



Lecture 2 Organic Chemistry (1)

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Intensive Teaching and Practicing

Point 1: Representing organic molecules

Organic molecules can be represented by the empirical formula and molecular formula.

Empirical formula is the simplest whole number ratio of the elements present in a compound.

Molecular formula is the total number of atoms of each element present in a molecule of the compound. A molecular formula is an integer multiple of the empirical formula.

The molecular formula of an organic compound may not be particularly useful, since there is usually more than one possible structure. We can present formulae in the following ways.

Structural formula shows the minimal detail that shows the arrangement of atoms in a molecule. For example, the structural formula of butane is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$.

Displayed formula shows all the covalent bonds present in a molecule. For example skeletal formula.

Skeletal formula is the simplest representation that is shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated function groups. Each 'zig-zag' represents one carbon atom. All other atoms that are not carbon or hydrogen, and their bonds, are included in the skeletal formula of an organic molecule.

The displayed and skeletal formulae of an alcohol called butan-2-ol are shown below:



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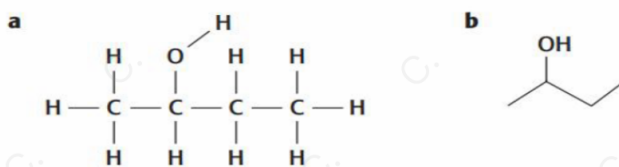
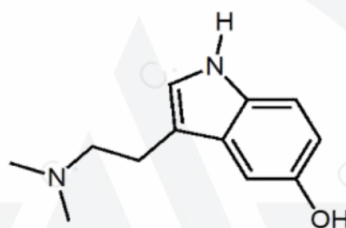


Fig 2. a. The displayed formula of butan-2-ol; b. the skeletal of butan-2-ol

The molecular formula of an alcohol called butan-2-ol is $C_4H_{10}O$

The structure formula of an alcohol called butan-2-ol is $CH_3CH(OH)CH_2CH_3$

Example 1. The structure below is a substance found in the skin of certain species of amphibians. In large quantities, the substance can have a psychoactive effect on humans, changing brain function and altering behaviour. What is the correct molecular formula of the substance? (Source: 2020, CCC, a, 07)



A) $C_{12}H_{16}N_2O$

B) $C_{10}H_{12}N_2O$

C) $C_{11}H_{14}N_2O$

D) $C_{12}H_{18}NO$

E) $C_{12}H_{14}N_2O$

Point 2: Functional groups

Different homologous series have different **functional groups**.

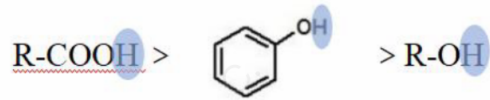
A functional group is the atom or group of atoms in a molecule that gives it its characteristic chemical properties - this is the reactive part of a molecule.

The table below shows the functional groups you are likely to meet.

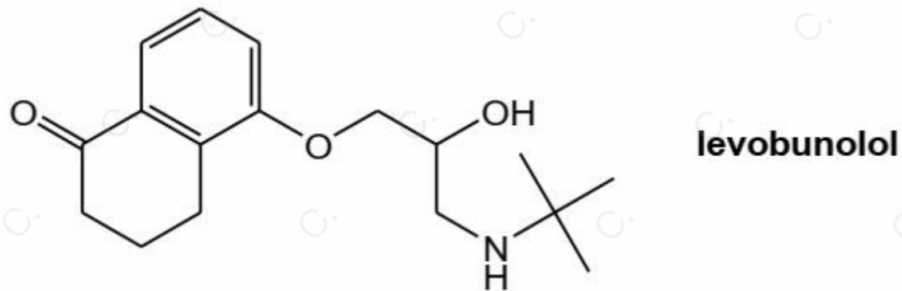
Homologous series / class name	Functional group	Functional group name	Example	General name	Name
alkane		alkyl		alkane	butane
alkene	C=C	alkenyl		alk-x-ene (or x-alkene)	but-1-ene (or 1-butene)
alkynes	C≡C	alkynyl		alk-x-yne (or x-alkyne)	but-1-yne (or 1-butyne)
alcohol	-OH	hydroxyl		alkan-x-ol (or x-alkanol)	propan-1-ol (or 1-propanol)
ether		ether		alkoxyalkane	methoxyethane
aldehyde		carbonyl		alkanal	propanal
ketone				alkan-x-one (or x-alkanone)	pentan-2-one (or 2-pentanone)
carboxylic acid		carboxyl		alkanoic acid	propanoic acid
halogenoalkane	-X X=Cl/Br/I	halo (chloro, bromo, iodo)		x-haloalkane	2-bromobutane
amine	-NH ₂ -NHR -NR ₂	amino		alkylamine or x-aminoalkane or alkan-x-amine (or x-alkanamine)	propylamine or 1-aminopropane or propan-1-amine (or 1-propanamine)
ester		ester		alkyl alkanoate	methyl propanoate
a	-C≡N	nitrile		alkanenitrile (C of C≡N included in chain)	propanenitrile
amide		carboxamide		alkanamide	propanamide

Fig 5 Functional groups that you are likely to meet.
(Chemistry for IB Diploma Coursebook 2nd edition)

Extention:Acidity of hydrogen in these three functional groups:



Example 2. Levobunolol (structure below) is used topically to treat glaucoma, an eye disorder which causes damage to the optic nerve. Which of the following functional groups are contained within the structure of levobunolol? (*source:2016, CCC, a, 10*)



- A) amine, ketone, ether, phenol
- B) amide, ketone, ether, alcohol
- C) amine, ketone, ester, alcohol
- D) amine, ketone, ether, alcohol
- E) amine, aldehyde, ether, alcohol



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Point 3: Organic naming

There are over 16 million known organic compounds. They can't all have simple names, and no-one would remember them if they did. For this reason, the International Union of Pure and Applied Chemistry (IUPAC) have developed systematic nomenclature, a set of rules that allows any compound to be given a unique name that can be deduced directly from its chemical structure. Conversely, a chemical structure can be deduced from its systematic name.

Systematic names can be divided into three parts: one describes the hydrocarbon framework, one describes the functional groups, and one indicates where the functional groups are attached to the skeleton.

You have already met the names for some simple fragments of hydrocarbon framework (methyl, ethyl, propyl). Adding a hydrogen atom to these alkyl fragments and changing -yl to -ane makes the alkanes and their names. You should hardly need reminding of their structures:



Names for the hydrocarbon framework

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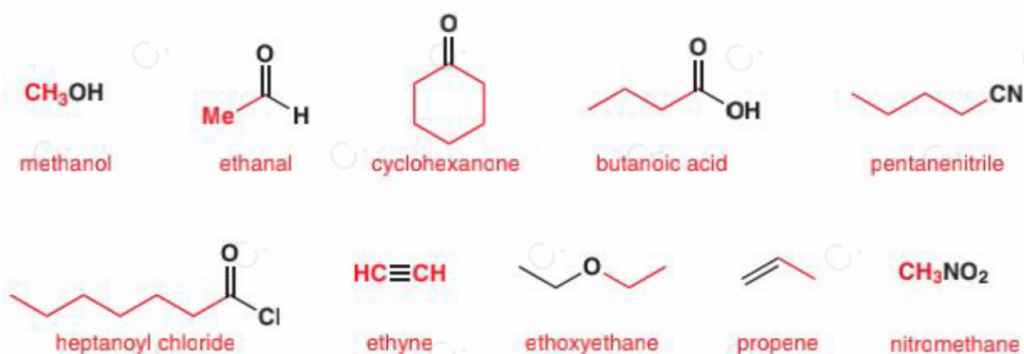
one carbon	methane	CH_4	
two carbons	ethane	$\text{H}_3\text{C}-\text{CH}_3$	
three carbons	propane	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_3$	cyclopropane 
four carbons	butane	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	cyclobutane 
five carbons	pentane	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	cyclopentane 
six carbons	hexane	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	cyclohexane 
seven carbons	heptane	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	cycloheptane 
eight carbons	octane	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	cyclooctane 
nine carbons	nonane	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	cyclononane 
ten carbons	decane	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	cyclodecane 

Fig. 2_organic chemistry Jonathan clayden 2nd Edition P34

The name of a functional group can be added to the name of a hydrocarbon framework either as a suffix or as a prefix. Some examples follow. It is important to count all of the carbon atoms in the chain, even if one of them is part of a functional group: pentanenitrile is actually BuCN. Compounds with functional groups attached to a benzene ring are named in a similar way.

Fig. 2_organic chemistry Jonathan clayden 2nd Edition P35

Numbers are used to locate functional groups

Sometimes a number can be included in the name to indicate which carbon atom the functional group is attached to. None of the above list needed a number—check that you can see why not for each one. When numbers are used, the carbon atoms are counted from one end.

In most cases, either of two numbers could be used (depending on which end you count from); the one chosen is always the lower of the two. Again, some examples will illustrate this point. Notice again that some functional groups are named by prefixes, some by suffixes, and that the number always goes directly before the functional group name.

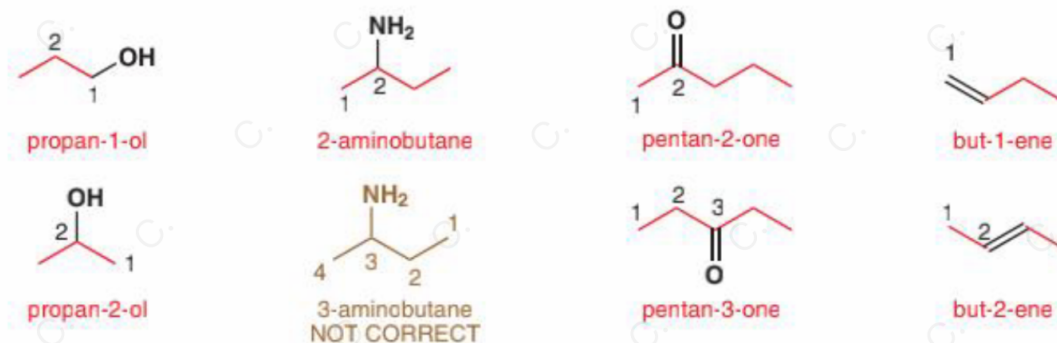


Fig. 2_organic chemistry Jonathan clayden 2nd Edition P35

One carbon atom can have as many as four functional groups: this limit is reached with tetrabromomethane, CBr_4 . Here are some other examples of compounds with more than one functional group.

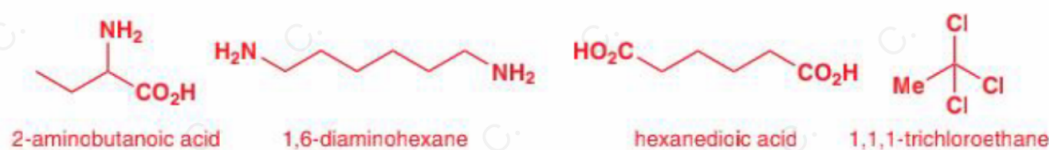


Fig. 2_organic chemistry Jonathan clayden 2nd Edition P35

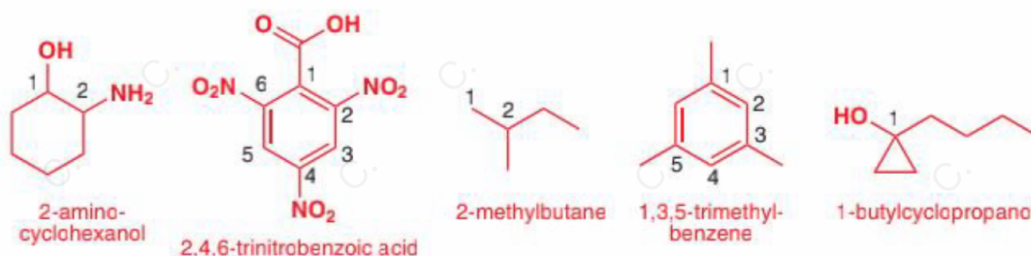
Again, the numbers indicate how far the functional groups are from the end of the carbon chain. Counting must always be from the same end for each functional group. Notice how we use di-, tri-, and tetra- if there is more than one of the same functional group.

With cyclic compounds, there isn't an end to the chain, but we can use numbers to show the distance between the two groups—start from the carbon atom carrying



one of the functional groups, then count round. These rules work for hydrocarbon frameworks that are chains or rings, but many skeletons are branched. We can name these by treating the branch as though it were a functional group.

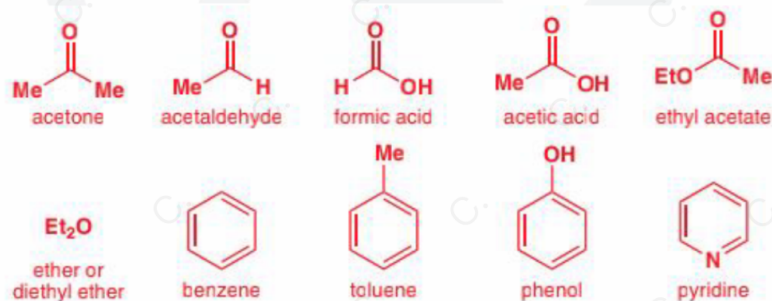
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Fig. 2_organic chemistry Jonathan clayden 2nd Edition P35

Names for well-known and widely used simple compounds

A few simple compounds are called by trivial names not because the systematic names are complicated, but just out of habit. We know them so well that we use their familiar names.

You may have met the compound on the right before and perhaps called it ethanoic acid, its systematic name. But in a chemical laboratory everyone would refer to this acid as acetic acid, its trivial name. The same is true for all these common substances.

Fig. 2_organic chemistry Jonathan clayden 2nd Edition P37

Trivial names like this are often long-lasting, well-understood historical names that are less easy to confuse than their systematic counterparts. 'Acetaldehyde' is easier to distinguish from 'ethanol' than is 'ethanal'.

Trivial names also extend to fragments of structures containing functional groups. Acetone, acetaldehyde, and acetic acid all contain the acetyl group (MeCO-, ethanoyl) abbreviated Ac and chemists often use this organic element symbol in writing AcOH for acetic acid or EtOAc for ethyl acetate. Chemists use special names for four

fragments because they have mechanistic as well as structural significance. These are vinyl and allyl, phenyl and benzyl.

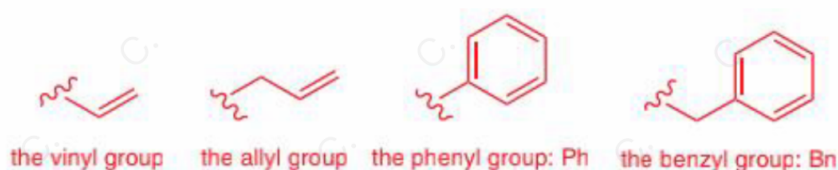


Fig. 2_organic cheimstry Jonathan clayden 2nd Edition P37

Giving the vinyl group a name allows chemists to use simple trivial names for compounds like vinyl chloride, the material that polymerizes to give PVC (polyvinyl chloride) but the importance of the name lies more in the difference in reactivity (Chapter 15) between the vinyl and allyl groups.

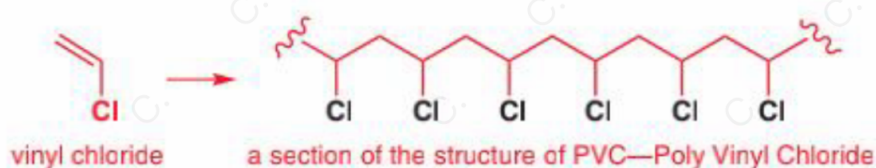
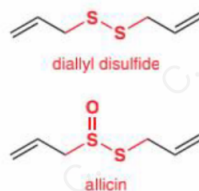
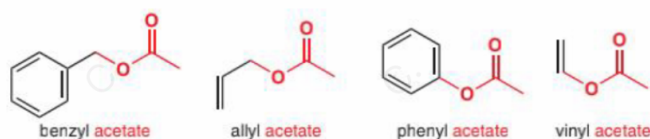


Fig. 2_organic cheimstry Jonathan clayden 2nd Edition P37

The allyl group gets its name from garlic (*Allium* sp.) because it makes up part of the structure of the compounds on the right responsible for the taste and smell of garlic. Allyl and vinyl are different in that the vinyl group is attached directly to a double-bonded C=C carbon atom, while the allyl group is attached to a carbon atom adjacent to the C=C double bond. The difference is extremely important chemically: allyl compounds are typically quite reactive, while vinyl compounds are fairly unreactive. For some reason, the allyl and vinyl groups have never acquired organic element symbols, but the benzyl group has and it is Bn. It is again important not to confuse the benzyl group with the phenyl group: the phenyl group is joined through a carbon atom in the ring, while the benzyl group is joined through a carbon atom attached to the ring. Phenyl compounds are typically unreactive but benzyl compounds are often reactive. Phenyl is like vinyl, and benzyl is like allyl. We shall review all the organic element symbols you have met at the end of the chapter.



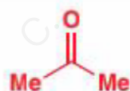
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Fig . 2_organic cheimstry Jonathan clayden 2nd Edition P37Fig . 2_organic cheimstry Jonathan clayden 2nd Edition P38

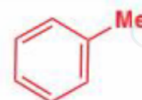
We've met a great many molecules in this chapter. Most of them were just there to illustrate points so don't learn their structures! Instead, learn to recognize the names of the functional groups they contain. However, there were 10 names for simple compounds and three for common solvents that we advised you to learn. Cover up the right-hand part of each column and draw the structures for these 14 compounds.

Important structures to learn

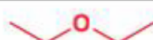
acetone



toluene



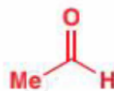
ether or diethyl-ether



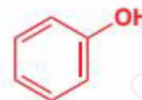
pyridine



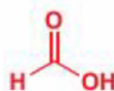
acetaldehyde



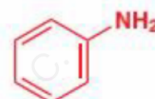
phenol



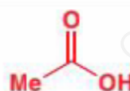
formic acid



aniline



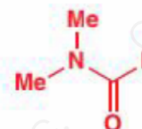
acetic acid or AcOH



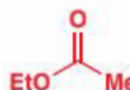
THF or tetrahydrofuran



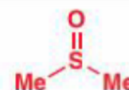
benzene

DMF, Me₂NCHO, or dimethylformamide

ethyl acetate or EtOAc






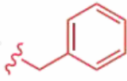









DMSO




That's all we'll say on the subject of nomenclature—you'll find that as you practise using these names and start hearing other people referring to compounds by name you'll soon pick up the most important ones. But, to reiterate, make sure you never pass a compound name by without being absolutely sure what it refers to—draw a structure to check.

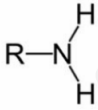
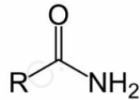
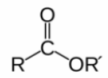
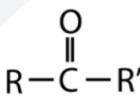
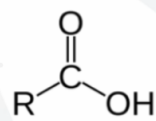
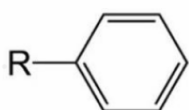
● Review box: Table of fragment names and 'organic elements'

R	alkyl		t-Bu	tert-butyl	
Me	methyl		Ar	aryl	any aromatic ring
Et	ethyl		Ph	phenyl	
Pr (n-Pr)	propyl		Bn	benzyl	
Bu (n-Bu)	butyl		Ac	acetyl	
i-Pr	isopropyl			vinyl	
i-Bu	isobutyl			allyl	
s-Bu	sec-butyl		X	halide	F, Cl, Br or I

We also summarized the rules of organic naming. Following the rules can help you solve most organic naming problems.

Rule 1: Identify the functional group

Class :	Alkane	Alkenes	Alkynes
Functional Group :	$-\text{C} - \text{C} -$	$-\text{C} = \text{C} -$	$-\text{C} \equiv \text{C} -$
Suffix	-ane	-ene	-yne
Class :	Alcohols	Aldehyde	
Functional Group :	$-\text{OH}$		
Name/Suffix	Hydroxyl	-ol	Aldehyde
			-al

Class :	Amine		Amide
Functional Group :			
Name	Amines		Carboxamide
Class :	Ether	Ester	Nitrile
Functional Group :	-O - C		-C ≡ N
Name	Ether	Ester	Nitrile
Class	Ketones	Carboxylic Acid	Arenes
Functional Group :			
Name/Suffix	Carbonyl	- one	Carboxyl
			Phenyl
Class	Halogenoalkanes		
Functional Group :	-F	-Cl	-Br
Prefix	Fluoro-	Chloro-	Bromo-

Rule 2: selecting the functional group

When organic compounds contain multiple functional groups, the most preferred functional group should be the main functional group, and other functional groups should be used as substituents.

The priority of functional groups is: carboxylic acid > sulfonic acid > carboxylic acid ester > acyl halide > amide > anhydride > nitrile > aldehyde > ketone > alcohol > mercaptan > phenol > mercaptan > amine > alkyne > olefin > ether > sulfide > halogenated hydrocarbon > nitro compound > nitroso compound.

-COOH > -SO₃H > -COOR > -COX > -CONH₂ > -COOCO- > -CN > -CHO > -CO- > -OH > -SH > -NH₂ > -C≡C- > -C=C- > -OR > -SR > -F > -Cl > -Br > -I > -NO₂ > -NO

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Rule 3: Longest carbon chain principle (find the longest chain of carbon atoms)

(1) When organic compound does not contain functional groups, the carbon chain with the most carbon atoms should be selected as the main chain.

Number of carbons	Stem used in naming
1	meth-
2	eth-
3	prop-
4	but-
5	bent-
6	hex-
7	hept-
8	oct-
9	nen-
10	dec-

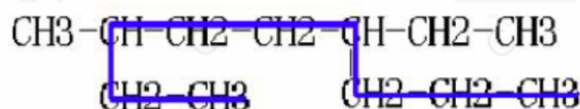
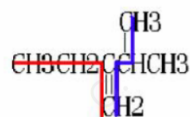


Fig 4

As shown in fig 4, the main chain is the carbon chain library covered by the blue line.

(2) If it is found that organic compound contains the longest carbon chain with multiple carbon atoms of the same number, the one with the most branched chains should be selected the longest carbon chain is the main chain.



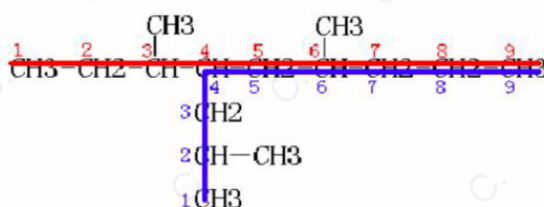
As shown in the figure, although both the carbon chain covered by the red line and the carbon chain covered by the blue line have four carbon atoms, the carbon chain covered by the red line has only one branch chain, while the carbon chain



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covered by the blue line has two branches. Therefore, the carbon chain covered by the blue line should be selected as the main chain.

(3) If an organic substance is found to contain multiple longest carbon chains with the same number of branched chains, the position of all substituents shall be considered, and the longest carbon chain with the largest number of branched chains and the smallest position of all substituents shall be selected as the main chain.



As shown in the figure, both the carbon chain covered by the red line and the carbon chain covered by the blue line have 7 carbon atoms, and both contain 3 branched chains. At this time, the position of substituents should be considered. The branched chain position of the carbon chain covered by the red line is 3,4,6, and the order of the branch chain of the carbon chain covered by the blue line is 2,4,6. Due to $2 < 3$, therefore, the substituent position of the carbon chain covered by the blue line is small. Therefore, the carbon chain covered by the blue line should be selected as the main chain.

(4) If an organic substance is found to contain multiple carbon atoms with the same number of branches and all substitutions. For the longest carbon chain with the same position occupied by the substituent, the longest carbon chain that can make **the least preferred substituent** occupy the smallest position should be selected.

(5) when there are two or more of the same groups, di-, tri-, tetra-, penta-, or hexa- are used.

(6) When organic compounds contain functional groups, **the main functional groups** must be selected into the main chain and as many as possible. **All functional groups** contained in the substance are selected into the main chain, and **the most preferred functional group** as the naming parent must be on the main chain, and the other principles are the same as (1) - (3).



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Example 3. (source, UKChO, 2011, 1d-1e)

The 'sharp' taste of the snack comes from citric acid. The IUPAC recommended name for citric acid is 2-hydroxypropane-1,2,3-tricarboxylic acid.

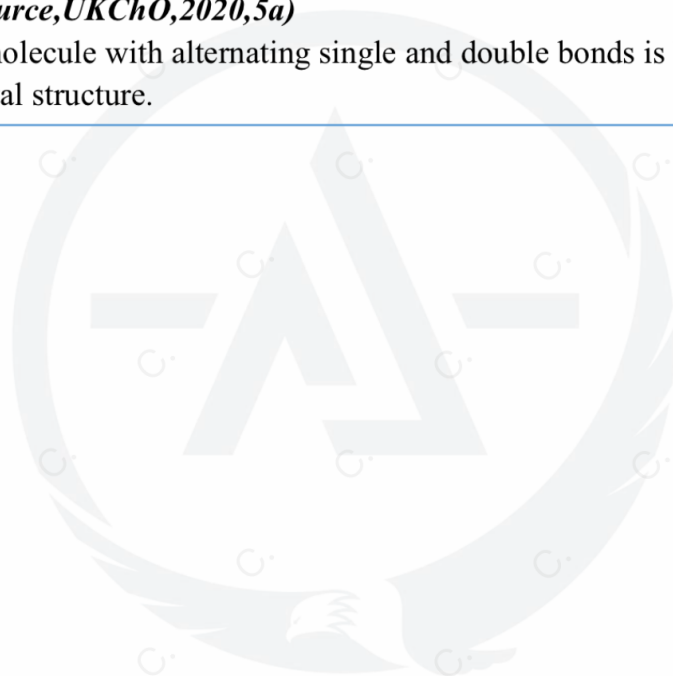
d) Draw the skeletal structure for citric acid.

A carbon atom bonded to four different groups is called a chiral centre or an asymmetric carbon atom.

e) How many chiral centres does a molecule of citric acid contain?

Exercise 1. (source, UKChO, 2020, 5a)

(a) A simple molecule with alternating single and double bonds is buta-1,3-diene. Draw its skeletal structure.





Point 4: Acidity, basicity, and pKa

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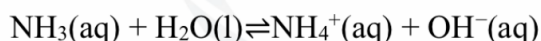
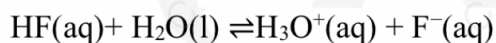
Arguably, the most important concept in organic chemistry is the concept of nucleophiles and electrophiles, as organic reactions are mostly reactions between them. The concept of nucleophiles and electrophiles is similar to acids and bases, in the sense that nucleophiles and electrophiles react with each other to form stable chemical species. Just instead of talking about proton affinity, the concept of nucleophiles and electrophiles deal with **electron affinity**.

In this chapter, we will learn the acidity and basicity of substances first.

4.1 Brønsted–Lowry acids and bases definition:

- Brønsted–Lowry acid is proton (H^+) donor
 $\text{HCl} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Cl}^-$, here HCl is an acid
- Brønsted–Lowry base is proton (H^+) acceptor
 $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$, here NH_3 acts as a base

Proton transfer between acids and bases is fast in both directions, so the dynamic equilibria:



give a more complete description of the behaviour of the acid HF and the base NH_3 , in water than the forward reaction alone. The central feature of Brønsted acid-base chemistry in aqueous solution is that of rapid attainment of equilibrium in the proton transfer reaction, and we concentrate on this aspect.

4.2 Conjugate acid and base pairs

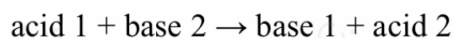
When a species donates a proton, it becomes the conjugate base. When a species gains a proton, it becomes the conjugate acid. Conjugate acids and bases are in equilibrium in solution.

The form of the two forward and reverse reactions given above, both of which depend on the transfer of a proton from an acid to a base, is expressed by writing the



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general Bronsted equilibrium as:



The species Base1, is called the conjugate base of Acid 1, and Acid 2 is the conjugate acid of Base 2. The conjugate base of an acid is the species that is left after a proton is lost. The conjugate acid of a base is the species formed when a proton is gained. Thus , **a conjugate acid is just another acid and a conjugate base is just another base.**

- ✓ In a reaction an acid loses an H^+ ion. The conjugate base of an acid is the species that is left after a proton is lost.

Acid	Conjugate base
HCl	Cl^-
H_2SO_4	HSO_4^-
H_2O	OH^-
CH_3COOH	CH_3COO^-
NH_4^+	NH_3

- ✓ The conjugate acid of a base is the species formed when a proton is gained.

Base	Conjugate acid
OH^-	H_2O
H_2O	H_3O^+
NH_3	NH_4^+
$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_3^+$
HSO_4^-	H_2SO_4

4.3 Lewis theory definition

Key point: An acid is an **electron pair acceptor**.

We denote a Lewis acid by A and a Lewis base by B , often omitting any other lone pairs that may be present. The fundamental reaction of Lewis acids and bases is the formation of a complex (or adduct) , A-B, in which A and B bond together by sharing the electron pair supplied by the base.

4.4 An isolated proton is extremely reactive—formation of H_3O^+ in water

Gaseous HCl is not an acid at all—it shows no tendency to dissociate into H^+ and Cl^- as the H–Cl bond is strong. But hydrochloric acid—that is, a solution of HCl in water—is a strong acid. The difference is that an isolated proton H^+ is too unstable to be encountered under normal conditions, but in water the hydrogen of HCl is transferred to a water molecule and not released as a free species.



4.4.1 A metal cation can accept an electron pair supplied by the base in a coordination compound.

The formation of a complex ion by a transition metal ion (Figure 8.6) is another example of a Lewis acid–base reaction. The transition metal ion is the Lewis acid and the ligand is the Lewis base. The ligands bond to the transition metal ion through the formation of coordinate covalent bonds. For example:

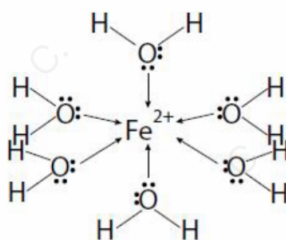
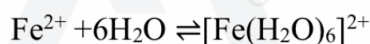


Figure 8.6 A transition metal complex ion.

(Chemistry for IB Diploma Cambridge textbook p311)

4.4.2 A molecule with an incomplete octet of valence electrons can complete its octet by accepting an electron pair.

A prime example is $\text{B}(\text{CH}_3)_3$ which can accept the lone pair of NH_3 , and other donors:





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Hence, B (CH₃)₃ is a Lewis acid.

4.4.3 A molecule or ion with a complete octet may be able to rearrange its valence electrons and accept an additional electron pair.

For example, CO₂ acts as a Lewis acid when it forms HCO₃²⁻; by accepting an electron pair from an O atom in an OH⁻ ion.



4.4.4 A molecule or ion may be able to expand its valence shell (or simply be large enough) to accept another electron pair.

An example is the formation of the complex [SiF₆]²⁻, when two F⁻ ions (the Lewis bases) bond to SiF₄ (the acid)



Exam tip :

For a substance to act as a Lewis base, it must have a lone pair of electrons, it is electron pair donor.

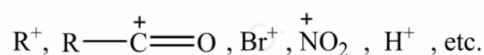
For a substance to act as a Lewis acid, it must have space to accept a pair of electrons in its outer shell, it is electron pair acceptor.

Actually, Lewis acid is an **electrophilic agent** and Lewis base is a **nucleophilic agent**

Can simply remember as:

Lewis acids mainly include the following types:

- ① Molecules that can accept electrons, such as BF₃, AlCl₃, SnCl₄, ZnCl₂, FeCl₃, etc;
- ② Metal ions, such as Li⁺, Ag⁺, Cu²⁺, etc;
- ③ Positive ions, such as:





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Lewis bases mainly include the following types:

- ① Compounds with lone pair electron, such as NH_3 , RNH_2 , ROH , ROR , $\text{RCH}=\text{O}$, $\text{R}_2\text{C}=\text{O}$, RSH , etc;
- ② Negative ions, such as X^- , HO^- , RO^- , HS^- , R^- , etc;
- ③ Alkenes or aromatic compounds, etc.

4.5 pH and pKa

4.5.1 The definition of pH

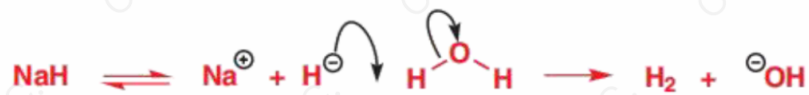
The amount of H_3O^+ in any solution in water is described using the pH scale. pH is simply a measure of the concentration of H_3O^+ on a logarithmic scale, and it is characteristic of any aqueous acid—it depends not only on what the acid is (hydrochloric, acetic, etc.) but also on how concentrated the acid is.

pH is the negative logarithm of the H_3O^+ concentration.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

4.5.2 Water can behave as an acid or as a base

So far we have seen water acting as a (very weak) base to form H_3O^+ . If we added a strong base, such as sodium hydride, to water, the base would deprotonate the water to give hydroxide ion, HO^- , and here the water would be acting as an acid. It's amusing to notice that hydrogen gas is the conjugate acid of hydride ion, but more important to note that hydroxide ion is the conjugate base of water.



Water is a weak acid and a weak base so we need a strong acid like HCl to give much H_3O^+ , and a strong base, like hydride ion, to give much hydroxide ion.

4.5.3 The ionization of water

The concentration of H_3O^+ ions in water is very low indeed at $10^{-7} \text{ mol dm}^{-3}$. Pure water at 25°C therefore has a pH of 7.00. Hydronium ions in pure water can arise only from water protonating (and deprotonating) itself. One molecule of water

acts as a base, deprotonating another that acts as an acid. For every H_3O^+ ion formed, a hydroxide ion must also be formed, so that in pure water at pH 7 the concentrations of H_3O^+ and hydroxide ions must be equal:

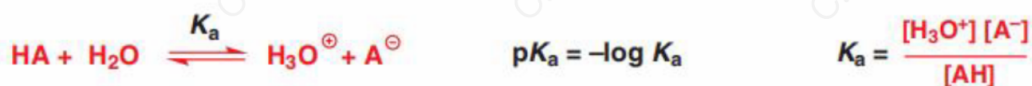
$$[\text{H}_3\text{O}^+] = [\text{HO}^-] = 10^{-7} \text{ mol dm}^{-3}.$$



The product of these two concentrations is known as the *ionization constant* (or as the *ionic product*) of water, K_w , with a value of $10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 25°C). This is a constant in aqueous solutions, so if we know the hydronium ion concentration (which we can get by measuring the pH), we also know the hydroxide concentration since the product of the two concentrations always equals 10^{-14} .

4.5.4 The definition of pKa

When we introduced you to pKa on p. 167, we said it is the pH at which an acid and its conjugate base are present in equal concentrations. We can now be more precise about the definition of pKa. pKa is the log (to the base ten) of the equilibrium constant for the dissociation of the acid. For an acid HA this is:



The concentration of water is ignored in the definition because it is also constant (at 25°C).

A low value of K_a corresponds to a high value of pKa and vice versa, so that the lower a pKa value is the stronger the acid.

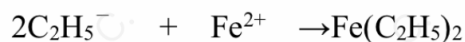
Acid	Formula	K_a	pKa
hydrofluoric acid	HF	5.62×10^{-4}	3.25
benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	6.31×10^{-5}	4.20
propanoic acid	$\text{CH}_3\text{CH}_2\text{COOH}$	1.35×10^{-5}	4.87
chloric(I) acid	HOCl	3.72×10^{-8}	7.43
hydrocyanic acid	HCN	3.98×10^{-10}	9.40

Table 8.4 K_a and pKa values of some acids – decreasing in strength downwards.

(Chemistry for IB Diploma Cambridge textbook p329)

4.6 Acid-Base theory in organic chemistry

Some substances that do not usually look like bases, such as ethylene and aromatic compounds, are bases according to Lewis acid-base theory. Such as:

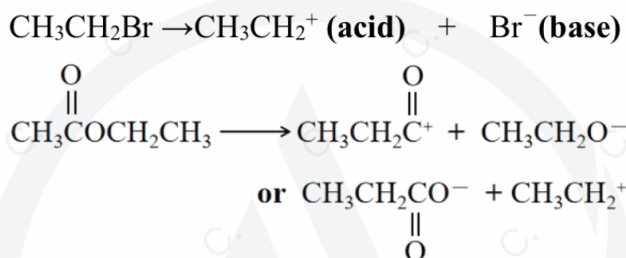


Due to the universal existence of coordination bonds in compounds, the definition of Lewis acids and bases can be more extensive.

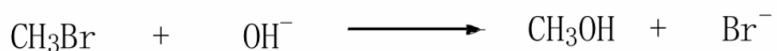
Acid: Cation or neutral molecule with empty orbital

Base: Anionic or neutral molecules that can bind to cations.

So we can split some organic compounds into two parts, here is an example:

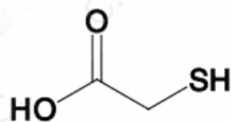


Some reactions in organic chemistry can be regarded as acid-base reactions. Like some substitution reactions. The so-called electrophilic reagent is Lewis acid; The nucleophile is Lewis base. Therefore, the electrophilic substitution reaction is the substitution reaction of Lewis acid, and the nucleophilic substitution reaction is the substitution reaction of Lewis base. For example:



**Example 4. (source, UKCHO, 2012, 3)**

Thioglycolic acid has two acidic protons. The pK_a values for the dissociation of these two protons are 3.67 and 10.31.



Thioglycolic acid

$$pK_a = -\log_{10} K_a$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pH = -\log_{10}[H^+]$$

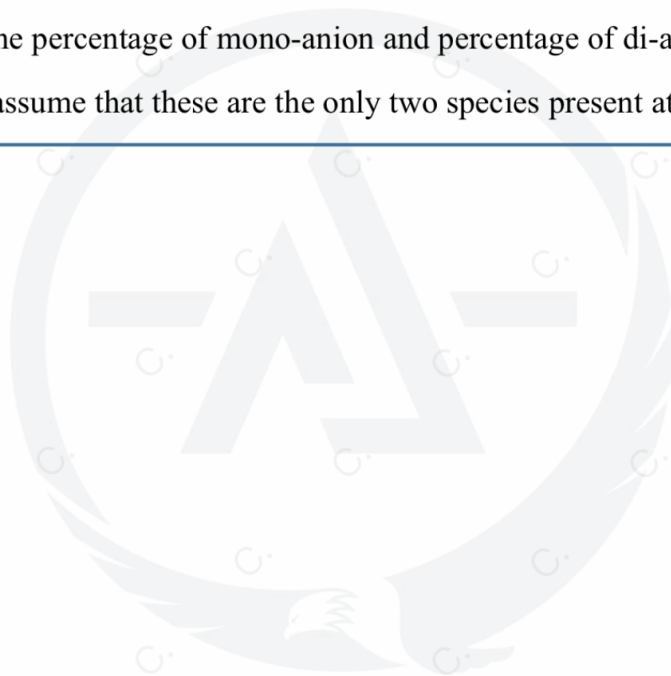
(c) Draw the predominant form of thioglycolic acid that is present in aqueous solution at

i) pH 0

ii) pH 7

iii) pH 14

(d) Calculate the percentage of mono-anion and percentage of di-anion present at pH 9.0. You may assume that these are the only two species present at this pH.



Point 5: Acidity of organic compounds

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5.1 Factors that affect acidity

It is handy to keep the relative acidity of protons in mind when attempting to solve organic chemistry problems. Now we will proceed to consider some factors that affect acidity:

1. Electronegativity

According to the definition of Lewis acid: An acid is an **electron pair acceptor**. The more easily they accept electrons, the greater the acidity.

Electronegativity is the ability to attract electrons. According to these two definitions, it can be clearly seen that:

In the same period, from left to right: the greater the electronegativity, the stronger the acidity. Here is a good example:

The acidity: $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$

2. Bond strength of H-X:

Since electronegativity decreases down the group as the atoms get bigger, it may seem that acidity should decrease going down the group. However, acidity actually increases down the group, which means that it must have increased due to a different reason. Down the group, the size of the atom increases significantly due to the increase in number of electron shells, which leads to an increase in the H-X bond length and a corresponding decrease in H-X bond strength. Thus, it is easier to break the H-X bond for the proton to dissociate and HX is more acidic.

In the same group, from top to bottom: the larger the radius, the stronger the acidity. Here is a good example:

The acidity: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

A comparison of thiol (R-S-H, $pK_a = 10.5$) with alcohol (R-O-H, $pK_a = 16-18$) is the other good example.

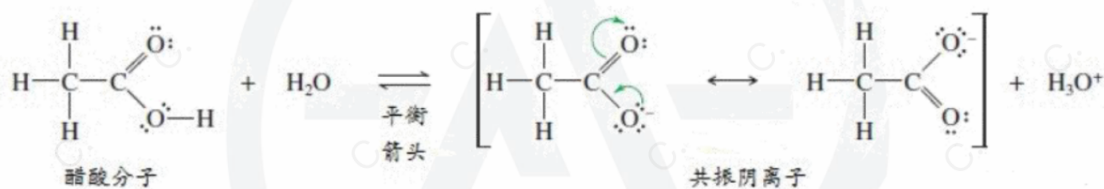
3. Inductive Effect:

Inductive effects are σ -effects that happen through the **polarisation of σ -bonds**, as electronegative atoms pull electron density in the σ -bonds towards them. This effect is obvious in trifluoroacetic acid: CF_3COOH (TFA), which is a strong acid due to the strongly electron-withdrawing nature of $-\text{CF}_3$ group that gives it pK_a of -1 as compared to acetic acid with pK_a of 4.76 . We can use the inductive effect to explain the acidity of the following substances:



4. Resonance effect

Just as how inductive effect is a σ -effect, the **resonance effect is a π -effect**. The negative charge can be delocalised over a π -system. We can use resonance theory to explain that carboxylic acid is more acidic than ethanol.



The resonance split the negative charge between the 2 oxygens. Due to resonance stabilization, the stability of acetate anion is greater than that of ethylic acid, so ethylic acid is more likely to lose protons and show a certain acidity. There is no π bond in ethanol molecule and no resonance structure in $\text{CH}_3\text{CH}_2\text{O}^-$, so the proton loss ability of ethanol is less than that of ethylic acid.

At point 6, we will study resonance more specifically.

5.2 Hydrocarmonic acid and the α Hydrogen activity

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5.2.1 The concept of Hydrocarmonic acid

Hydrocarbon can be regarded as a hydrocarmonic acid. The ability of hydrogen on carbon to dissociate with positive ions represents the acidity of hydrocarmonic acid. You can use PKa. To represent PKa. The smaller, the stronger the acidity. Table 13-1 lists the PK of some hydrocarbonate..

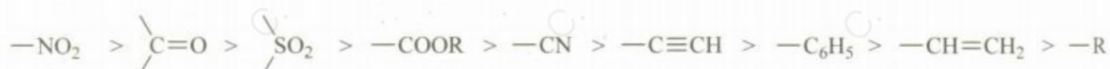
5.2.2 The acidity of α -hydrogen

The carbon directly connected to the functional group is called a carbon, and the hydrogen on a carbon is called a hydrogen.

PKa of some organic compounds

Compounds	CH ₃ SOCH ₃	CH ₃ CN	CH ₃ COC ₆ H ₅	CH ₃ NO ₂
pKa	29	25	16	10.21

The data in the table shows that CH₃NO₂ has the strongest α hydrogen acidity. This is because -NO₂ has strong electron absorption ability(**Inductive Effect**). That means, the acidity of α -hydrogen depends on the ability of electron absorption of the functional groups and other groups linked to α -carbon. The stronger the total electron absorption capacity, the more acidity of α -hydrogen is. The order of electron absorption capacity of some common groups is as follows:





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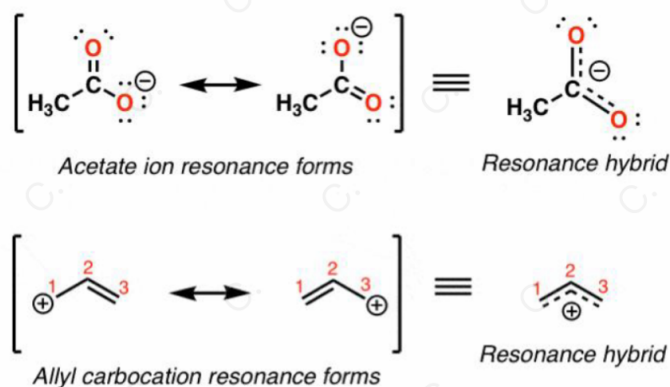
Point 6: Resonance

Resonance theory can not only explain the acidity and basicity of organic compounds, but also explain some laws of organic reactions. At this point, we will learn the basic knowledge of resonance theory in detail.

6.1 What is resonance theory?

Resonance is to signify that there is more than one possible way in which the valence electrons can be arranged in a Lewis structure. Resonance structures are usually shown with a double headed arrow between them. The resonance hybrid averages the bond characteristics over the molecule, resulting in it having a lower energy than any single contributing structure.

Take CH_3COO^- as an example:



*The "double-headed" arrow denotes that two molecules are resonance isomers (NOT in equilibrium)

CH_3COO^- usually show the characteristics of these two structures. Different structures are called resonant structures or resonant forms because they are not different compounds, but different ways to draw the same compound. The actual molecule is called a resonant mixture of its resonant form.

6.2 How to write resonance structures

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6.2.1 Introducing Curved Arrows

We can convert one resonance form into another by showing the movement of electrons between bonds and lone pairs (or vice versa). We just need a graphical tool to do it.—It's called the “curved arrow”.

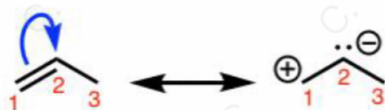
Electrons move **from** the tail **to** the head



6.2.2 Every Resonance Form For A Molecule Can Be “Found” Through The Application Of Three Electron-Pushing Arrow “Moves”

Examples of the three legal “moves” of resonance.

π Bond \rightarrow Lone pair



Tail is at π bond between C₁ and C₂

Head is at C₂

Arrow shows movement of electrons from the C₁-C₂ π bond to become a lone pair on carbon 2.

Arrows also explain the changes in formal charge.

C₁ was *sharing* an electron pair with C₂. Now it *lacks* its share of this pair, which was 1 electron (50% of 2). It has lost an electron, so it becomes more *positive* by 1.

C₂ was *sharing* an electron pair with C₁. Now it *owns* this pair. So it has *gained* an electron and becomes more *negative* by 1.



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Lone pair → π Bond**Tail** is on lone pair of C_2 **Head** is between C_1 and C_2 Arrow shows movement of electrons from the lone pair on C_2 to become a π bond between C_1 and C_2 .

C_1 had six valence electrons and a formal charge of +1. Now it *shares* a pair of electrons with C_2 (the π bond), so it has gained an electron and its charge becomes more negative by 1 (from +1 to 0).

C_2 had a formal charge of -1 and *owned* a lone pair of electrons, but now it *shares* a pair of electrons with C_1 . So it has *lost* an electron, and its formal charge becomes more *positive* by 1 (from -1 to 0).

 π Bond → π Bond**Tail** is at π bond between C_1 and C_2 **Head** is at π bond between C_2 and C_3 Arrow shows movement of electrons from the C_1 - C_2 π bond (which breaks) to the C_2 - C_3 π bond (which forms).

C_1 goes from *sharing* an electron pair with C_2 to *lacking* an electron pair. It has lost an electron, and its formal charge goes from 0 to +1

C_2 goes from having six valence electrons and a formal charge of +1 to *sharing* a pair of electrons with C_3 (the π bond). It has gained an electron and its formal charge goes from 0 to +1.

Lone pair → Lone pair (ILLEGAL)

It is not possible to draw **one** arrow to show this. This "move" is not allowed.

This is illegal. Note how the charge on C_1 has gone from +1 to -1 (it has become more negative by 2).

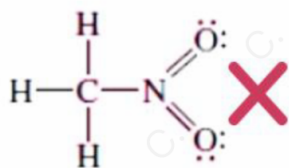
We cannot draw a single curved arrow for this transformation.



6.2.3 Principles of writing resonance

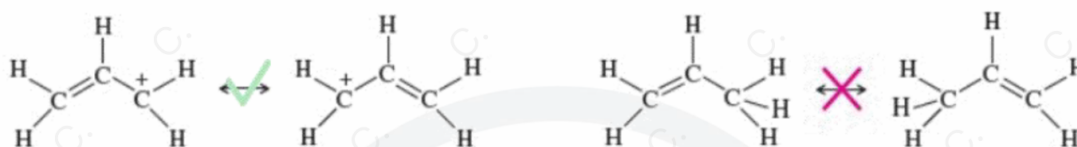
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1. Only reasonable Lewis structure is allowed.

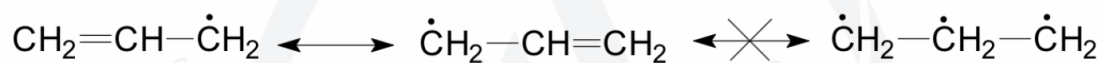


The nitrogen atom does not satisfy the octet rule.

2. The position and number of atoms cannot be changed, only change the position of electron.

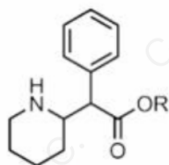


3. The number of unpaired electrons in all resonance forms must be the same.

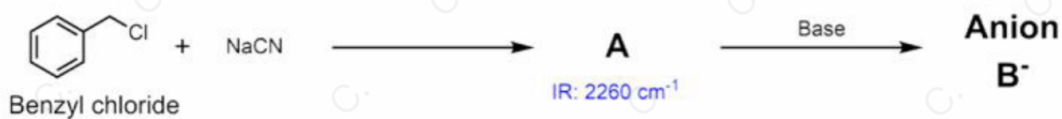


Example 5. (source, UKChO, 2015, 3b)

The drug Ritalin® has long been used as a treatment for attention-deficit hyperactivity disorder (ADHD). More recently it has been in the news as a possible performance-enhancing drug taken by students studying for exams. The structure of Ritalin is shown below, where R represents a hydrocarbon group.

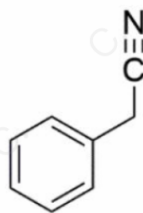


Ritalin is synthesised according to the scheme below. Some of the characteristic IR stretching frequencies of the intermediates are shown.



Previous conclusion:

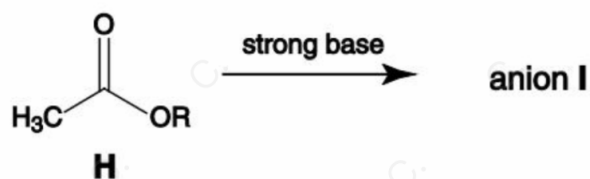
Compound A



(b) Compound **A** is then deprotonated to form **Anion B⁻**. Draw the structure of **Anion B⁻**.

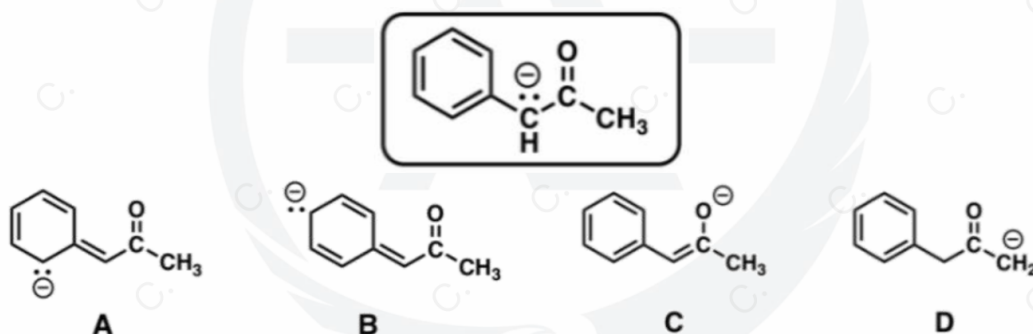
**Exercise 2.** (source, UKChO, 2012, 4b)

Ester **H** is deprotonated by strong bases to give the reactive carbon nucleophile, anion **I**. The R group in the structure is an alkyl chain which remains unchanged throughout the entire synthesis.

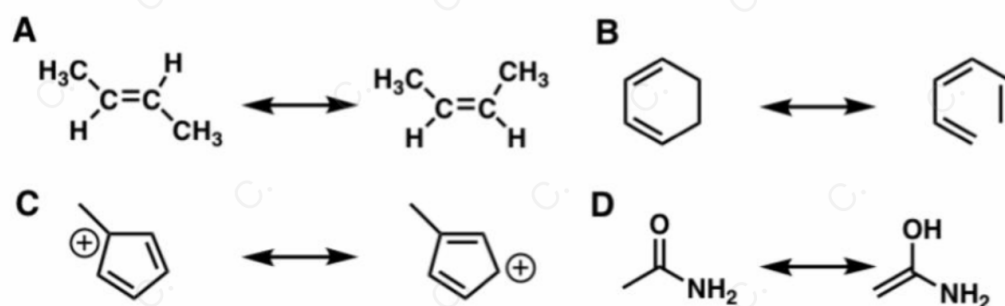


(b) Draw the structure for the anion **I**.

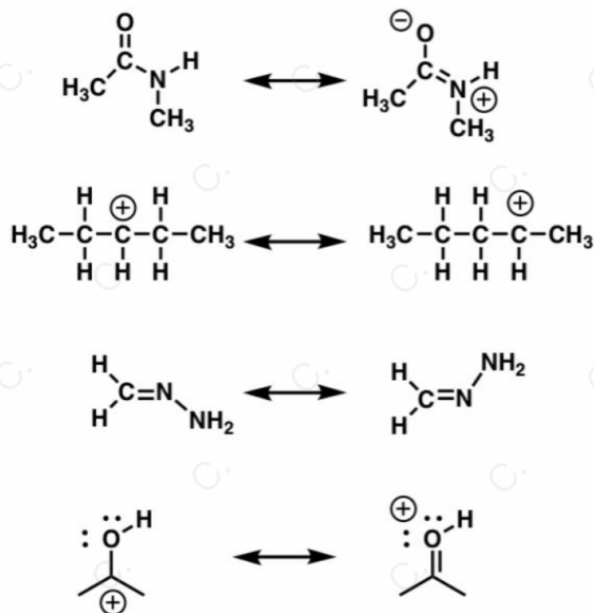
Example 6: Which of these molecules is **NOT** a resonance form of ?



Exercise 3: Which of these molecules represents a pair of resonance forms?



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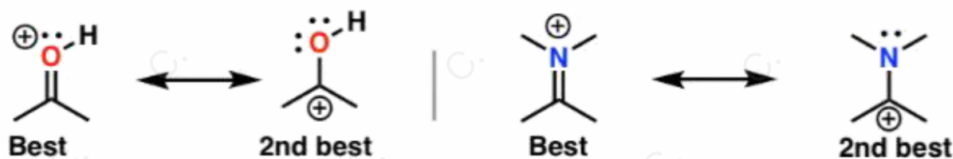
Exercise 4. Which of these drawings represents a pair of resonance forms?


6.3 Which resonance form contributes the most

Here's an important point about resonance forms. It is tempting to think that these resonance forms are in "equilibrium" between each other. Instead, the "true" state of the molecule will be a "hybrid" of these resonance forms. But not all resonance forms are of equal significance. In the case of the acetate ion and the allyl cation, both resonance forms are equal in energy, so the "hybrid" is a 1:1 mixture of the two. However, this is only rarely the case. So how do we evaluate how "important" each one is.

Rule 1: Full octets are preferable to empty octets.

It's best to give all atoms full octets of electrons (if possible)



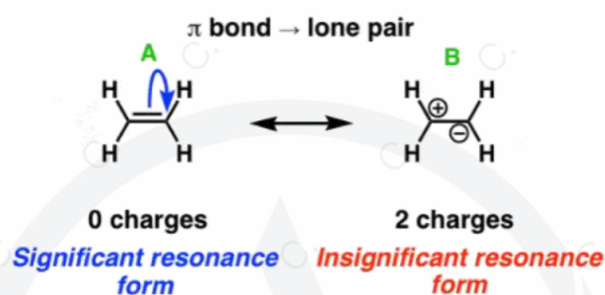


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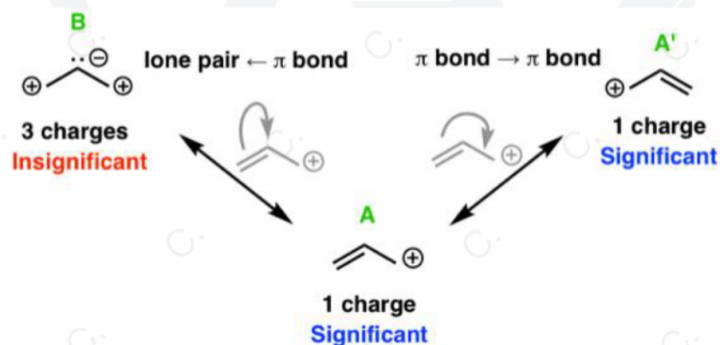
Rule 2: As many chemical bonds as possible.

Rule 3: Neutral resonance structures are more “important” than charged resonance structures.

For Example 1—Ethylene (aka ethene):



For Example 2—The allyl cation:

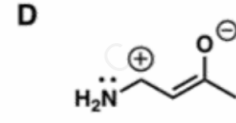
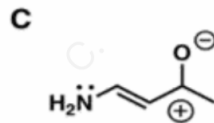
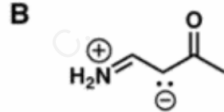
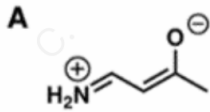
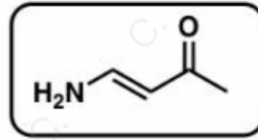


Rule 4: Place negative charges on the atom best able to stabilize it (i.e. The least basic atom).

“Basicity is the opposite of stability”, this is the same as saying, “Put the negative charge on the least basic atom”.



Exercise 5: Which resonance form contributes the most to the resonance hybrid of:

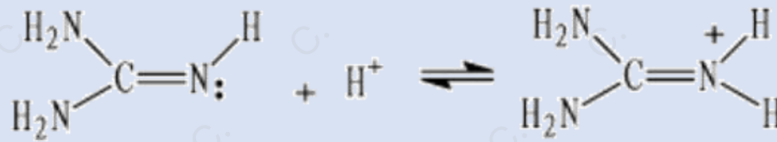




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Extention: Use resonance theory to explain why is RNH_2 a weak base and guanidine (CH_5N_3) a strong base?

Answer: CH_5N_3 is a Lewis base which can accept proton (H^+)



After binding with protons, the conjugated acid is more stable because of the formation of resonant "hybrid".





Summary

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1. Representing organic molecules

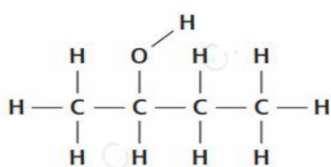
For example,

Naming: _____

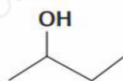
molecular formula: _____

structural formula: _____

displayed formula: _____



skeletal formula:



2. Functional groups

remember the differentials : alkane and alkene ,

-ane -ene -yne,

-ol -al,

ether , ester ,

amino, amide

Remember the functional group:

Homologous series / class name	Functional group	Functional group name	Example	General name	Name
alkane		alkyl	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	alkane	butane
alkene	C=C	alkenyl	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array}$	alk-x-ene (or x-alkene)	but-1-ene (or 1-butene)
alkynes	C≡C	alkynyl	$\begin{array}{ccc} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}\equiv\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ & \text{H} & \text{H} \end{array}$	alk-x-yne (or x-alkyne)	but-1-yne (or 1-butyne)
alcohol	-OH	hydroxyl	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	alkan-x-ol (or x-alkanol)	propan-1-ol (or 1-propanol)
ether		ether	$\begin{array}{cccc} \text{H} & & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array}$	alkoxyalkane	methoxyethane
aldehyde		carbonyl	$\begin{array}{ccc} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{H} & \text{H} \end{array}$	alkanal	propanal
ketone			$\begin{array}{ccccc} \text{H} & \text{O} & \text{H} & \text{H} & \text{H} \\ & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & \\ \text{H} & & \text{H} & \text{H} & \text{H} \end{array}$	alkan-x-one (or x-alkanone)	pentan-2-one (or 2-pentanone)
carboxylic acid		carboxyl	$\begin{array}{ccc} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C} \\ & & \\ \text{H} & \text{H} & \text{O}-\text{H} \end{array}$	alkanoic acid	propanoic acid
halogenoalkane	-X X=Cl/Br/I	halo (chloro, bromo, iodo)	$\begin{array}{cccc} \text{H} & \text{Br} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	x-haloalkane	2-bromobutane
amine	-NH ₂ -NHR -NR ₂	amino	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{N} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	alkylamine or x-aminoalkane or alkan-x-amine (or x-alkanamine)	propylamine or 1-aminopropane or propan-1-amine (or 1-propanamine)
ester		ester	$\begin{array}{ccc} \text{H} & \text{O} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array}$	alkyl alkanoate	methyl propanoate
a	-C≡N	nitrile	$\begin{array}{ccc} \text{H} & \text{H} & \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}\equiv\text{N} \\ & & \\ \text{H} & \text{H} & \end{array}$	alkanenitrile (C of C≡N included in chain)	propanenitrile
amide		carboxamide	$\begin{array}{ccc} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C} \\ & & \\ \text{H} & \text{H} & \text{NH}_2 \end{array}$	alkanamide	propanamide

3. Organic naming

Rule 1: Identify the functional group

Rule 2: selecting the functional group

The priority of functional groups is:

_____ > -SO₃H > -COOR > -COX > -CONH₂ > -COOCO- > -CN > -CHO > -CO- > -OH > -SH > -NH₂ > -C≡C- > -C=C- > -OR > -SR > -F > -Cl > -Br > -I > -NO₂ > -NO



Rule 3: _____ carbon chain principle (contains the functional group)

Rule 4: The end closest to the functional group begins to label the carbon atom

Rule 5: For the longest carbon chain with the same position occupied by the substituent, the longest carbon chain that can make **the _____ preferred substituent** occupy the smallest position should be selected.

Rule 6: when there are two or more of the same groups, di-, tri-, tetra-, penta-, or hexa- are used.

4. Bronsted–Lowry acids and bases and Lewis acid and bases

1) Bronsted–Lowry theory: bronsted acid is proton _____ and bronsted base is _____;

2) Lewis theory: Lewis acid is _____ donor and Lewis base is acceptor.

5. Some factors that affect acidity

(1) Electronegativity:

In the same period, from left to right: the _____ the electronegativity, the stronger the acidity.

(2) The length of the H-X bond:

In the same group, from top to bottom: the _____ the radius, the stronger the acidity.

(3) Inductive Effect:

Acidity of _____ increases as electron-withdrawing substituents are added

(4) Resonance effect

The conjugated bases of acids have more resonance hybrids, and the acidity will be stronger

5. Resonance

The resonance effect is a π -effect. The _____ charge can be delocalised over a π -system.