Structure and bonding

Key point. Organic chemistry is the study of carbon compounds. Ionic bonds involve elements gaining or losing electrons but the carbon atom is able to form four covalent bonds by sharing the four electrons in its outer shell. Single (C–C), double (C=C) or triple bonds (C≡C) to carbon are possible. When carbon is bonded to a different element, the electrons are not shared equally, as electronegative atoms (or groups) attract the electron density whereas electronegative atoms (or groups) repel the electron density. An understanding of the electron-withdrawing or -donating ability of atoms, or a group of atoms, can be used to predict whether an organic compound is a good acid or base.

1.1 Ionic versus covalent bonds

- Ionic bonds are formed between molecules with opposite charges. The negatively charged anion will electrostatically attract the positively charged cation. This is present in (inorganic) salts.

\[
\text{Cation}^{\oplus} \quad \text{Anion}^{\ominus} \quad \text{e.g. Na}^{\oplus} \quad \text{Cl}^{\ominus}
\]

- Covalent bonds are formed when a pair of electrons is shared between two atoms. A single line represents the two-electron bond.

\[
\text{Atom} \quad \text{Atom} \quad \text{e.g. Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]
- **Coordinate (or dative) bonds** are formed when a pair of electrons is shared between two atoms. One atom donates both electrons and a single line or an arrow represents the two-electron bond.

  ![Coordinate Bonds](image)

- **Hydrogen bonds** are formed when the partially positive (δ+) hydrogen of one molecule interacts with the partially negative (δ−) heteroatom (e.g. oxygen or nitrogen) of another molecule.

  ![Hydrogen Bonds](image)

### 1.2 The octet rule

To form organic compounds, the carbon atom shares electrons to give a stable ‘full shell’ electron configuration of eight valence electrons.

**Methane (CH₄)**

![Lewis Structure of Methane](image)

C is in group 14 and so has 4 valence electrons

H is in group 1 and so has 1 valence electron

A single bond contains two electrons, a double bond contains four electrons and a triple bond contains six electrons. A lone (or non-bonding) pair of electrons is represented by two dots (••).

**Carbon dioxide (CO₂)**

**Hydrogen cyanide (HCN)**

![Carbon Dioxide and Hydrogen Cyanide](image)

### 1.3 Formal charge

Formal positive or negative charges are assigned to atoms, which have an apparent ‘abnormal’ number of bonds.
Example: Nitric acid (HNO₃)

\[
\begin{array}{cccc}
\text{H} & \text{N} & \text{O} & \text{N} \\
\end{array}
\]

Nitrogen with 4 covalent bonds has a formal charge of +1

\[
\text{Formal charge: } 15 - 4 - 0 - 10 = +1
\]

The nitrogen atom donates a pair of electrons to make this bond.

Carbon forms four covalent bonds. When only three covalent bonds are present, the carbon atom can have either a formal negative charge or a formal positive charge.

- **Carbanions**—three covalent bonds to carbon and a formal negative charge.

  \[
  \text{Formal charge on C: } 14 - 3 - 2 - 10 = -1
  \]

  The negative charge is used to show the 2 non-bonding electrons.

- **Carbocations**—three covalent bonds to carbon and a formal positive charge.

  \[
  \text{Formal charge on C: } 14 - 3 - 0 - 10 = +1
  \]

  The positive charge is used to show the absence of 2 electrons.

### 1.4 Sigma (\(\sigma\)) and Pi (\(\pi\)) bonds

The electrons shared in a covalent bond result from overlap of atomic orbitals to give a new molecular orbital. Electrons in 1s and 2s orbitals combine to give sigma (\(\sigma\)) bonds.

When two 1s orbitals combine in-phase, this produces a bonding molecular orbital.

Nitric acid is used in synthesis to nitrate aromatic compounds such as benzene (Section 7.2.2)

The stability of carbocations and carbanions is discussed in Section 4.3

Carbanions are formed on deprotonation of organic compounds. Deprotonation of a carbonyl compound, at the \(\alpha\)-position, forms a carbanion called an enolate ion (Section 8.4.3)

Carbocations are intermediates in a number of reactions, including \(S_N1\) reactions (Section 5.3.1.2)

Molecular orbitals and chemical reactions are discussed in Section 4.10
When two 1s orbitals combine *out-of-phase*, this produces an *antibonding molecular orbital*.

Electrons in p orbitals can combine to give sigma (σ) or pi (π) bonds.

- **Sigma (σ−) bonds** are strong bonds formed by head-on overlap of two atomic orbitals.
- **Pi (π−) bonds** are weaker bonds formed by side-on overlap of two p-orbitals.

Only σ- or π-bonds are present in organic compounds. All single bonds are σ-bonds while all multiple (double or triple) bonds are composed of one σ-bond and one or two π-bonds.

**1.5 Hybridisation**

- The ground-state electronic configuration of carbon is 1s²2s²2pₓ¹2pᵧ¹.
- The six electrons fill up lower energy orbitals before entering higher energy orbitals (Aufbau principle).
- Each orbital is allowed a maximum of two electrons (Pauli exclusion principle).
- The two 2p electrons occupy separate orbitals before pairing up (Hund’s rule).
The carbon atom can mix the 2s and 2p atomic orbitals to form four new hybrid orbitals in a process known as *hybridisation*.

- **sp³ Hybridisation.** For four single σ-bonds – carbon is sp³ hybridised (e.g. in methane, CH₄). The orbitals move as far apart as possible, and the lobes point to the corners of a tetrahedron (109.5° bond angle).

  ![sp³ hybridisation](image1)

  methane: 4 × C–H σ-bonds

- **sp² Hybridisation.** For three single σ-bonds and one π-bond – the π-bond requires one p-orbital, and hence the carbon is sp² hybridised (e.g. in ethene, H₂C═CH₂). The three sp²-orbitals point to the corners of a triangle (120° bond angle), and the remaining p-orbital is perpendicular to the sp² plane.

  ![sp² hybridisation](image2)

  ethene: 4 × C–H σ-bonds, 1 × C–C σ-bond, 1 × C–C π-bond

- **sp Hybridisation.** For two single σ-bonds and two π-bonds – the two π-bonds require two p-orbitals, and hence the carbon is sp hybridised (e.g. in ethyne, HC≡CH). The two sp-orbitals point in the opposite directions (180° bond angle), and the two p-orbitals are perpendicular to the sp plane.

  ![sp hybridisation](image3)

  ethyne: 2 × C–H σ-bonds, 1 × C–C σ-bond, 2 × C–C π-bonds

Alkenes have a C=C bond containing one strong σ-bond and one weaker π-bond (Section 6.1)

All carbonyl compounds have a C=O bond, which contains one strong σ-bond and one weaker π-bond (Section 8.1)

Alkynes have a C≡C bond containing one strong σ-bond and two weaker π-bonds (Section 6.1)
For a single C—C or C—O bond, the atoms are sp\(^3\) hybridised and the carbon atom(s) is tetrahedral.
For a double C≡C or C≡O bond, the atoms are sp\(^2\) hybridised and the carbon atom(s) is trigonal planar.
For a triple C=C or C≡N bond, the atoms are sp hybridised and the carbon atom(s) is linear.

The shape of organic molecules is therefore determined by the hybridisation of the atoms.

Functional groups (Section 2.1) that contain π-bonds are generally more reactive as a π-bond is weaker than a σ-bond. The π-bond in an alkene or alkyne is around +250 kJ mol\(^{-1}\), while the σ-bond is around +350 kJ mol\(^{-1}\).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Mean bond enthalpies (kJ mol(^{-1}))</th>
<th>Mean bond lengths (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>+347</td>
<td>153</td>
</tr>
<tr>
<td>C≡C</td>
<td>+612</td>
<td>134</td>
</tr>
<tr>
<td>C≡≡C</td>
<td>+838</td>
<td>120</td>
</tr>
</tbody>
</table>

The shorter the bond length, the stronger the bond. For C—H bonds, the greater the ‘s’ character of the carbon orbitals, the shorter the bond length. This is because the electrons are held closer to the nucleus.

A single C—C σ-bond can undergo free rotation at room temperature, but a π-bond prevents free rotation around a C≡C bond. For maximum orbital overlap in a π-bond, the two p-orbitals need to be parallel to one another. Any rotation around the C≡C bond will break the π-bond.

1.6 Inductive effects, hyperconjugation and mesomeric effects

1.6.1 Inductive effects

In a covalent bond between two different atoms, the electrons in the σ-bond are not shared equally. The electrons are attracted towards the most electronegative atom. An
arrow drawn above the line representing the covalent bond can show this. (Sometimes an arrow is drawn on the line.) Electrons are pulled in the direction of the arrow.

An inductive effect is the polarisation of electrons through $\sigma$-bonds

An alkyl group (R) is formed by removing a hydrogen atom from an alkane (Section 2.2).

An aryl group (Ar) is benzene (typically called phenyl, Ph) or a substituted benzene group (Section 2.2)

When the atom (X) is more electronegative than carbon

- electrons attracted to X
- negative inductive effect. $\delta^-$

When the atom (Z) is less electronegative than carbon

- electrons attracted to C
- positive inductive effect. $\delta^+$

$\delta^-$ groups  
$X = \text{Br, Cl, NO}_2, \text{OH, OR, SH, SR, NH}_2, \text{NHR, NR}_2, \text{CN, CO}_2\text{H, CHO, C(O)R}$

$\delta^+$ groups  
$Z = \text{R (alkyl or aryl), metals (e.g. Li or Mg)}$

The inductive effect of the atom rapidly diminishes as the chain length increases

The higher the value the more electronegative the atom

$K = 0.82$  
$C = 2.55$  
$I = 2.66$  
$\text{Cl} = 3.16$  
$\text{Br} = 2.96$  
$N = 3.04$  
$O = 3.44$  
$F = 3.98$

The overall polarity of a molecule is determined by the individual bond polarities, formal charges and lone pair contributions and this can be measured by the dipole moment ($\mu$). The larger the dipole moment (often measured in debyes, D), the more polar the compound.

1.6.2 Hyperconjugation

A $\sigma$-bond can stabilise a neighbouring carbocation (or positively charged carbon, e.g. $\text{R}_3\text{C}^+$) by donating electrons to the vacant p-orbital. The positive charge is delocalised or ‘spread out’ and this stabilising effect is called resonance.

Hyperconjugation is the donation of electrons from nearby $\text{C}–\text{H}$ or $\text{C}–\text{C} \sigma$-bonds

The stability of carbocations is discussed in Section 4.3.1

1.6.3 Mesomeric effects

Whilst inductive effects pull electrons through the $\sigma$-bond framework, electrons can also move through the $\pi$-bond network. A $\pi$-bond can stabilise a negative charge, a
positive charge, a lone pair of electrons or an adjacent bond by resonance (i.e. 
delocalisation or ‘spreading out’ of the electrons). Curly arrows (Section 4.1) are 
used to represent the movement of $\pi$- or non-bonding electrons to give different 
resonance forms. It is only the electrons, not the nuclei, that move in the resonance 
forms, and a double-headed arrow is used to show their relationship.

1.6.3.1 Positive mesomeric effect

- When a $\pi$-system donates electrons, the $\pi$-system has a positive mesomeric 
effect, $+M$. 

\[ \begin{array}{c}
\text{donates electrons:} \\
\text{+M group}
\end{array} \]

- When a lone pair of electrons is donated, the group donating the electrons has a 
positive mesomeric effect, $+M$.

\[ \begin{array}{c}
\text{donates electrons:} \\
\text{+M group}
\end{array} \]

1.6.3.2 Negative mesomeric effect

- When a $\pi$-system accepts electrons, the $\pi$-system has a negative mesomeric 
effect, $-M$.

\[ \begin{array}{c}
\text{accepts electrons:} \\
\text{–M groups}
\end{array} \]

The actual structures of the cations or anions lie somewhere between the 
two resonance forms. All resonance forms must have the same overall charge 
and obey the same rules of valency.

$-M$ groups generally contain an electronegative atom(s) and/or a $\pi$-bond(s):
\[ \text{CHO, C(O)R, CO}_2\text{H, CO}_2\text{Me, NO}_2, \text{CN, aromatics, alkenes} \]

$+M$ groups generally contain a lone pair of electrons or a $\pi$-bond(s):
\[ \text{Cl, Br, O\text{H}, O\text{R, S\text{H}, S\text{R, N\text{H}_2, NHR, N\text{R}_2}}, aromatics, alkenes} \]

Aromatic (or aryl) groups and alkenes can be both $+M$ and $-M$. 

This carbocation is called an allylic cation (see Section 5.3.1.2)

This anion, formed by deprotonating an aldehyde at the $\alpha$-position, is called an enolate ion 
(Section 8.4.3)

Functional groups are discussed in Section 2.1
In neutral compounds, there will always be a $+M$ and $-M$ group(s): one group donates ($+M$) the electrons, the other group(s) accepts the electrons ($-M$).

All resonance forms are not of the same energy. Generally, the most stable resonance forms have the greatest number of covalent bonds, atoms with a complete valence shell of electrons, and/or an aromatic ring. In phenol (PhOH), for example, the resonance form with the intact aromatic benzene ring is expected to predominate.

As a rule of thumb, the more resonance structures an anion, cation or neutral $\pi$-system can have, the more stable it is.

### 1.6.3.3 Inductive versus mesomeric effects

Mesomeric effects are generally stronger than inductive effects. A $+M$ group is likely to stabilise a cation more effectively than a $+I$ group.

Mesomeric effects can be effective over much longer distances than inductive effects provided that conjugation is present (i.e. alternating single and double bonds). Whereas inductive effects are determined by distance, mesomeric effects are determined by the relative positions of $+M$ and $-M$ groups in a molecule (Section 1.7).

### 1.7 Acidity and basicity

#### 1.7.1 Acids

An acid is a substance that donates a proton (Brønsted-Lowry). Acidic compounds have low $pK_a$ values and are good proton donors as the anions (or conjugate bases), formed on deprotonation, are relatively stable.

In water:

$$
HA + H_2O \rightleftharpoons H_3O^+ + A^-
$$

**Acid** + **Base** \[\rightleftharpoons\] **Conjugate acid** + **Conjugate base**

The more stable the conjugate base the stronger the acid

$$
K_a \approx \frac{[H_3O^+][A^-]}{[HA]}
$$

As $H_2O$ is in excess

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

The higher the value of $K_a$, the lower the $pK_a$ value and the more acidic is HA.
The $pK_a$ value equals the pH of the acid when it is half ionised. At pH’s above the $pK_a$ the acid (HA) exists predominantly as the conjugate base ($A^-$) in water. At pH’s below the $pK_a$ it exists predominantly as HA.

<table>
<thead>
<tr>
<th>pH</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>strongly acidic</td>
</tr>
<tr>
<td>7</td>
<td>neutral</td>
</tr>
<tr>
<td>14</td>
<td>strongly basic</td>
</tr>
</tbody>
</table>

The $pK_a$ values are influenced by the solvent. Polar solvents will stabilise cations and/or anions by solvation in which the charge is delocalised over the solvent (e.g. by hydrogen-bonding in water).

The more electronegative the atom bearing the negative charge, the more stable the conjugate base (which is negatively charged).

<table>
<thead>
<tr>
<th>$pK_a$</th>
<th>Most Acidic</th>
<th>Least Acidic</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>HF</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>16</td>
<td>H$_2$O</td>
<td>NH$_3$</td>
</tr>
<tr>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Therefore, $F^-$ is more stable than $H_3C^-$. The conjugate base can also be stabilised by $-I$ and $-M$ groups which can delocalise the negative charge. (The more ‘spread out’ the negative charge, the more stable it is).

$-I$ and $-M$ groups therefore lower the $pK_a$ while $+I$ and $+M$ groups raise the $pK_a$.

### 1.7.1.1 Inductive effects and carboxylic acids

The carboxylate ion ($RCO_2^-$) is formed on deprotonation of a carboxylic acid ($RCO_2H$). The anion is stabilised by resonance (i.e. the charge is spread over both oxygen atoms) but can also be stabilised by the R group if this has a $-I$ effect.

The greater the $-I$ effect, the more stable the carboxylate ion (e.g. $FCH_2CO_2^-$ is more stable than $BrCH_2CO_2^-$) and the more acidic the carboxylic acid (e.g. $FCH_2CO_2H$ is more acidic than $BrCH_2CO_2H$).
Most acidic as F is more electronegative than Br and has a greater −I effect

Least acidic as the CH₃ group is a +I group

1.7.1.2 Inductive and mesomeric effects and phenols

Mesomeric effects can also stabilise positive and negative charges.

The negative charge needs to be on an adjacent carbon atom for a −M group to stabilise it.

The positive charge needs to be on an adjacent carbon atom for a +M group to stabilise it.

On deprotonation of phenol (PhOH) the phenoxide ion (PhO⁻) is formed. This anion is stabilised by the delocalisation of the negative charge on to the 2-, 4- and 6-positions of the benzene ring.

- If −M groups are introduced at the 2-, 4- and/or 6-positions, the anion can be further stabilised by delocalisation through the π-system as the negative charge can be spread onto the −M group. We can use double-headed curly arrows to show this process.
- If −M groups are introduced at the 3- and/or 5-positions, the anion cannot be stabilised by delocalisation, as the negative charge cannot be spread onto the −M group. There is no way of using curly arrows to delocalise the charge on to the −M group.
- If −I groups are introduced on the benzene ring, the effect will depend on their distance from the negative charge. The closer the −I group is to the negative charge, the greater the stabilising effect will be. The order of −I stabilisation is therefore 2-position > 3-position > 4-position.
- The −M effects are much stronger than −I effects (Section 1.6.3).

Examples

The NO₂ group is strongly electron-withdrawing; −I and −M
1.7.2 Bases

A base is a substance that accepts a proton (Brønsted-Lowry). Basic compounds are good proton acceptors as the conjugate acids, formed on protonation, are relatively stable. Consequently, strong bases (B⁺ or B⁻) give conjugate acids (BH⁺ or BH) with high pKₐ values.

In water:

\[
\text{Base} + \text{H}_2\text{O} \rightleftharpoons \text{Conjugate acid} + \text{Conjugate base} \quad \text{basicity constant}
\]

The strength of bases is usually described by the \( K_a \) and pKₐ values of the conjugate acid.

\[
\text{Conjugate base} + \text{H}_2\text{O} \rightleftharpoons \text{Base} + \text{H}_3\text{O}^{+}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^{+}]}{[\text{BH}^\text{−}]} \]

As H₂O is in excess

- If B is a strong base then BH⁺ will be relatively stable and not easily deprotonated. BH⁺ will therefore have a high pKₐ value.
- If B is a weak base then BH⁺ will be relatively unstable and easily deprotonated. BH⁺ will therefore have a low pKₐ value.
The cation can be stabilised by $+\text{I}$ and $+\text{M}$ groups, which can delocalise the positive charge. (The more ‘spread out’ the positive charge, the more stable it is.)

### 1.7.2.1 Inductive effects and aliphatic (or alkyl) amines

On protonation of amines (e.g. RNH$_2$), ammonium salts are formed.

$$
\begin{array}{c}
\text{R} \quad \text{NH}_2 \\
\text{primary amine}
\end{array}
\quad + \quad \begin{array}{c}
\text{H}^+ \quad \\
\text{ammonium ion}
\end{array}
$$

The greater the $+\text{I}$ effect of the R group, the greater the electron density at nitrogen and the more basic the amine. The greater the $+\text{I}$ effect, the more stable the ammonium ion and the more basic the amine.

<table>
<thead>
<tr>
<th>$+\text{I}$ group</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>no $+\text{I}$ group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>p$K_a$</td>
<td>9.3</td>
<td>10.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$+\text{I}$ groups</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>three $+\text{I}$ groups</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>Et</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>Et</td>
</tr>
<tr>
<td>p$K_a$</td>
<td>10.9</td>
<td>10.9</td>
</tr>
</tbody>
</table>

The p$K_a$ values should increase steadily as more $+\text{I}$ alkyl groups are introduced on nitrogen. However, the p$K_a$ values are determined in water, and the more hydrogen atoms on the positively charged nitrogen, the greater the extent of hydrogen bonding between water and the cation. This solvation leads to the stabilisation of the cations containing N–H bonds.

In organic solvents (which cannot solvate the cation) the order of p$K_a$’s is expected to be as follows.

$tertiary \quad secondary \quad primary \quad ammonia$

$$R_2\text{N} \quad R_2\text{NH} \quad R\text{NH}_2 \quad \text{NH}_3 \quad (R = +\text{I alkyl group})$$

The presence of $-\text{I}$ and/or $-\text{M}$ groups on nitrogen reduces the basicity and so, for example, primary amides (RCONH$_2$) are poor bases.

The C=O group stabilises the lone pair on nitrogen by resonance – this reduces the electron density on nitrogen.

If ethanamide was protonated on nitrogen, the positive charge could not be stabilised by delocalisation. Protonation therefore occurs on oxygen as the charge can be delocalised on to the nitrogen atom.
1.7.2.2 Mesomeric effects and aryl (or aromatic) amines

The lone pair of electrons on the nitrogen atom of aminobenzene (or aniline, PhNH₂) can be stabilised by delocalisation of the electrons onto the 2-, 4- and 6-positions of the benzene ring. Aromatic amines are therefore less basic than aliphatic amines.

- If –M groups are introduced at the 2-, 4- and/or 6-positions (but not the 3- or 5-positions) the anion can be further stabilised by delocalisation, as the negative charge can be spread on to the –M group. This reduces the basicity of the amine.

- If –I groups are introduced on the benzene ring, the order of –I stabilisation is 2-position > 3-position > 4-position. This reduces the basicity of the amine.

\[
\begin{align*}
\text{Most basic as no} & \quad \text{The NO}_2 \text{can stabilise the lone pair inductively} \quad \text{Least basic – the NO}_2 \\
\text{–I or –M groups} & \quad \text{can stabilise the lone pair inductively} \quad \text{can stabilise the lone pair inductively and by resonance} \\
on \text{the ring} & \quad \text{by resonance} \\
pK_a & \quad 4.6 \quad 2.45 \quad -0.28
\end{align*}
\]

These are \(pK_a\) values of the conjugate acids

- If +M groups (e.g. OMe) are introduced at the 2-, 4- or 6-position of aminobenzene (PhNH₂), then the basicity is increased. This is because the +M group donates electron density to the carbon atom bearing the amine group. Note that the nitrogen atom, not the oxygen atom, is protonated – this is because nitrogen is less electronegative than oxygen and is a better electron donor.
The OMe group is –I but +M

\[ \text{NH}_2 \quad \text{OMe} \quad \text{NH}_2 \quad \text{OMe} \quad \text{NH}_2 \quad \text{OMe} \]

These are \( pK_a \) values of the conjugate acids formed by protonation of the \( \text{–NH}_2 \) group

\[ \begin{align*}
\text{Least} & \quad \text{basic as the OMe group cannot donate electron density to the carbon atom bearing the nitrogen} \\
\text{OMe} & \quad \text{4.2} \\
\text{Most} & \quad \text{basic as the OMe group can donate electron density to the nitrogen and it has a weak –I effect (as well apart from the nitrogen)} \\
\text{OMe} & \quad \text{5.3}
\end{align*} \]

Curly arrows can be used to show the delocalisation of electrons on to the carbon atom bearing the nitrogen.

Curly arrows are introduced in Section 4.1

1.7.3 Lewis acids and bases

- A Lewis acid is any substance that accepts an electron pair in forming a coordinate bond (Section 1.1). Examples include \( \text{H}^+ \), \( \text{BF}_3 \), \( \text{AlCl}_3 \), \( \text{TiCl}_4 \), \( \text{ZnCl}_2 \) and \( \text{SnCl}_4 \). They have unfilled valence shells and so can accept electron pairs.
- A Lewis base is any substance that donates an electron pair in forming a coordinate bond. Examples include \( \text{H}_2\text{O} \), \( \text{ROH} \), \( \text{RCHO} \), \( \text{R}_2\text{C}=	ext{O} \), \( \text{R}_3\text{N} \) and \( \text{R}_2\text{S} \). They all have a lone pair(s) of electrons on the heteroatom (O, N or S).

- A heteroatom is any atom that is not carbon or hydrogen

Reactions of ketones are discussed in Chapter 8

1.7.4 Basicity and hybridisation

The greater the ‘s’ character of an orbital, the lower in energy the electrons and the more tightly the electrons are held to the nucleus. The electrons in an sp-orbital are therefore less available for protonation than those in an sp\(^2\)- or sp\(^3\)-orbital, and hence the compounds are less basic.
1.7.5 Acidity and aromaticity

Aromatic compounds are planar, conjugated systems which have $4n + 2$ electrons (Hückel’s rule) (Section 7.1). If, on deprotonation, the anion is part of an aromatic $\pi$-system then the negative charge will be stabilised. Aromaticity will therefore increase the acidity of the compound.

If a lone pair of electrons on a heteroatom is part of an aromatic $\pi$-system, then these electrons will not be available for protonation. Aromaticity will therefore decrease the basicity of the compound.

1.7.6 Acid-base reactions

The $pK_a$ values can be used to predict if an acid-base reaction can take place. An acid will donate a proton to the conjugate base of any acid with a higher $pK_a$ value.
This means that the product acid and base will be more stable than the starting acid and base.

\[
\begin{align*}
\text{ethyne} & \quad \text{amide ion} & \quad \text{ethynyl anion} & \quad \text{ammonia} \\
\text{HC} & \equiv \text{C} & + & \overset{\ominus}{\text{NH}_2} & \quad \text{HC} & \equiv \text{C} & + & \overset{\ominus}{\text{NH}_3} \\
pK_a^{25} & & & & & & & & \\
\text{Ammonia has a higher pK}_a \text{ value than ethyne} & & & & & & & &
\end{align*}
\]

Deprotonation of terminal alkynes is discussed in Section 6.3.2.5

\[
\begin{align*}
\text{propanone} & \quad \text{hydroxide ion} & \quad \text{enolate ion} & \quad \text{water} \\
\text{CH}_3\text{COCH}_3 & + & \overset{\ominus}{\text{OH}} & \quad \text{CH}_3\text{COCH}_2 & + & \overset{\ominus}{\text{H}_2\text{O}} \\
pK_a^{20} & & & & & & & & \\
\text{Water has a lower pK}_a \text{ value than propanone} & & & & & & & &
\end{align*}
\]

For deprotonation of carbonyl compounds to form enolate ions, see Section 8.4.3

**Worked Example**

(a) Giving your reasons, rank the following carbanions 1–4 in order of increasing stability.

\[
\begin{align*}
1 & \quad \overset{\ominus}{\text{CH}_3} & \quad \overset{\ominus}{\text{CH}_3} & \quad \overset{\ominus}{\text{CH}_3} \\
2 & \quad \overset{\ominus}{\text{CH}_3} & \quad \overset{\ominus}{\text{CH}_3} & \quad \overset{\ominus}{\text{CH}_3} \\
3 & \quad \overset{\ominus}{\text{CH}_2} & \quad \overset{\ominus}{\text{CH}_2} & \quad \overset{\ominus}{\text{CH}_2} \\
4 & \quad \overset{\ominus}{\text{CH}_2} & \quad \overset{\ominus}{\text{CH}_2} & \quad \overset{\ominus}{\text{CH}_2} \\
\end{align*}
\]

(b) Identify, giving your reasons, the most acidic hydrogen atom(s) in compound 5.

\[
\begin{align*}
\overset{\ominus}{\text{O}} & \quad \overset{\ominus}{\text{N}} & \quad \overset{\ominus}{\text{N}} \\
\text{HO}_2 & \quad \text{NH}_2 \\
5 & & 6
\end{align*}
\]

(c) Identify, giving your reasons, the basic functional group in compound 6.

**Answer**

(a)

For the tert-butyl anion 3, because the three \(\text{CH}_3\) are electron-donating groups (+I), this makes 3 less stable than the methyl anion 2.

**Hint:** Determine whether the groups attached to the negatively charged carbons in 1–4 can stabilise the lone pair by I and/or M effects

**Hint:** Consider a \(\delta^+\) hydrogen atom bonded to an electronegative atom that, on deprotonation, gives the more stable conjugate base

**Hint:** Show all the lone pairs in 6 and consider their relative availability. Compare the stability of possible conjugate acids

Inductive and mesomeric effects (resonance) are discussed in Sections 1.6.1 and 1.6.3
The benzyl anion 4 is more stable than the methyl anion 2 because it is stabilised by resonance – the negative charge is delocalised on to the 2, 4 and 6 positions of the ring.

Enolate ion 1 is the most stable because the anion is stabilised by resonance and one resonance form has the negative charge on oxygen – a negative charge on oxygen is more stable than a negative charge on carbon.

(b) Hydrogen atoms bonded to oxygen are more acidic than those bonded to carbon. As oxygen is more electronegative than carbon, the conjugate base is more stable. The carboxylic acid group is more acidic than the alcohol group in 5 because deprotonation of the carboxylic acid gives a conjugate base that is stabilised by resonance.

(c) The tertiary amine is the most basic group in 6. The lone pairs on the nitrogen atoms in the tertiary amide and aniline groups are both delocalised and less available for protonation (the oxygen atom of the tertiary amide is less basic than the tertiary amine because oxygen is more electronegative than nitrogen, hence the oxygen lone pairs are less available). On protonation of the tertiary amine, the conjugate acid is stabilised by three +I effects.

Problems

1. Using the I and M notations, identify the electronic effects of the following substituents.
(a) –Me (b) –Cl (c) –NH₂ (d) –OH (e) –Br (f) –CO₂Me (g) –NO₂ (h) –CN

2. (a) Use curly arrows to show how cations A, B and C (shown below) are stabilised by resonance, and draw the alternative resonance structure(s).

(b) Would you expect A, B or C to be the more stable? Briefly explain your reasoning.

3. Provide explanations for the following statements.

(a) The carbocation CH₃OCH₂⁺ is more stable than CH₃CH₂⁺.
(b) 4-Nitrophenol is a much stronger acid than phenol (C₆H₅OH).
(c) The pKₐ of CH₃COCH₃ is much lower than that of CH₃CH₃.
(d) The C–C single bond in CH₃CN is longer than that in CH₂=CH–CN.
(e) The cation CH₂=CH–CH₂⁺ is resonance stabilised whereas the cation CH₂=CH–NMe₃⁺ is not.

4. Why is cyclopentadiene (pKₐ 15.5) a stronger acid than cycloheptatriene (pKₐ ~ 36)?

5. Which hydrogen atom would you expect to be the most acidic in each of the following compounds?

(a) 4-Methylphenol (or p-cresol, 4-HOC₆H₄CH₃)
(b) 4-Hydroxybenzoic acid (4-HOC₆H₄CO₂H)
(c) H₂C=CHCH₂CH₂C≡CH
(d) HOCH₂CH₂CH₂C≡CH

6. Arrange the following sets of compounds in order of decreasing basicity. Briefly explain your reasoning.

(a) 1-Aminopropene, ethanamide (CH₃CONH₂), guanidine [HN=C(NH₂)₂], aniline (C₆H₅NH₂).
(b) Aniline (C₆H₅NH₂), 4-nitroaniline, 4-methoxyaniline, 4-methylaniline.

7. For each of the following compounds D–F, identify the most acidic hydrogen atom(s). Briefly explain your reasoning.
8. For each of the following compounds **G**–**I**, identify the most basic group. Briefly explain your reasoning.

8.

9. Given the approximate $pK_a$ values shown below, for the following acid-base reactions (a)–(e), determine whether the position of the equilibrium lies over to the reactant side or the product side.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhOH</td>
<td>9.9</td>
</tr>
<tr>
<td>H_2O</td>
<td>15.7</td>
</tr>
<tr>
<td>CH_3COCH_3</td>
<td>20</td>
</tr>
<tr>
<td>H_2</td>
<td>35</td>
</tr>
<tr>
<td>NH_3</td>
<td>38</td>
</tr>
<tr>
<td>H_2C=CH_2</td>
<td>44</td>
</tr>
</tbody>
</table>

(a) **NaH** + PhOH $\rightleftharpoons$ PhO$^-$ Na$^{+}$ + H_2

(b) CH_3COCH_3 + NaOH $\rightleftharpoons$ CH_3COCH_2Na$^+$ + H_2O

(c) H_2C=CH_2 + NaNH_2 $\rightleftharpoons$ H_2C=CH Na$^{+}$ + NH_3

(d) CH_3COCH_2Na$^+$ + PhOH $\rightleftharpoons$ CH_3COCH_3 + PhO$^-$ Na$^{+}$

(e) H_2C=CH Na$^{+}$ + H_2O $\rightleftharpoons$ H_2C=CH_2 + NaOH