

### Organic chemicals & nomenclature (IUPAC)

How do these compounds behave in aqueous solution? What are products and byproducts of reactions? Organics:

Natural

Synthetic

Xenobiotic (from the Greek "Xenon" the stranger)

#### Properties

- Solubility volatility adsorptivity (bioaccumulate into fatty tissue)
- Toxicity (carcinogenic; mutagenic; teratogenic [birth defects])
- Both *acute* and *chronic*
- Biodegradability (recalcitrant = not degradable or very resistant; persistent = long lived or slow to degrade)

General: organics burn easily, are not very water soluble, have relatively low boiling points, have non-ionic (covalent {i.e. electron sharing} or polar covalent) bonds and thus slower reaction rates, are often very high in molecular weight, and are degradable by microorganisms Particular: Natural compounds contain C, H, O, N, P and S Xenobiotics may contain halogens (Cl, Br, F) Ability of Carbon to have numerous valence states and bonds with particular geometry leads to the incredible diversity and complexity of organic chemistry

#### Carbon

Four outer shell electrons wants to complete "octet" bonds are tetrahedral single C-C bonds allow free rotation about axis of bond double bonds and triple bonds are rigid Carbon may link up in unbranched (aka straight) chains, branched chains, and rings (cyclic compounds)

#### Models vs Reality

We use a representational shorthand to write out chemical structures. Thus a 2-D representation of a 3-D phenomenon. We also tend to draw orthogonally (straight lines and right angles), and that is not true either. The tetrahedral nature of the carbon bond angles won't allow it. But it is quicker and we learn to compensate.

For example we can write the formula for methane, the simplest hydrocarbon, as CH<sub>4</sub> and draw the structure as:

Another example is ethane, the simplest 2-carbon hydrocarbon, C<sub>2</sub>H<sub>6</sub>, which we draw as but we can also write CH<sub>3</sub>-CH<sub>3</sub>.

Another caution: isomerism

We get in trouble when we try to use simple chemical formulae, as in inorganic chemistry (e.g.  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ ) to unambiguously describe reactions or identify organic compounds. If we say  $\text{C}_2\text{H}_6\text{O}$ , for example do we mean:

$\text{CH}_3\text{-O-CH}_3$  (dimethyl ether) or, do we mean:

$\text{CH}_3\text{-CH}_2\text{OH}$  ethanol.

Another example:  $\text{C}_4\text{H}_{10}$  which can be drawn as:

$\text{CH}_3\text{-CH}_3\text{-CH-CH}_3$  (isobutane or 2-methylpropane) or

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{CH}_3$  (butane)

**Aromatic compounds contain a benzene ring. All other organics are aliphatics.**

Hydrocarbons contain only hydrogen and carbon.

Saturated hydrocarbons have only single carbon-carbon bonds.

All the other bonds to carbon are satisfied by hydrogen.

Unsaturated hydrocarbons have one or more double or triple carbon-carbon bonds.

The homologous series of saturated hydrocarbons is called the alkanes (or paraffins). You must know these by rote to ten (decane).

The first part of the name gives the number of carbons in the chain, it is the root or parent name, the -ane ending means that it is saturated and contains no double bonds. If these compounds are substituents on other carbon chains then we drop the ane and add yl. Thus methyl groups, ether groups.

The Alkanes are colorless odorless and relatively insoluble. Their chemical formula is  $\text{C}_n\text{H}_{2n+2}$ .

If the compound is an unbranched chain then it is often called "n-alkane" for normal. See step-by-step naming rules.

Cyclic alkanes have formula  $\text{C}_n\text{H}_{2n}$ . Note examples.

Now, the homologous series of unsaturated hydrocarbons are called **alkenes**:

Ethene, propene, butene, pentene etc...

Note that there are structural isomers. So you must name the position of the double bond, using the lowest numbered carbon in the parent chain that has the bond.

- Substituents follow the same rules as in alkanes. If two double bonds then the compound is a diene -- butadiene, pentadiene with the appropriate numbers in prefix.
- If the alkene is a substituent on another chain then the suffix becomes enyl, as in ethenyl (common: vinyl). Propenyl.

### OTHER SUBSTITUENTS

Halides-do not change the name of the compound they are bound to. Naming conventions follow similar rules as if it were an alkyl group.

Obviously other organic functional groups may bond with a carbon of an aliphatic compound. Some of these substituents are so important to the behavior of the compound that they give the compound a new name.

In particular **alcohols**, **thiols (-SH)**, **amines**, **aldehydes** and **carboxylic acid** functional groups affect the aqueous chemical properties of organic compounds enormously.

- **Alcohols. -OH** group substituents. Select longest chain to which hydroxyl is attached. Drop final a and add ol. This is parent alcohol. Number the chain to give the alcohol the lower number when counting from end of chain. If two hydroxyl substituents, then it is a **diol** (common: glycol).
  1. If hydroxyl substituent is on a carbon atom connected to one other carbon atom (e.g. at the end of a chain) then the alcohol is a primary.
  2. If the hydroxyl group is on a carbon atom bonded to two other carbons, then it is a secondary alcohol (2-butanol aka sec-butanol).
  3. And tertiary, the carbon bonds to three other carbons and to the hydroxyl group (e.g. tert-butyl alcohol).
- **Aldehydes** and **Ketones. -HC=O** or **C=O**. Functional group at **end of chain** (**aldehyde**) gives the name -al. Functional group in **middle of chain** (**ketone**) gives -one suffix (propanone). If not name giver then an oxo- substituent.
- **Thiols. -SH** functional group. If naming compound, it is a -thiol suffix (ethanethiol). If a substituent, it is mercapto- prefix.
- **Carboxylic acid. -COOH** functional group. If it names the compound then the suffix is -oic acid. Methanoic, ethanoic, propanoic etc. But these "fatty" acids have many common names. Formic, Acetic, propionic, butyric, valeric, caproic, etc. If a substituent, then prefix carboxy-.
- **Ethers. R-O-R'**. Where R and R' are any alkyl groups. If naming the compound, identify R and R' and end with ether e.g. ethylmethyl ether. If a substituent then alkyloxy- prefix (methoxy e.g.).
- **Amine. -NH<sub>2</sub>, R-NH<sub>2</sub>, R-NH-R', or R-NR'-R''** where R is any alkyl group. If naming, then list R groups followed by amine (Ethyl amine). If a substituent then amino- prefix. If R, then primary amine. If R and R', secondary amine. If R, R', and R'' then tertiary amine. Can also have quaternary amine (bactericide and toxicant, suspected carcinogen)

Chemical species	Structure	Biological importance
Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$	Organic, amino, and fatty acids
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$	Functional group of reducing sugars such as glucose
Alcohol	$\begin{array}{c} \text{H} \\   \\ -\text{C}-\text{OH} \\   \\ \text{H} \end{array}$	Lipids, carbohydrates
Keto	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$	Pyruvate, citric acid cycle intermediates
Ester	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad \parallel \\ -\text{C}-\text{O}-\text{C}- \\   \\ \text{H} \end{array}$	Lipids, amino acid attachment to tRNAs
Ether	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{O}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	Archaeobacterial lipids, sphingolipids

Covalent bonds	Bond energy
<b>Single bonds</b>	
H-H	436
C-H	411
C-O	369
C-N	294
C-S	260
<b>Double bonds</b>	
C=C	616
C=O	704
O=O	402
<b>Triple bonds</b>	
C≡C	805
N≡N	955
Noncovalent interactions	Energy
Hydrogen bonds	4.2-8.4
Hydrophobic interactions	4.2-8.4
van der Waal's attractions	4.2-8.4

*\*The bond energies are given as the amount of heat, in kilojoules per mole, needed to break the bonds.*

## Nomenclature of Alkanes, Alkyl Halides and Alcohols

### Branched-chain alkanes:

1. Locate longest chain of carbon atoms; this chain determines name.
2. Number the longest chain, beginning with the end nearer the substituent.
3. Use number from rule 2 to designate location of substituent.
4. With two or more substituents, give each a number based on location along chain.
- 4a. Use alphabetical naming hierarchy (e.g. ethyl before methyl).
5. With two or more on same carbon atom, use that number twice (or more).
6. When two or more substituents are identical, use prefixes di-, tri-, tetra- etc.
7. When two chains are of equal length, choose the chain with the greater number of substituents.
8. When branching first occurs at equal distance from either end, choose the name that gives the lower number at the first point of difference.

### Alkyl Halides:

Halogens as substituents

Cl	Chloro
Br	Bromo
F	Fluoro
I	Iodo-

Use rules 3, 4, 5, and 6 to indicate halide substituents in the name of the compound.

### Alcohols:

Hydroxyl group (-OH) often results in compound being named as an alcohol.

1. Select longest continuous carbon chain to which the hydroxyl is directly attached. Change name of alkane by dropping final -e and adding -ol. This is base name of the alcohol.
2. Number the chain to give the carbon with the -OH the lower number. Use number to indicate position along carbon chain.

Hydroxyl group also is sometimes considered as a substituent. If so, it is called hydroxy and is indicated in name following rules used for alkyl or halo substituents.

## Substitutive and parental names (prefixes and suffixes) for some important functional groups

Functional Group	Formula	Prefix (substituents)	Suffix (parent)	Examples	Name
Alcohol	-OH	hydroxy-	-ol	CH <sub>3</sub> -CH <sub>2</sub> OH CH <sub>3</sub> -CHOH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> CH <sub>2</sub> OH-CH=CH	Methanol 2-pentanol (isopentanol) 3-hydroxy-1-propane
If 2 hydroxy, then glycol	-OH	dihydroxy-	-glycol; -diol	CH <sub>2</sub> OH-CH <sub>2</sub> -CHOH-CH <sub>3</sub> CH <sub>2</sub> OH-CH <sub>2</sub> OH	1,3-butanediol 1,2-ethanediol (ethylene glycol)
Aldehyde	-CHO		-al	CH <sub>3</sub> -CHO	ethanal (acetaldehyde)
ketone	-(C)OR	oxo	-one	CH <sub>3</sub> -CO-CH <sub>3</sub>	2-propanone (2-oxopropane)
Carboxylic acid	-COOH	carboxy	-oic acid	CH <sub>3</sub> -COON CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -COOH	ethanoic acid (acetic acid) pentanoic acid (valeric acid)
alkanedioic acids			Common name dioic	COOH-COOH COON-CH <sub>2</sub> -COOH COOH-(CH <sub>2</sub> ) <sub>2</sub> -COOH	oxalic acid malonic acid succinic acid
Ester	-COOR -(C)OOR	alkoxycarbonyl	Alkyl, -oate	CH <sub>3</sub> -COO-CH <sub>3</sub>	methylethanoate (methyl acetate)
Amine	-NH <sub>2</sub>	amino	RR'R"-amine	CH <sub>3</sub> -CH <sub>2</sub> -CHNH <sub>2</sub> -CH <sub>3</sub> CH <sub>3</sub> -NH-CH <sub>3</sub> CH <sub>3</sub> -CH <sub>2</sub> -N(CH <sub>3</sub> ) <sub>2</sub>	1,2-ammobutane (sec-butylamine) dimethylamine ethyl dimethylamine
Ether	R-O-R	alkyloxy-	RR'ether	CH <sub>3</sub> -C(OCH <sub>3</sub> )H-CH <sub>2</sub> -CH <sub>3</sub>	Isobutylmethylether (2-methyloxybutane)
Nitrile	-C≡N	cyano-	-nitrile	CH <sub>3</sub> -CH(CN)-CH <sub>3</sub> CH <sub>3</sub> -CN	2-cyanopropane acetonitrile
Thiols	-SH	mercapto-	-thiol	CH <sub>3</sub> -CH <sub>2</sub> SH	Ethanethiol
Benzene	Benzene ring	Phenyl (not benzyl)		CH( ) <sub>2</sub> -CH <sub>3</sub>	1,1-diphenylethane
Nitro	-NO <sub>2</sub>	nitro-			
Sulfonic acids	-SO <sub>3</sub> H	Sulfo-	Sulfonic acid		

## Structure-Function Relationships

CMPD	Formula	~ mw	BP	DENSITY @ 20' g/L	pKa	solubility g/100 ml
methane	CH <sub>4</sub>	16	-161.5	gaseous		0.005
ethane	C <sub>2</sub> H <sub>6</sub>	30	-88.6	gaseous		
propane	C <sub>3</sub> H <sub>8</sub>	44	-42.1	gaseous		
butane	C <sub>4</sub> H <sub>10</sub>	58	-0.5	gaseous		
pentane	C <sub>5</sub> H <sub>12</sub>	72	36.1	0.626		insoluble
hexane	C <sub>6</sub> H <sub>14</sub>	86	68.7	0.659		insoluble
heptane	C <sub>7</sub> H <sub>16</sub>	100	98.4	0.684		insoluble
octane	C <sub>8</sub> H <sub>18</sub>	114	125.7	0.703		insoluble
nonane	C <sub>9</sub> H <sub>20</sub>	128	1500.8	0.718		insoluble
decane	C <sub>10</sub> H <sub>22</sub>	142	174.1	0.73		insoluble
cyclopropane	C <sub>3</sub> H <sub>6</sub>	42	-33	gaseous		
cyclobutane	C <sub>4</sub> H <sub>8</sub>	56	13	gaseous		
cyclopentane	C <sub>5</sub> H <sub>10</sub>	70	49	0.751		
cyclohexane	C <sub>6</sub> H <sub>12</sub>	84	81	0.779		
chloromethane	CH <sub>3</sub> Cl	50.4	-24.2	gaseous		1
dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	84.9	40.1	1.33		2
trichloromethane	CHCl <sub>3</sub>	119.4	61.2	1.49		1
tetrachloromethane	CCl <sub>4</sub>	153.8	76.8	1.59		0.08
methanol	CH <sub>3</sub> OH	32	64.6	0.69		infinite
methanal	H <sub>2</sub> CO	30	-21			very sol.
methanoic acid	HCOOH	46	100.7		3.752	infinite
ethanoic "	CH <sub>3</sub> COOH	60	118	1.02	4.754	infinite
propanoic	CH <sub>3</sub> CH <sub>2</sub> COOH	74	141		4.873	infinite
butanoic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	88	164		4.839	infinite
pentanoic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	102	187		4.818	4.97
hexanoic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	116	205		4.883	1.08
chloroethanoic acid	CH <sub>2</sub> ClCOOH	94.5			2.854	V. SOL.
dichloroethanoic acid	CHCl <sub>2</sub> COOH	130			1.479	V. SOL.
trichloroethanoic acid	CCl <sub>3</sub> COOH	163			1.699	V. SOL.
2-chloropropanoic acid	CH <sub>3</sub> CHClCOOH	106			2.833	SOL
3-chloropropanoic acid	CH <sub>2</sub> ClCH <sub>2</sub> COOH	106			3.983	SOL

As chain lengths (and mw) increase, by and densely increase. Compounds get more hydrophobic. Water solubility drops with chain length. Polar functional groups (aldehydes, carboxylic acids and alcohol, thiols, and amines) greatly affect solubility. Hydrogen bonds with water become possible.

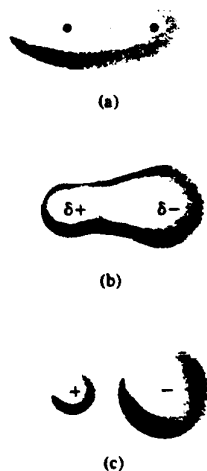
Other factors beside chain length and the polarity of substituents affect the properties of organic chemicals. In particular the polarity of the molecule itself characterized by its dipole moment. This measure of the attractive forces of different atoms for their shared electrons is a vector quantity. Thus molecules with offsetting dipoles, like tetra-chloromethane have a net dipole moment of zero. Chloromethane has a large dipole moment. Similarly planar molecules like dimethyl-ether or carbon dioxide will have dipoles that sum to zero, thus giving the molecule relatively little polar nature in aqueous solution even though the carbon-oxygen bond is polar in nature.

Halogen substituents affect compounds in complex ways. Density and molecular weight are obvious. Chlorine is a large and heavy atom compared to carbon and especially compared to hydrogen. Yet the dipole moment of the carbon-halogen bond also plays a part. Note how the solubility of chloromethane is increased 200 fold by the replacement of a hydrogen with chloride. When another chloride is added one would expect the dipole moment to be offset to some degree and the solubility to drop; it doesn't, but rather is doubled. Trichloro-methane sees the solubility fall and with carbon tetrachloride fall even further. Note the effect of chloride substituent on the acidity constant of acetic acid, withdrawing electrons from the carbon and making the carboxyl group much more eager to shed its proton. The effect is more pronounced in 2-cl-propanoic acid than in 3-chloropropanoic acid.

← Increasing electronegativity →

																		H 2.1																			
Decreasing electronegativity ↓		Li 1.0	Be 1.5															B 2.0	C 2.5	N 3.0	O 3.5	F 4.0															
		Na 0.9	Mg 1.2															Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0															
		K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8																			
		Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5																			
		Cs 0.7	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2																			
		Fr 0.7	Ra 0.9	Ac	Th 1.3	Pa 1.4	U 1.4	Np-No 1.4-1.3																													

The Pauling electronegativity values. Electronegativity generally increases across a period and decreases down a group.



The three possible types of bonds: (a) a covalent bond formed between identical atoms; (b) a polar covalent bond, with both ionic and covalent components; and (c) an ionic bond, with no electron sharing.