Conjugated Systems

- We met in Chem 2321 unsaturated bonds as either a C= C bond or C≡C bond.
- If these unsaturated bonds are well separated then they react independently however if there are close together they interact with each other.
- When we have an alternating C=C double bond and C-C single bond this is called a conjugated system. See below.
- Conjugated systems have properties and reactivity which are sometimes quite different from their non-conjugated counterparts.

\[
\begin{align*}
\text{H}_2\text{C} & \equiv \text{CH} \text{-} \text{CH} - \text{CH} \equiv \text{CH}_2 \\
\text{H}_2\text{C} & \equiv \text{CH} \text{-} \text{CH} - \text{CH} \equiv \text{CH}_2 \\
\end{align*}
\]

- 1,3-Butadiene (conjugated; alternating double and single bonds)
- 1,4-Pentadiene (nonconjugated; nonalternating double and single bonds)

Natural Conjugated compounds

- Many of the pigments in nature are conjugated systems for example Lycopene is the red colour in tomatoes.
- Some are hormones for example progesterone, this prepares the uterus for ovum implantation. While others are aromatic compounds.

Synthesis of Conjugated Compounds

- Conjugated dienes can be prepared by methods we have already discussed for example below.

\[
\begin{align*}
\text{Cyclohexene} & \overset{\text{Br}_2}{\longrightarrow} \text{3-Bromocyclohexene} \\
& \overset{\text{KNO}_3\text{H}_2\text{O}}{\longrightarrow} \text{1,3-Cyclohexadiene} (76\%) \\
\end{align*}
\]

- Industrially, 1,3-butadiene is used in polymer synthesis and is made by thermal cracking over a chromium oxide/aluminum oxide catalyst.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 & \overset{600^\circ\text{C}}{\longrightarrow} \text{H}_2\text{C} \equiv \text{CHCHCHCH}_2 + 2\text{H}_2 \\
\text{Butane} & \overset{\text{Catalyst}}{\longrightarrow} \text{1,3-Butadiene} \\
\end{align*}
\]
• Ok let’s consider some physical properties of conjugated dienes: One property is that the central C2-C3 bond in dienes is shorter than the corresponding bond in butane.

• Another is their **stability**; indeed they are more stable than we might expect consider: (remember less negative more stable as less heat evolved!)

<table>
<thead>
<tr>
<th>Alkene or diene</th>
<th>Product</th>
<th>$\Delta H_{\text{hydro}}$ (kJ/mol)</th>
<th>Calculated (kJ/mol)</th>
<th>Difference (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH=CH=CH$_2$</td>
<td>CH$_3$CH$_2$CH=CH$_2$</td>
<td>$-126$</td>
<td>$-30.1$</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH=CH=CH$_2$</td>
<td>CH$_3$CH$_2$CH=CH$_2$</td>
<td>$-119$</td>
<td>$-28.4$</td>
<td></td>
</tr>
<tr>
<td>H$_2$C=CHCH=CH$_2$</td>
<td>CH$_3$CH=CH=CH$_2$</td>
<td>$-236$</td>
<td>$-56.4$</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH=CH=CH$_2$</td>
<td>CH$_3$CH$_2$CH=CH$_2$</td>
<td>$-299$</td>
<td>$-54.7$</td>
<td></td>
</tr>
<tr>
<td>H$_2$C=CHCH=CH$_2$</td>
<td>CH$_3$CH=CH=CH$_2$</td>
<td>$-253$</td>
<td>$-60.5$</td>
<td></td>
</tr>
</tbody>
</table>

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• We can get a rough handle on the stability increase if we deduct the expected $\Delta H_{\text{hydro}}$ for the observed (remember less negative more stable!)

- $\Delta H_{\text{hydro}}$ is used to compare the stability of different compounds.

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• So what accounts for the increased stability of conjugated dienes?

- Well according to valence bond theory this is due to the orbital’s hybridization.
- This is due to the increased *s-character* of the of the sp$^2$ bond 33% versus sp$^3$, 25%.
- This increase *s-character* results in the orbital having more spherical nature and the electrons are held closer to the nucleus.
- The result of this is that the bonds are shorter and therefore more stable.

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• If we consider MO theory: As a brief review remember when we combine the *p*-orbitals we get a bonding and antibonding MO.
- The antibonding orbital has a node (area of zero probability of finding an electron) between the two atoms.

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A little Bit of Theory

• No let's consider four adjacent p-orbitals

Due to these different MO orbitals there is partial double bond character between C2-C3 as you would expect this results in a short bond
• This is not possible in non-conjugated systems
• As reminder focusing of charge leads to instability and delocalization of charge leads to stability
• Here we delocalize the electrons over the carbon framework, which leads to stability

Electrophilic Additions

• One of the major difference in the way conjugated dienes react compared to typical alkenes is in electrophilic additions
• Normal alkenes react as summarized below

Conjugated dienes can undergo 1,2 or 1,4 addition as shown below
**Electrophilic Additions**

- What's the mechanism?

![Electrophilic Additions Diagram](image)

**Kinetic v. Thermodynamic Control**

- Consider the process below: Why do we get different product ratios at different temperatures?

![Kinetic v. Thermodynamic Control Diagram](image)

- To understand this consider we have a reaction where A can be converted to B or C.

**Kinetic v. Thermodynamic Control**

- Now let's consider B forms faster than C, \(\Delta G^\text{‡}_B > \Delta G^\text{‡}_C\), however C is more stable than C, \(\Delta G^\circ_B < \Delta G^\circ_C\).

**Kinetic v. Thermodynamic Control**

- What happens when we carry the reaction out at low temperature?
  - Due to the extra energy the processes are readily reversible and an equilibrium is reached.
- Since C is more thermodynamically stable it is formed in preference; it doesn't matter that C forms slower than B as the reaction for B is reversible.
- These reactions are said to be under thermodynamic control.

**Kinetic v. Thermodynamic Control**

- What happens when we carry the reaction out at higher temperature?
  - Both processes will be irreversible at this temperature therefore no equilibrium is reached.
  - Since B has the lower activation energy it is formed in preference it doesn't matter that C is more stable.
  - These reactions are said to be under kinetic control.
Kinetic v. Thermodynamic Control

- Worked example: 14.5 and 14.6

Diels-Alder Reaction

- One of the major uses of dienes is in the Diels-Alder cycloaddition, one of which is shown below.

\[
\begin{align*}
\text{1,3-Butadiene} & \quad \text{3-Buten-2-one} \quad \text{3-Cyclohexenyl methyl ketone (98%)}
\end{align*}
\]

Diels-Alder Reaction

- The mechanism of the D-A reactions is different than other reactions and is called a pericyclic process.
- Pericyclic processes take place in a single concerted step.
- We can picture the addition occurring between a head-on (s) overlap between the p-orbitals of the diene and alkene as shown below.

Diels-Alder Reaction

- The reaction takes place between a diene and an alkene, the dienophile (diene loving).
- The reaction generally is quicker if we have an electron withdrawing group on the dienophile.

Some Diels-Alder dienophiles:

- Ethylene unreactive
- Propenal (Acrolein)
- Ethyl propenoate (Ethyl acrylate)
- Maleic anhydride
- Benzoinone
- Propenoic acid (Propenoic acid)
- Methyl propenoate
**Diels-Alder Reaction**

- One of the useful features is that the reaction is that it is **stereospecific**: the stereochemistry of the starting material is maintained in the product.
- This is shown by the reaction of cis and trans alkenes below.

![Diels-Alder Reaction](image1)

**Diels-Alder Reaction**

- Another stereochemical feature is that the **endo** product is formed and not the **exo**.
- Endo and exo refer to stereochemistry of bicycles.
- A substituent is said to be exo if it is trans to the larger of the two bridges.

![Diels-Alder Reaction](image2)

**Diels-Alder Reaction**

- The endo product results as shown below, the dienophile approaches from directly below the diene to maximize orbital overlap.

![Diels-Alder Reaction](image3)

**Diene**

- The diene must have **s-cis** not s-trans geometry to react.

![Diene](image4)
**Diene**

- These two structures prevent s-cis alignment

![Chemical structures](image)

- However 1,

![Chemical structures](image)

**Polymerizations**

- Just like alkenes, dienes can undergo polymerizations. The initiator can be either a radical or an acid.
- Note the reaction occurs via 1,4 addition

![Polymerization structures](image)

**Polymerizations**

- As one might expect, the C=C bond geometry affects the physical properties of the resultant polymer.
- For example, the E-isomer of rubber has different properties than natural rubber; it is harder and more brittle.

![Polymerization structures](image)
Polymerizations

- Another example is neoprene

\[
\text{Chloroprene (2-Chloro-1,3-butadiene)} \quad \Rightarrow \quad \text{Neoprene (Z)}
\]

- Rubber can be hardened by vulcanization.
- This introduces sulfur cross-links and leads to improved wear and abrasion

Ultraviolet Spectroscopy

- The ultraviolet region of the spectrum extends from \(4 \times 10^{-7}\) to \(10^{-8}\) nm.
- Absorptions in this region are normally measured in nanometers (nm) where 1 nm = \(10^{-9}\) m.
- Thus the UV range of interest is from 200 to 400 nm.
- If the absorption of IR increases the bending and stretching vibrations of a molecule what does UV absorption do?

UV Spectrum of 1,3-Butadiene

- Remember 1,3-butadiene has four \(\pi\)-MOs, with the lower energy (bonding) orbitals filled in the ground state.
- Conversely the higher energy antibonding orbitals are empty.
- One UV irradiation we can promote an electron from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular orbital (LUMO).
- This is call a \(\pi\) to \(\pi^*\) transition and requires a certain energy (wavelength of light) dependent on the molecule.

- When we record a UV spectrum we irradiate the sample with a continuously changing wavelength of light.
- When the wavelength of light matches the energy need for electron promotion we get absorption. Therefore we plot wavelength against absorbance which is defined as:

\[
A = \log \frac{I_0}{I}
\]

- \(I_0\) is the intensity of the incident light and \(I\) is the intensity of the light transmitted.
- As you will notice a UV spectrum is displayed with zero absorption on the baseline in contrast to IR.
The exact amount of UV absorbed is expressed in molar absorptivity \( \varepsilon \):

\[ \varepsilon = \frac{A}{C \times l} \]

- \( A \) = Absorbance
- \( C \) = Concentration in mol/L
- \( l \) = Sample pathlength in cm
- We note the peaks position by \( \lambda_{\text{max}} \)

As you may expect the exact wavelength that affects the \( \pi \) to \( \pi^* \) transition is dependent on the energy gap between the HOMO and LUMO.

The energy gap between the HOMO and LUMO to a large degree depends on the nature of the conjugated system.

Therefore we can get an idea of the HOMO-LUMO gap by measuring the UV spectrum.

Interestingly the gap between the HOMO and LUMO decreases as the extent of conjugation increases.

Hence 1,3-butadiene absorbs at \( \lambda_{\text{max}} = 217 \text{ nm} \) while 1,3,5-hexatriene absorbs at \( \lambda_{\text{max}} = 258 \text{ nm} \).

Remember longer wavelength means lower energy.

So why do you think some organic compounds are coloured?

Well remember the visible region of the spectrum is right next to the UV region and runs from 400 to 800 nm.

As the conjugation increase absorption shifts to longer and longer wavelengths and before you know it the absorption goes above 400 nm and you detect this absorption with your visible wavelength detectors (commonly known as eyes).

For example \( \beta \)-carotene has 11 C=C bonds and a \( \lambda_{\text{max}} = 455 \text{ nm} \).

Now white light is made up of many different colours and between 400-500nm is blue light.

As the sun light hits the \( \beta \)-carotene the blue light is absorbed with the remaining reflected to our eyes. So we see the white light minus the blue light which we detect as yellow-orange.
Conjugation and Colour

\[ \lambda_{	ext{max}} = 455 \text{ nm} \]

\( \beta \)-Carotene