Summary

• Hopefully you are starting to build up a picture of molecular structure
• You should know how to draw molecules and both their Lewis structure and simple molecular orbitals

\[ \begin{align*}
\text{H} & \quad \text{C} \quad \text{H} \\
\text{C} & \quad \text{H} \quad \text{H} \\
\text{O} & \quad \equiv \\
\text{H} & \quad \text{O} \quad \equiv \\
\text{H} & \quad \text{C} \quad \text{H}
\end{align*} \]

• You should also be aware that IR spectroscopy provides information about functional groups in the molecule

• For the molecule to absorb IR there must be a change in dipole moment - so electrons cannot be evenly distributed in a bond
• Today we look at this effect...
**Formal charges**

- MO theory tells us that electrons shared out over whole molecule
- But it is useful to "localise" electrons and charge in order to understand reactivity & properties
- Localise electrons in **bonds**
- Localise charge as **formal charge (fc)**
- NOTE: this is just "bookkeeping" charge distributed over molecule

\[
\text{fc} = \text{old group number} - \text{number of unshared electrons} - \frac{1}{2} \text{number of shared electrons}
\]

Carbon: \(\text{fc} = 4 - 0 - \frac{1}{2}(8) = 0\)

Nitrogen: \(\text{fc} = 5 - 0 - \frac{1}{2}(8) = +1\)
Formal charges II

- Atoms in neutral molecules can have formal charges
- This can frequently be used to understand their chemistry

\[
\text{B}^\cdot + 3\text{H}^\cdot + \text{H}^\ominus \rightarrow H \begin{array}{c} H \\ H \end{array} \begin{array}{c} B \\ H \end{array} \begin{array}{c} H \\ H \end{array} \\
\text{boron; } fc = 3-0-\frac{1}{2}(8) = -1
\]

\[
\text{O}^\cdot + \text{O}^\cdot + \text{O}^\cdot \rightarrow \text{O} = \text{O} = \text{O} \\
\text{central oxygen; } fc = 6-2-\frac{1}{2}(6) = +1
\]

\[
\text{H}^\cdot + 3\text{H}^\cdot + \text{N}^\cdot + 2\text{O}^\cdot \rightarrow \text{H} \begin{array}{c} H \\ H \\ O \end{array} \begin{array}{c} C \\ N \\ O \end{array} \\
\text{nitr} \text{ogen; } fc = 5-0-\frac{1}{2}(8) = +1
\]

\[
\text{O}^\cdot + \text{O}^\cdot + \text{O}^\cdot \rightarrow \text{O} = \text{O} = \text{O} \\
\text{terminal oxygen; } fc = 6-6-\frac{1}{2}(2) = -1
\]

\[
\text{O}^\cdot + \text{O}^\cdot + \text{O}^\cdot \rightarrow \text{O} = \text{O} = \text{O} \\
\text{neutral}
\]

\[
\text{H}_3\text{C} - \text{N}^\oplus \\
\text{atom's formal charges}
\]

\[
\text{H}_3\text{C} - \text{N}^\oplus \\
\text{atom's formal charges}
\]
Carbanions and carbocations

- Learn to count to four!
- Carbon has four bonds in stable molecules
- If there are only three bonds present carbon has either a formal positive charge or a formal negative charge

**Carbanion**

3 covalent bonds and a formal negative charge

\[
\text{carbon; } fc = 4 - 2 - \frac{1}{2}(6) = -1
\]

**Carbocation**

3 covalent bonds and a formal positive charge

\[
\text{carbon; } fc = 4 - 0 - \frac{1}{2}(6) = +1
\]

- Here the Θ & ⊕ are not the same as formal charge!
- Negative charge shows the two non-bonding electrons
- Positive charge shows the absence of 2 electrons
Polarisation

- IR has shown us that electrons not evenly distributed in a bond
- Different atoms have different electronegativities
- The more electronegative an atom the closer the electrons will be held to it
- This effects the shape of the bonding & antibonding MOs
Polarisation II

- These effects occur in σ-bonds
- Below highlights the effect of the more common functional groups
- Power of effect diminishes with distance from X or Z
- NOTE: Formal charges effect bond polarisation

\[
\begin{align*}
\text{X} = \text{Br, Cl, NO}_2, \text{OH, OR, SH, SR, NH}_2, \text{NHR, NR}_2, \text{CN, CO}_2\text{H, CHO, C(O)R} \\
\text{If X is more electronegative than carbon} \\
\text{Electrons are attracted to X} \\
\text{The more electronegative X the stronger the effect} \\
\text{This effects orbitals & reactivity}
\end{align*}
\]

\[
\begin{align*}
\text{Z} = \text{R (alkyl or aryl), metals (Li, Mg etc)} \\
\text{If Z is less electronegative than carbon} \\
\text{Electrons are attracted to C} \\
\text{The more electropositive Z the stronger the effect} \\
\text{This effects orbitals & reactivity}
\end{align*}
\]
Polarisation III

- Electrons shared evenly in alkene
- Electrons not shared evenly in carbonyl group
- Polarisation of bond effects reactivity
- Carbonyl C=O is a stronger bond than C=C - but more reactive!
Resonance

- Electrons can also move in $\pi$-bonds
- $\pi$-bonds can stabilise $\Theta, \Theta$ & lone pairs
- Electrons are **delocalised** or spread out
- We draw the **extremes** or resonance forms - electrons "inbetween"
- "Curly arrow" shows the movement of 2 electrons only

Positive charges can be stabilised

\[
\begin{align*}
R^1 & \equiv \begin{array}{c} \text{R1} \\ \text{R2} \end{array} & \text{R3} \\
\begin{array}{c} \text{R1} \\ \text{R2} \end{array} & \equiv & \begin{array}{c} \text{R1} \\ \text{R2} \end{array} & \equiv & \begin{array}{c} \text{R1} \\ \text{R2} \end{array} & \equiv & \begin{array}{c} \text{R1} \\ \text{R2} \end{array}
\end{align*}
\]

2 p orbitals with 1 electron each

May look complicated but it is just the same as benzene!
Resonance II

Negative charges can be stabilised

\[
\begin{align*}
R^1\equiv & \quad R^3 \\
\quad & \quad R^2
\end{align*}
\]

MO diagram identical to previous slide except an addition 2 electrons

Neutral compounds can also have delocalised electrons

\[
\begin{align*}
R\equiv & \quad R^2 \\
\quad & \quad R^2
\end{align*}
\]

Delocalisation

This effect is general - any 2 p-orbitals separated by 1 bond can overlap!

\[
\begin{align*}
R\equiv & \quad R^2 \\
\quad & \quad R^2
\end{align*}
\]

MO diagram is again identical to previous slide except it will be polarised
Nucleophiles

- **Electron rich** - form a covalent bond by **donating two electrons**
- Nucleophiles are either **negatively charged**
- Or they are neutral with a **lone pair**

### Anions

- $\text{H}^- \quad \equiv \quad \left[ \begin{array}{c} \vdots \\ \vdots \\ \vdots \end{array} \right]^{-}$
  - 3 lone pairs
- $\text{Br}^- \quad \equiv \quad \left[ \begin{array}{c} \vdots \\ \vdots \end{array} \right]^{-}$
  - 4 lone pairs
- $\text{Pr}^- \quad \equiv \quad \left[ \begin{array}{c} \vdots \\ \vdots \end{array} \right]^{-}$
  - 1 lone pair

### Lone pairs on heteroatoms

- Water: lone pairs as **nucleophile**
- Ammonia: lone pairs as **nucleophile**
- Dimethyl sulfide (DMS): lone pairs as **nucleophile**
Nucleophiles II

High energy or reactive $\sigma$ bonds are nucleophiles

$Y=$Li, Mg

$\pi$ bonds can also act as nucleophiles
**Strength of nucleophiles**

Anions are normally more nucleophilic than lone pairs

\[
\text{HO}^- > \text{H}_2\text{O}
\]

- More electronegative an atom the less nucleophilic it is
- Reason is the atom holds on to the electrons more readily
- This parallels BASICITY (roughly)

```
most nucleophilic  R_3\text{C}^-  >  R_2\text{N}^-  >  \text{RO}^-  >>  \text{F}^-

least nucleophilic
```

- Basicity = donation of 2 electrons to H\(^+\) or H
- Basicity measured in pK\(_a\) (higher the value the more basic)
- Nucleophilicity = donation of 2 electrons to anything else
- Nucleophilicity similar to basicity but effected by steric (size)
Electrophiles

- **Electron deficient** - form a covalent bond by **accepting** two electrons
- Nucleophiles are often **positively charged**
- But can be neutral

**Electrophiles with an empty atomic orbital**

[Diagram showing electrophiles with empty orbitals and their reactions with nucleophiles]
Electrophiles II

Electrophiles with an empty molecular orbital

- $Y$ must be able to accept and stabilise electrons of $\sigma$ bond
- If $Y$ can it is a **leaving group**
- The more stable or electronegative $Y$ is the better leaving group it is
**Strength of electrophiles**

- Charged species are always more powerful **electrophiles** than neutral compounds.
- The more stable the cation the less reactive the electrophile.

\[
\begin{align*}
\text{H} & \quad \text{O}^- \quad \text{C}^+ \\
\text{O}^+ \quad \text{C}^- \quad \text{H}
\end{align*}
\]

- Electrophilic strength of the **electrophilic site** of a neutral species depends on the **partial positive charge** (\(\delta^+\)).
- H or C atoms are **electrophilic** if attached to **electronegative** atoms.
- More electronegative the atom the more **electrophilic** H or C.

\[
\begin{align*}
\delta^+ \quad & \quad \delta^- \\
\text{H–Cl} & \quad \text{H–OH} & \quad \text{H–NH}_2
\end{align*}
\]

H more electrophilic as chloride more electronegative than nitrogen.

\[
\begin{align*}
\text{O}^\delta^- & \quad \text{R–Cl}^\delta^- \\
\text{C}^\delta^+ & \quad \text{O}^\delta^- \\
\text{C}^\delta^+ & \quad \text{O}^\delta^-
\end{align*}
\]

C in acid chloride is more electrophilic than C in ketone as both O & Cl are electronegative.