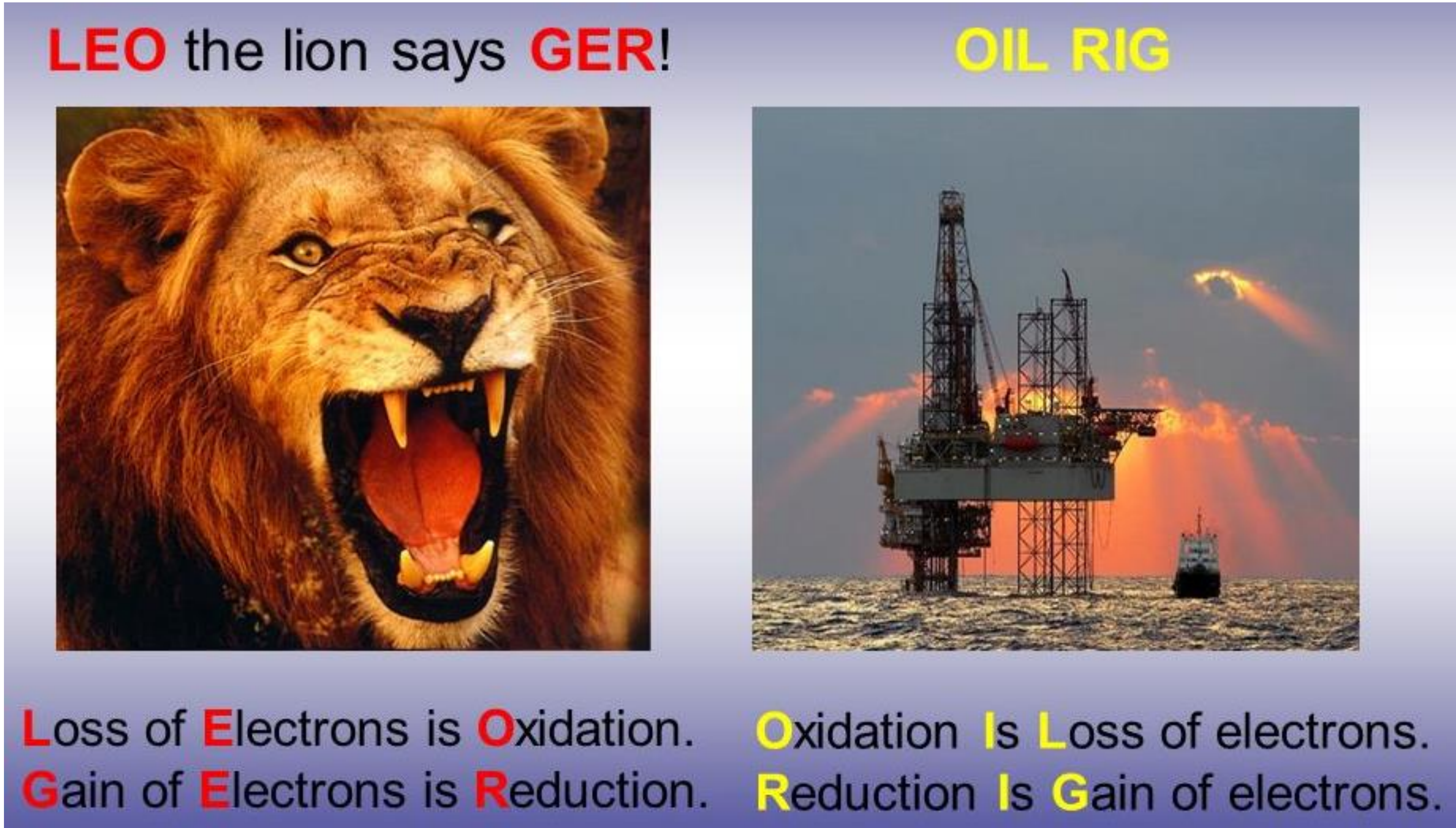
If oxygen is present:

$$O_2 + 2H_2 \longrightarrow 2H_2O$$

Degradation of Chlorinated VOCs

- How does PCE breakdown to TCE?

Oxidation
and
Reduction

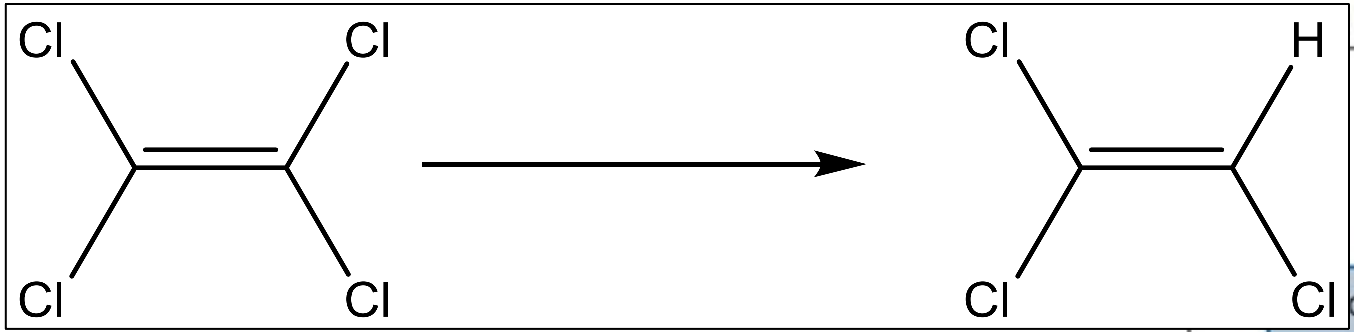


Degradation of Chlorinated VOCs

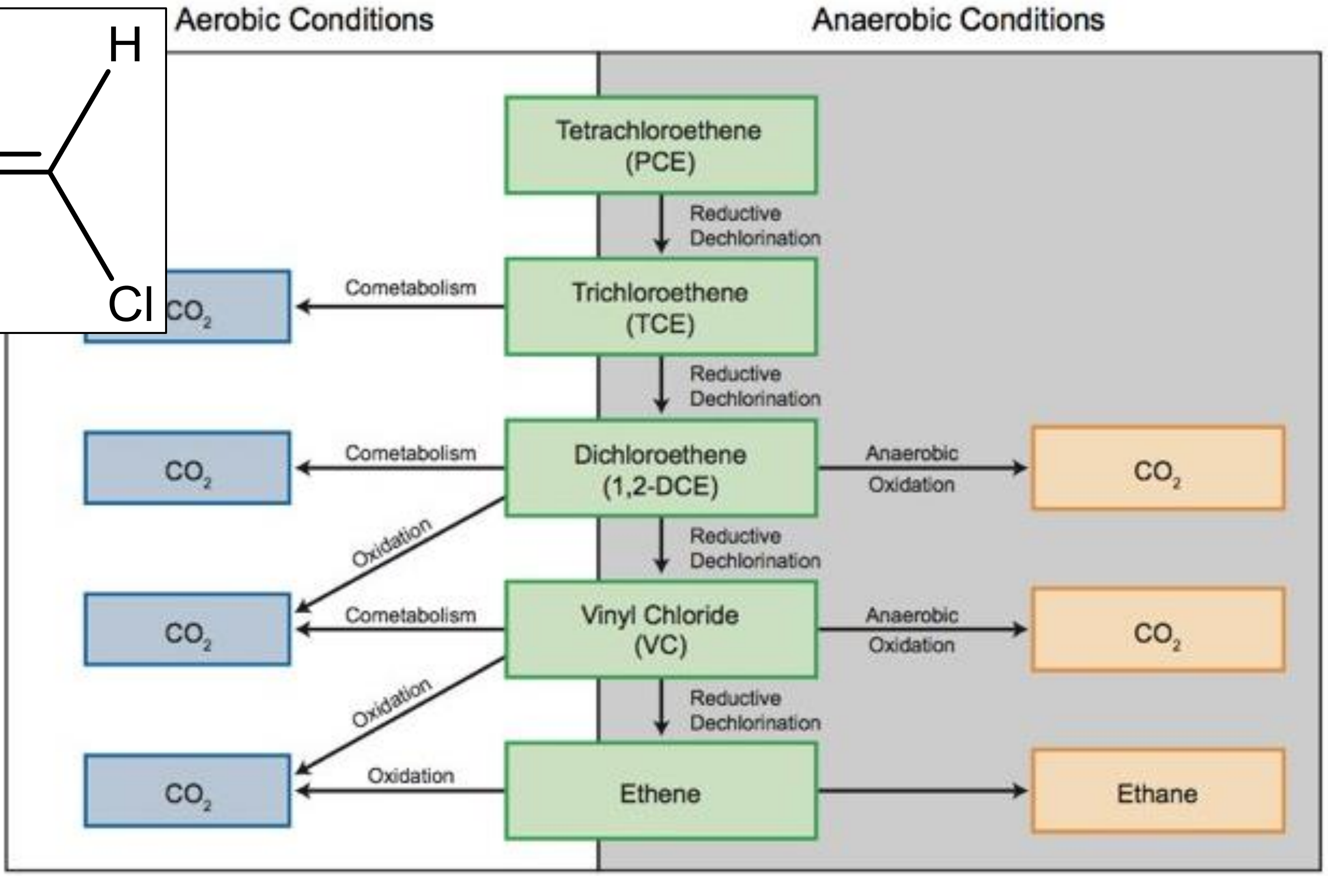
- How does PCE breakdown to TCE?

$$H_2 \longrightarrow 2H^+ + 2e^-$$

Electron donor, oxidized



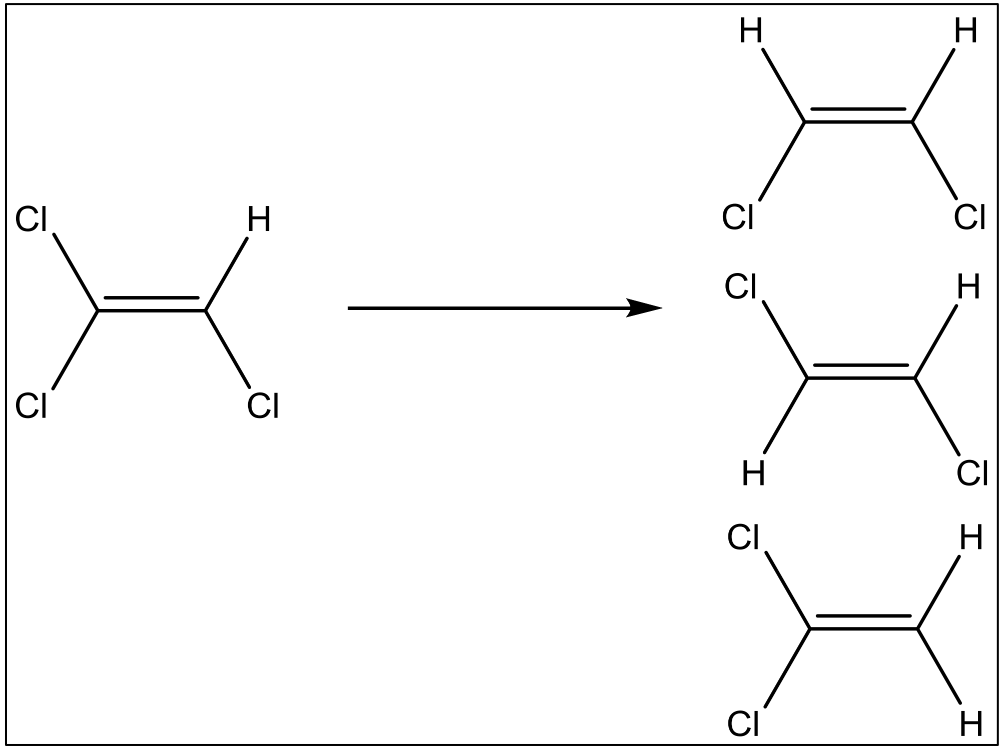
Electron acceptor, reduced



Degradation of Chlorinated VOCs

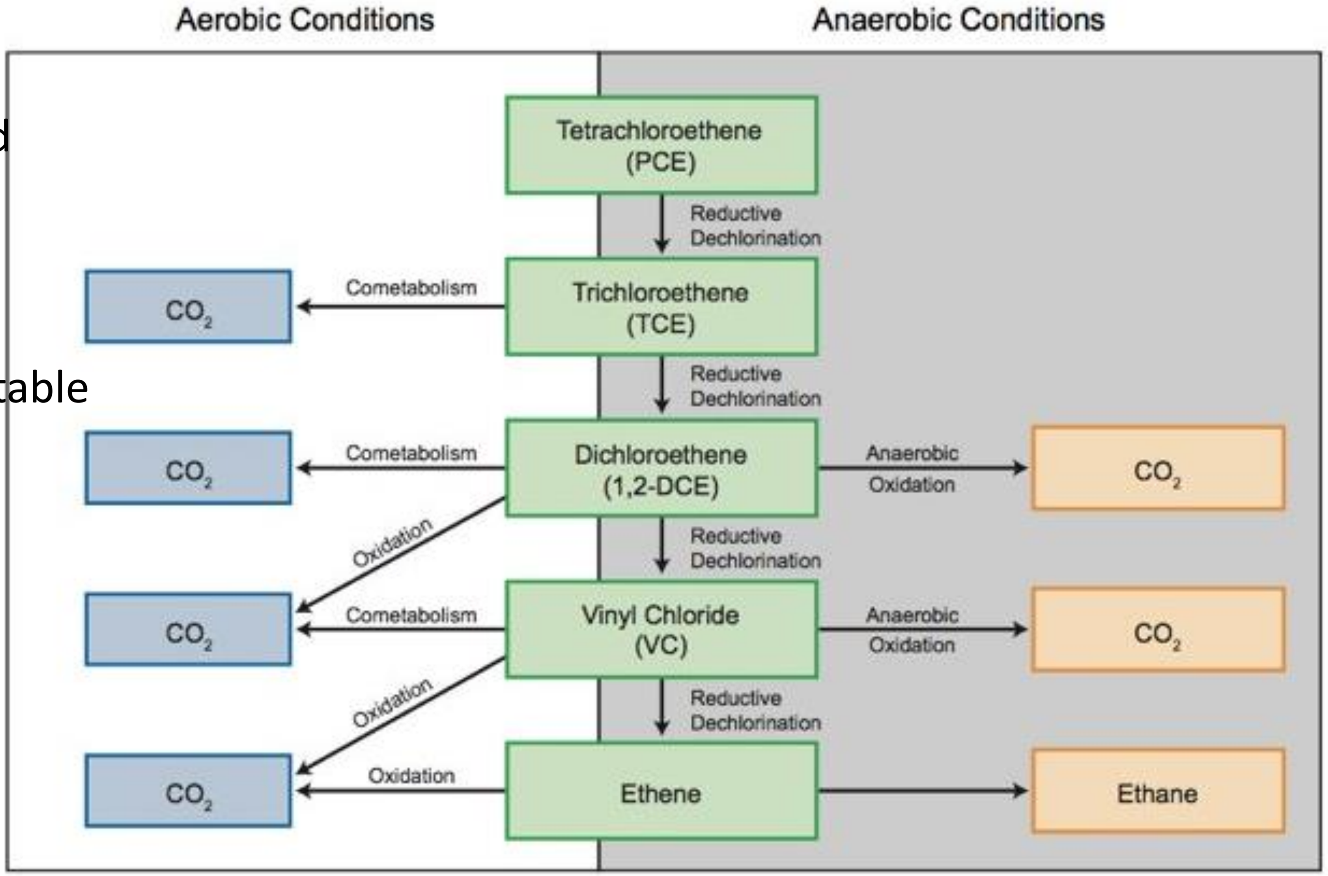
- How does TCE breakdown to DCE's?

$$H_2 \longrightarrow 2H^+ + 2e^-$$



Favored

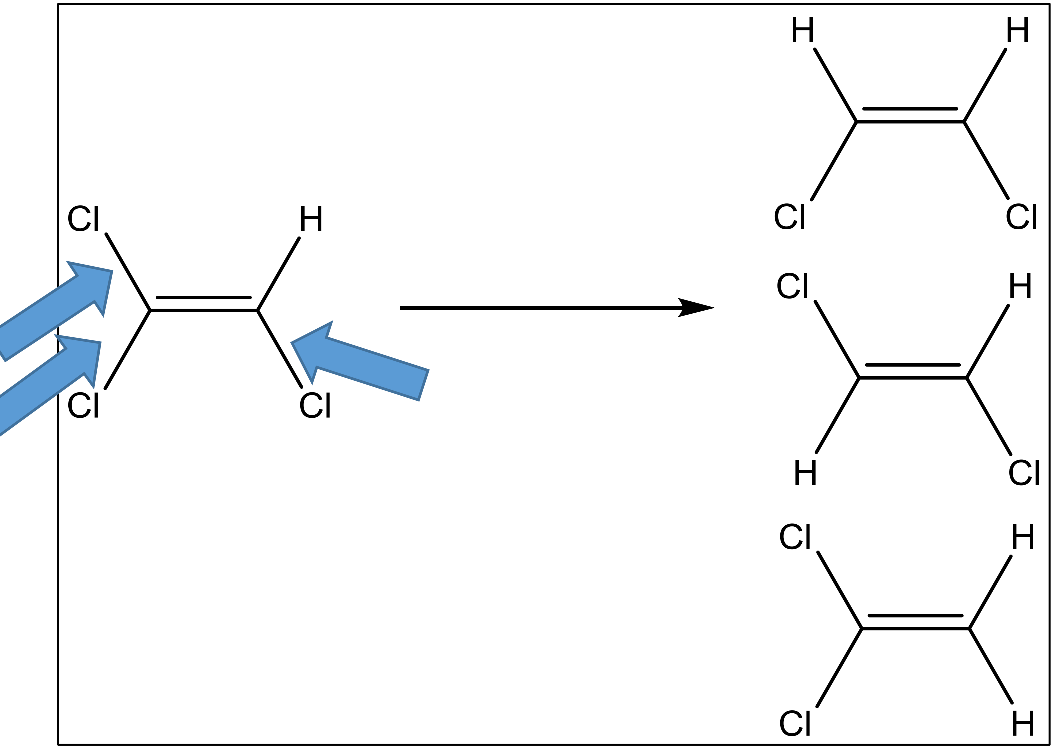
Most stable

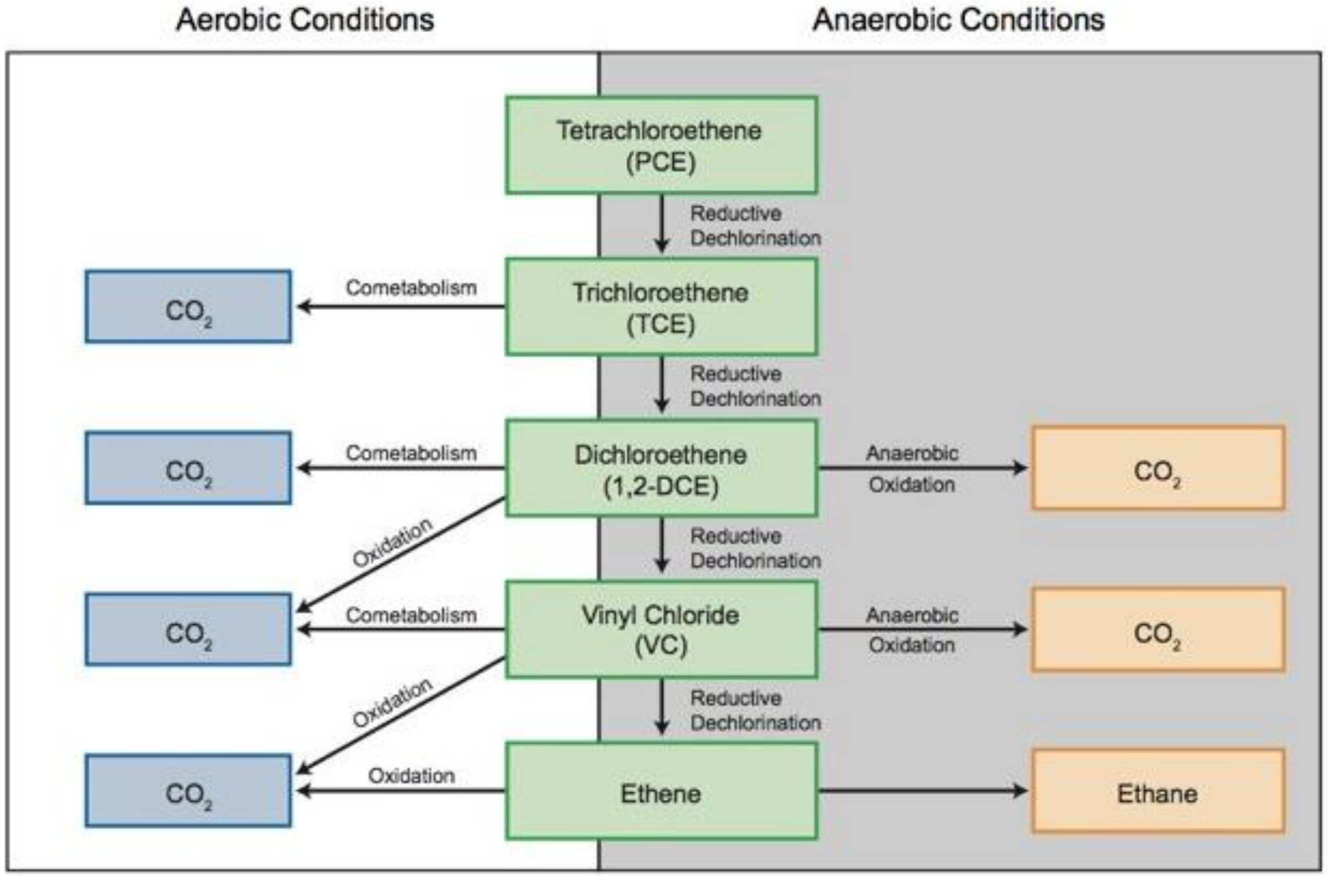


Degradation of Chlorinated VOCs

- Why does TCE breakdown to DCE's?

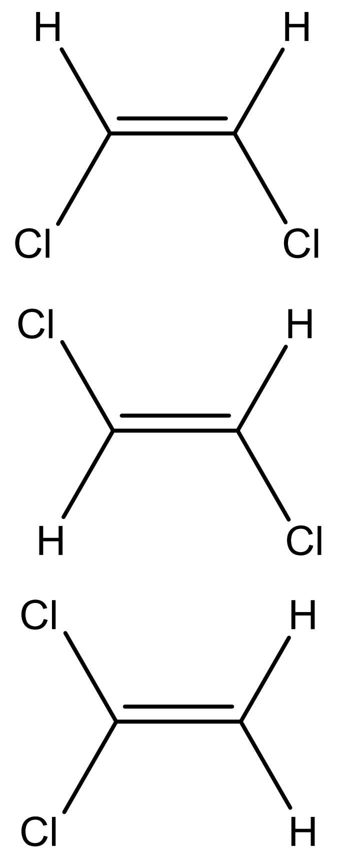
$$H_2 \longrightarrow 2H^+ + 2e^-$$

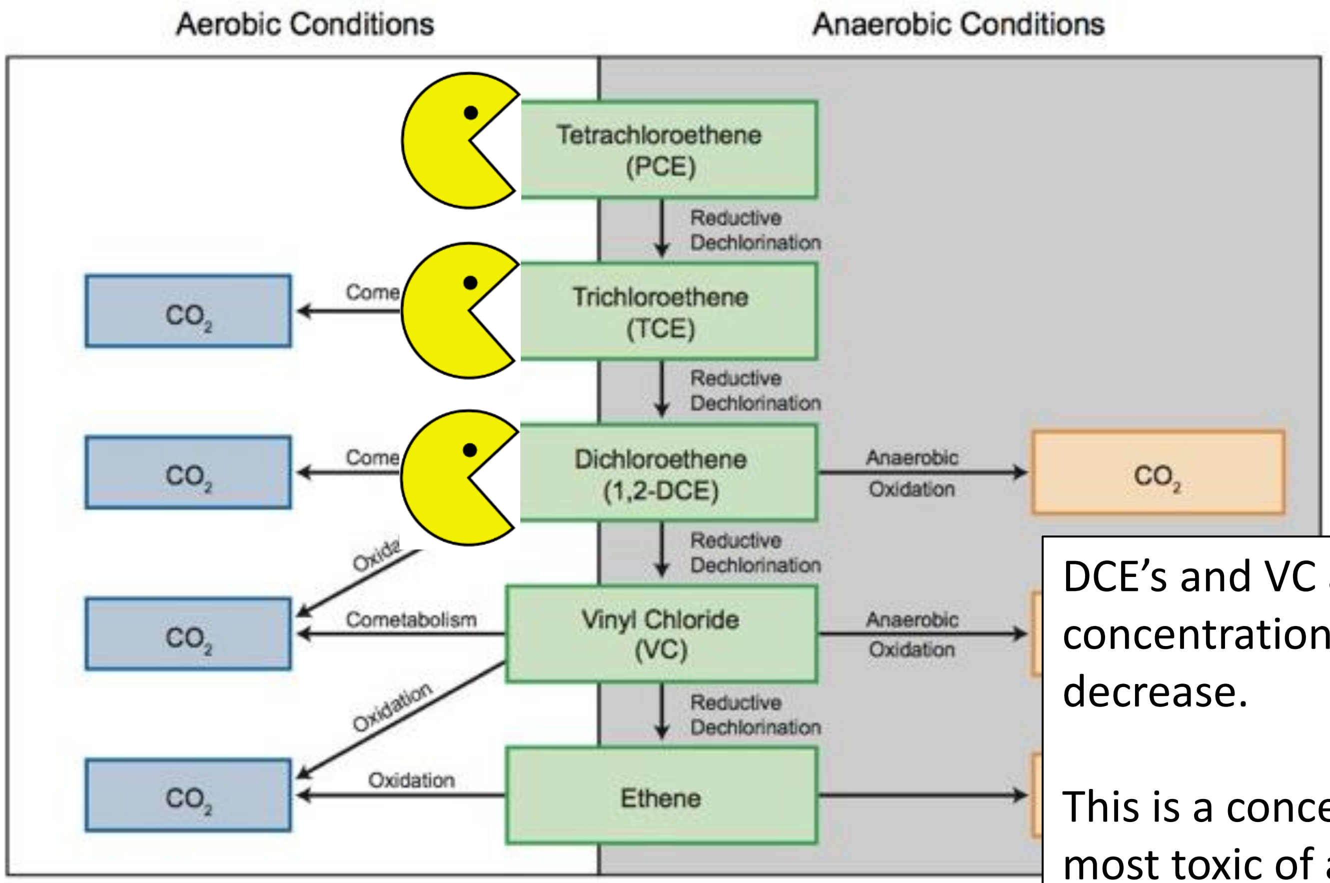




Degradation of Chlorinated VOCs

- Why don't DCE's continue to break down as fast as PCE and TCE?





DCE's and VC accumulate until the concentration of PCE and TCE decrease.

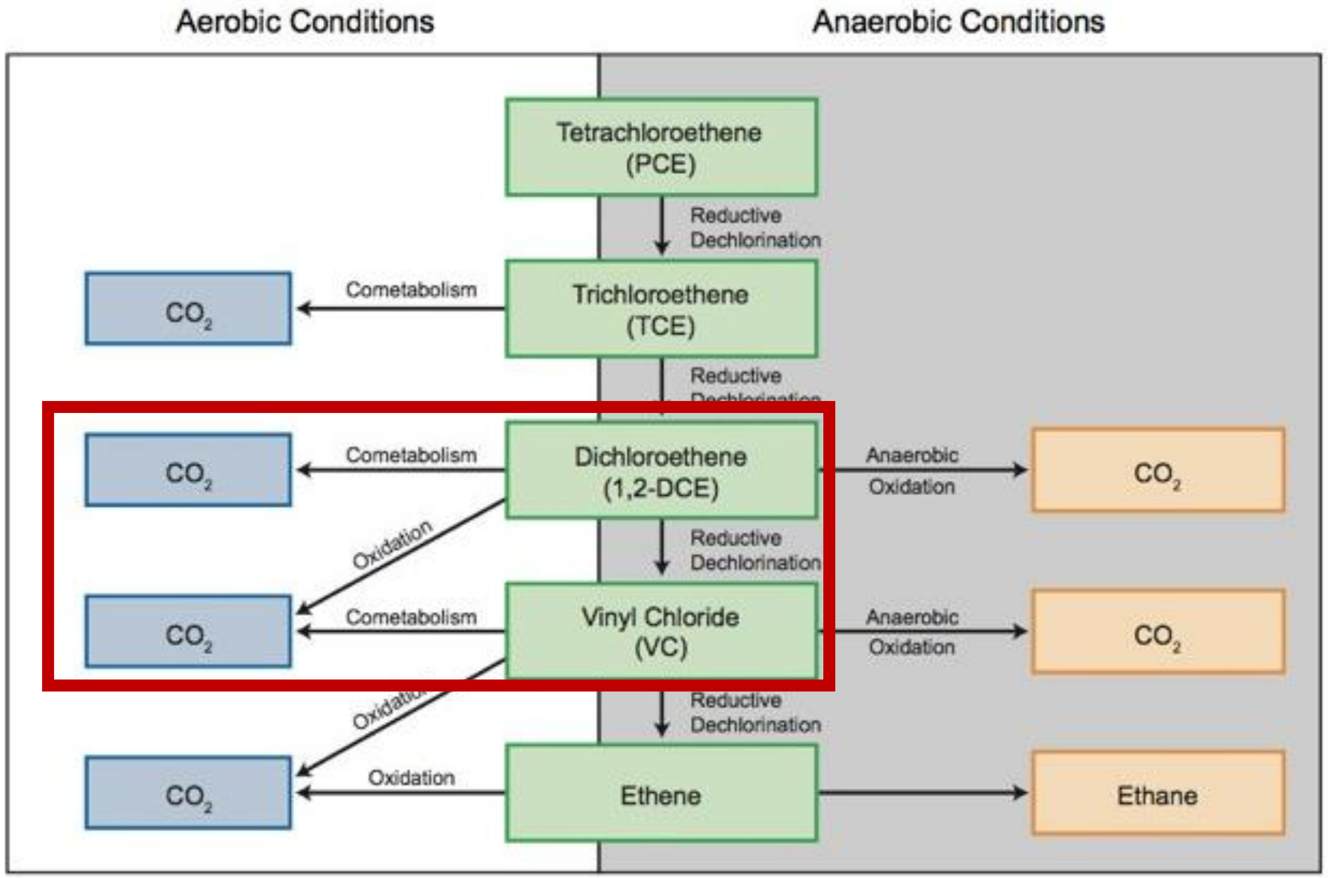
This is a concern because VC is the most toxic of a CVOC's.

Degradation of Chlorinated VOCs

- Biodegradation of DCE's, and VC can also proceed via oxidation pathways under aerobic conditions

- Why? Because they are polar and will migrate into the aqueous phase (lots of oxygen)

- How?
  - VC acts as the electron donor (oxidized)
  - Oxygen is the electron acceptor (reduced)



Abiotic (chemical) Transformation

- Abiotic Reductive Dechlorination – oxidation/reduction reaction (uses oxidized metals to attract Cl)
- Hydrolysis – substitution reaction (OH in place of Cl)

Summary of CVOC's fate in the environment.

1. Compound's tendency to volatilize
2. Compound's tendency to dissolve in water (polarity)

Table 2.5 Characteristics of Chlorinated Aliphatic Hydrocarbons and Dechlorination Products

Compound	Molecular Formula	Molecular Weight (g/mol)[a/]	Density (g/mL @ approx. 20 to 25 °C)[b/]	Henry's Law Constant (atm-m^3/mol)[e/]	Solubility (mg/L @ approx. 20 to 25 °C)[c/]	Vapor Pressure (mm Hg @ 20 °C)[d/]	Octanol/Water Partition Coefficient (log Kow)[f/]	Octanol/Carbon Partition Coefficient (log Koc)[g/]
Chloroethenes								
Tetrachloroethene (PCE)	C_2Cl_4	165.8 (1)	1.62 (1)	0.0132 (2)	150 (3)	14.0 (3)	2.53 (4)	2.42 (5)
Trichloroethene (TCE)	C_2HCl_3	131.4 (1)	1.46 (1)	0.0072 (2)	1,100 (3)	60.0 (3)	2.42 (4)	2.03 (5)
cis-1,2- Dichloroethene (*cis*-DCE)	$C_2H_2Cl_2$	96.94 (1)	1.28 (1)	0.0030 (2)	3,500 (3)	200 (6)	0.70	1.65 (7)
trans-1,2- Dichloroethene (*trans*-DCE)	$C_2H_2Cl_2$	96.94 (1)	1.26 (1)	0.0073 (2)	6,300 (4)	340 (6)	2.06 (7)	1.77 (5)
1,1-Dichloroethene (1,1-DCE)	$C_2H_2Cl_2$	96.94 (1)	1.22 (1)	0.021 (2)	2,250 (5)	500 (3)	2.13 (4)	1.81 (5)
Vinyl Chloride (VC)	C_2H_3Cl	62.51 (1)	Gas	0.218 (2)	1,100 (3)	2,660 (3)	0.60 (4)	1.23 (5)
Ethene	C_2H_4	28.05 (1)	Gas	8.60 (7)	131 (7)	30,800 (7)	1.13 (8)	2.48 (7)

Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents

Summary of CVOC's fate in the environment.

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2. Compound's tendency to dissolve in water (polarity)

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1,1-Dichloroethene (1,1-DCE)	$C_2H_2Cl_2$	96.94 (1)	1.22 (1)	0.021 (2)	2,250 (5)	500 (3)	2.13 (4)	1.81 (5)
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Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents

Summary of CVOC's fate in the environment.

1. Compound's tendency to volatilize
2. Compound's tendency to dissolve in water (polarity)
3. Compound's tendency to sink or float (density)

Table 2.5 Characteristics of Chlorinated Aliphatic Hydrocarbons and Dechlorination Products

Compound	Molecular Formula	Molecular Weight (g/mol)[a/]	Density (g/mL @ approx. 20 to 25 °C)[b/]	Henry's Law Constant (atm-m^3/mol)[e/]	Solubility (mg/L @ approx. 20 to 25 °C)[c/]	Vapor Pressure (mm Hg @ 20 °C)[d/]	Octanol/Water Partition Coefficient (log Kow)[f/]	Octanol/Carbon Partition Coefficient (log Koc)[g/]
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Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents

Summary of CVOC's fate in the environment.

1. Compound's tendency to volatilize
2. Compound's tendency to dissolve in water (polarity)
3. Compound's tendency to sink or float (density)
4. Compound's tendency to degrade in the environment
    1. PCE and TCE (anaerobic)
    2. DCE's and VC (anaerobic and aerobic)

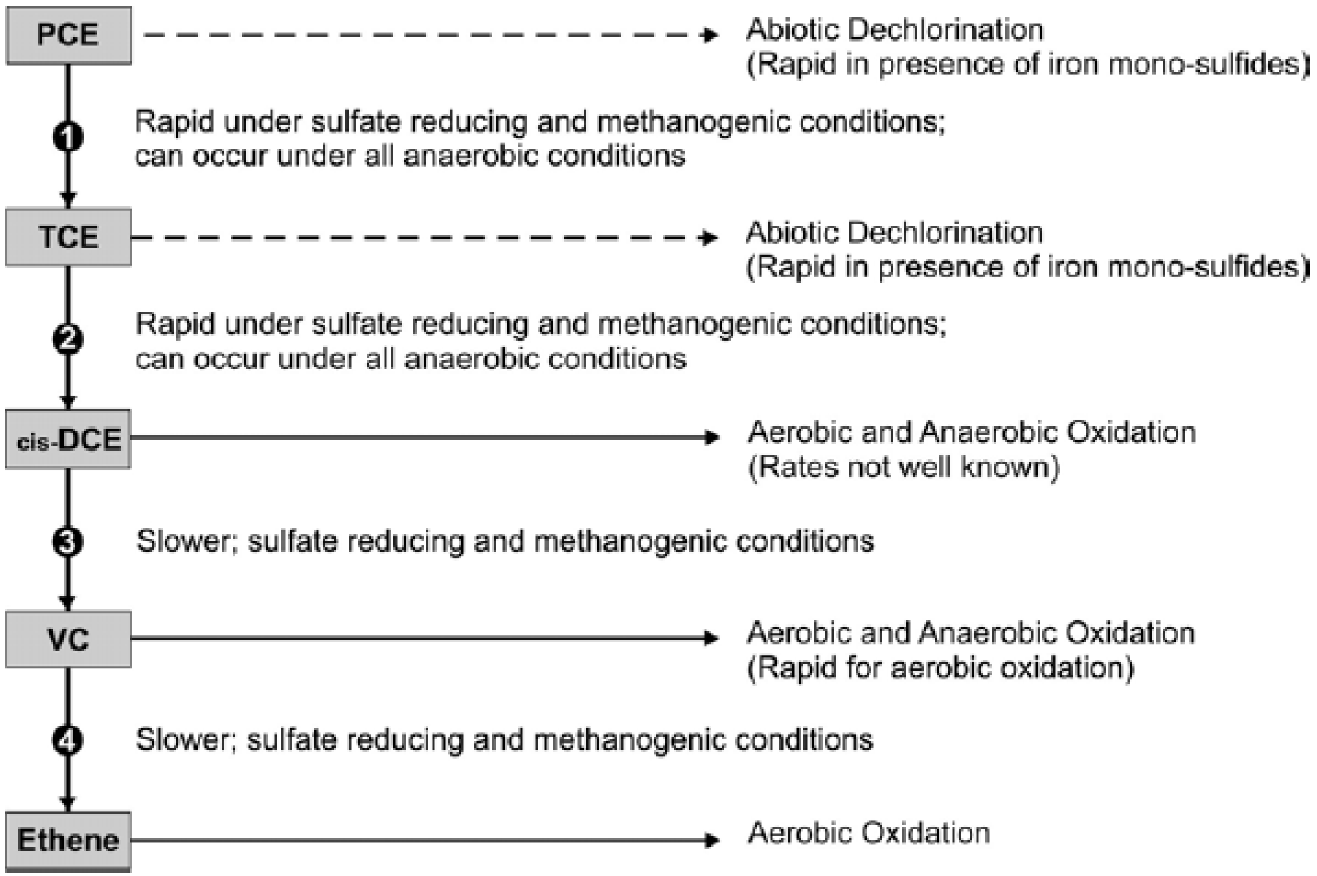
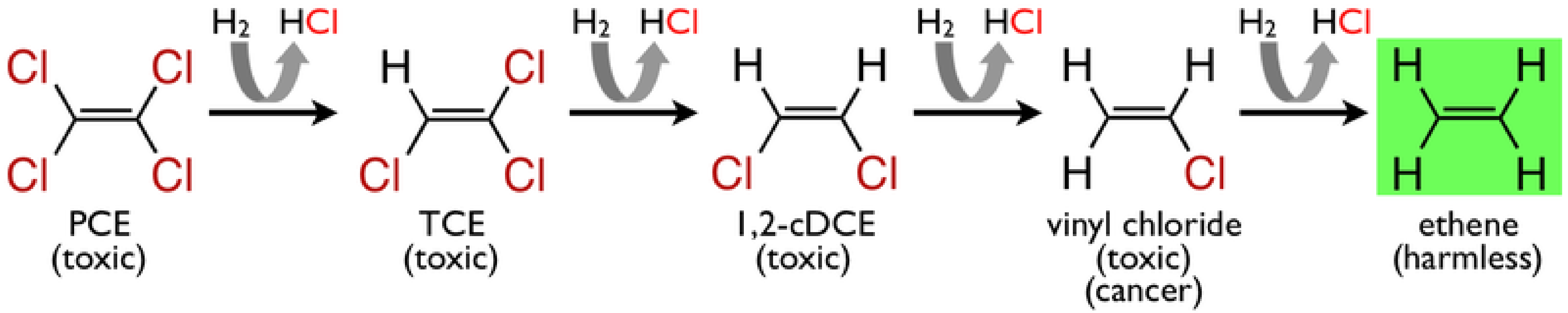


Figure 2.2 **Reaction Sequence and Relative Rates of Degradation for Chlorinated Ethenes (modified from Wiedemeier et al., 1999)**

Reaction Summary – oxidation/reduction rxn

- Hydrogen (H_2) loses its electrons and becomes oxidized.
- Hydrogen substitutes in place of the Cl atom.
- Haloalkene gains electrons and becomes reduced.



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