SECTION 13 – CONJUGATED SYSTEMS AND UV SPECTROSCOPY

13-1 -- Three Classes of Dienes
- Conjugated Dienes
- Cumulenes (“Allenes”)  
- Other, Isolated Double Bonds (d.b.’s)

13-1 -- Relative Stabilities of Dienes
- Heats of Formation (ΔH°f) – Values and Comparisons

13-2 -- Double Bonds of Conjugated Dienes
- Prefer to be Coplanar
- “Cisoid” or S-Cis Conformation
- “Transoid” or S-Trans Conformation
- Resonance Description

13-4 -- Reactions of Dienes – Summary (3 Main Reactions)
13-4 -- Additions of Electrophiles
- Markovnikov Addition
- 1,2-Addition Product vs. 1,4-Addition Product
- Mechanism of the Reaction
- Equilibration via an Sn1 Mechanism
- Kinetic Control vs. Thermodynamic Control

13-6 -- Addition of Halogens (X₂)
- Also Gives 1,2-Addition Product and 1,4-Addition Product
- Mechanism of the Reaction
- With Br₂, Mechanism May Go via a Bromonium Ion Intermediate

13-6 -- The Diels-Alder Reaction (Huge Topic!)
- General Form of the Reaction
- The Diene (4e- Component) and the Dienophile (2e- Component)
- Diene Conformation Must be S-Cis
- Diels-Alder Reaction is Concerted – All Bonding Changes Occur Simultaneously
- Formation of 1 New π-Bond and 2 New σ-Bonds
- Diels-Alder Reaction is Stereospecific
- Formation of Products that are Enantiomers and/or Meso Compounds
- Electronic Requirements of the Diels-Alder Reaction
- The “Endo Effect”
- Endo Substituents vs. Exo Substituents

13-13 -- Ultraviolet-Visible (UV-Vis) Spectroscopy
- Excitation of Electrons (e−’s)
- Promoting e− from Bonding Molecular Orbital (MO) or Non-Bonding MO
• Bonding Molecular Orbitals (MO’s) and Antibonding MO’s
• Non-Bonding MO’s
• The “Excited State”
• Lowest-Energy Transitions (the HOMO-LUMO gap, and ΔE)
• Conjugated π-Systems
• The Electromagnetic Spectrum and Complimentary Colors
• A Typical UV-Vis Spectrum
• Beer’s Law (A = ε · c · b)
• The Extinction Coefficient (ε) = “Molar Absorptivity”
• $\lambda_{max}$ Increases with Increasing Conjugation
• Delocalization of π-MO’s
• Systems with Non-Bonding e⁻’s and π-Electrons
• $\pi \rightarrow \pi^*$ Transitions vs. $n \rightarrow \pi^*$ Transitions
• 3 General Rules for $\lambda_{max}$
• What are Chromophores?
Section 13 - Conjugated Systems and Ultraviolet Spectroscopy.

3 Classes of Dienes.

1. Conjugated dienes = double bonds separated by one single bond.
   \[
   \begin{array}{c}
   \text{\textcolor{red}{C=CC}}\\
   \text{\textcolor{blue}{C=C}}
   \end{array}
   \]

2. Cumulenes ("allenes") = compounds with double bonds that share a single sp-hybridized carbon.
   \[
   \begin{array}{c}
   \text{\textcolor{red}{C=C=C}}
   \end{array}
   \] (not planar)

3. Other Isolated Double Bonds = nothing special here.
   \[
   \begin{array}{c}
   \text{\textcolor{red}{C=C}}\text{\textcolor{blue}{C=C}}
   \end{array}
   \]

Relative Stabilities of Dienes.

\[
\begin{array}{c|c|c}
\text{Structure} & \Delta H^\circ & \text{more stable than above by } \sim 7 \text{ kcal/mol} \\
\hline
\begin{array}{c}
\text{\textcolor{red}{C==C}}
\end{array} & 25.4 \text{ kcal/mol} & \text{unfair though because it has a more substituted d.b. (stable) } - 2 \text{ kcal/mol} \\
\begin{array}{c}
\text{\textcolor{red}{C=CC}}
\end{array} & 18.3 \text{ kcal/mol} & \text{conjugation } \text{worth about } 5 \text{ kcal/mol.} \\
\begin{array}{c}
\text{\textcolor{blue}{C=C=CC}}
\end{array} & 31.2 \text{ kcal/mol} & \\
\end{array}
\]

least stable arrangement of double bonds (d.b.'s).
- conjugated dienes = favorable interaction between double bonds makes conjugated double bonds 
  ~5 kcal/mol more stable than isolated d.b.'s.

- cumulenes
  \[ \implies \text{less stable than isolated d.b.'s.} \]

**Double Bonds of Conjugated Dienes Prefer to be Coplanar.**

\[ \implies 2 \text{ conformations:} \]

- “cisoid” or
  \[ \text{s-cis} \]
  \[ \Rightarrow \text{single bond} \]

- “transoid” or
  \[ \text{s-trans} \]
  \[ \Rightarrow \text{slightly more stable than s-cis conformer.} \]

**Why? = 2 reasons:**

- a transfer of e⁻-density from one \(\pi\) to \(\pi^*\) orbital allows for a little more delocalization and additional stability.
Calculations show that the stabilizing interaction between double bonds (d.b.'s) is a transfer of $e^-$-density $\pi_2 \rightarrow \pi_1^*$ and $\pi_1 \rightarrow \pi_2^*$ (both directions).

**Resonance description:**

![Resonance structures]

Minor contributors

(b) $s$-trans = more stable than $s$-cis (by $\sim 3$ kcal/mol) because of steric interactions.

1,3-butadiene:

- Small barrier height ($E_a$)
- In the transition state, the d.b.'s are perpendicular, so no conjugation.

- This energy diagram illustrates that conjugation is worth 7 kcal/mol in stability (lower $E$), but $\Delta H^\circ$ (page 13-1) claims conjugation is worth 5 kcal/mol.

$\rightarrow$ so, $5 - 7$ kcal/mol
Reactions of Dienes - 3 main ones we’ll look at.

1. Additions of Electrophiles - Markovnikov addition.

Example: \( \text{CH}_2=\text{CH}-\text{CH}==\text{CH}_2 + \text{HCl} \)

- 1,2-addition product
- 1,4-addition product ("conjugate addition product")

Mechanism:

\[ \text{CH}_2==\text{CH}-\text{CH}==\text{CH}_2 + \text{HCl} \]

1. Localized 1° carbocation (not nearly as stable as allylic carbocation).

\[ \text{CH}_3-\text{CH}==\text{CH}-\text{CH}_2 \]

2° carbocation more stable, but actually part of an "allylic cation" system.

\[ \text{CH}_3-\text{CH}==\text{CH}-\text{CH}_2 \]

\[ \text{CH}_2-\text{CH}-\text{CH}==\text{CH}_2 \]

\[ \text{CH}_3-\text{CH}==\text{CH}-\text{CH}_2 \]

1,4-product

1,2-product

\[ \text{CH}_3-\text{CH}==\text{CH}-\text{CH}_2 \]

Local resonance-stabilized.
in general, 1,2-addition is faster, but if products can equilibrate, the more stable product (often 1,4-addition product) will dominate.

- more highly substituted alkene.
- 1,2-addition product is stable too, though just to a lesser extent.

\[
\begin{align*}
\text{H}_2\text{C} & \equiv \text{CH}-\text{CH} = \text{CH}_2 \\
\Downarrow \text{H} - \text{Cl} \uparrow \\
\text{CH}_3-\text{CH} = \text{CH} - \text{CH}_2
\end{align*}
\]

\[\sigma^+\]

\[
\text{Cl} \quad \text{1,2-product}
\]

\[
\Theta \quad \text{1,4-product}
\]

- farther away and smaller $\sigma^+$ (positive charge)

* 1,2-addition and 1,4-addition products can equilibrate via an $S_{N1}$ mechanism under appropriate conditions.

\[\text{Cl} \text{ acts as the leaving group (it's an "okay" l.g.)}\]

reaction is initially under kinetic control, but if addition of $\text{Cl}^-\text{Cl}^+$ is reversible, the product mixture is under thermodynamic control.
(2) Addition of Halogens - also gives 1,2-addition and 1,4-addition products.

\[ \text{ex: } \begin{array}{c}
\text{Br}_2 \\
\rightarrow \\
\text{Br} \quad + \quad \text{Br}
\end{array} \]

* reaction may go via:

\[
\begin{array}{c}
\text{Br} \\
\leftrightarrow \\
\text{Br} \quad \text{Br}
\end{array}
\]

or via bromonium ion: not too important.

"S_N2" gives 1,2-product \{ \text{Br}^+ \}

"S_N2" gives 1,4-product \{ \text{Br}^- \}

(3) Diels-Alder Reaction = HUGE TOPIC !!

→ general form:

\[
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array} \rightarrow \begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array} \]

\text{dienophile} \quad \text{newly formed bonds} \quad \text{diene, a triene, an alkyne, etc.}

\text{dione} \quad \text{4e}^- \text{ component} \quad \text{2e}^- \text{ component}

\text{can be an alkene, another diene, a triene, an alkyne, etc.}
Diels-Alder Reaction - 5 considerations...

1) Diene conformation.
   - must have s-cis conformation.
   - dienes that cannot be s-cis do not react.

   ex: 

   problem: ends too far apart if s-trans, and product would be a trans-cyclohexene (very strained).

   (can't form)

   ex: 

   * equilibrium lies to the left (trans form), so this molecule cannot act as a diene.

   * dienes constrained (forced) to be s-cis react rapidly:

   ex: 

   ex:
SECTION 13 – CONJUGATED SYSTEMS AND ULTRAVIOLET (UV) SPECTROSCOPY

Were the FREE Section 13 Notes Useful?

Want the FULL VERSION of the Section 13 Notes?

*Download Them Instantly at:*

[ChemistryNotes.com](http://ChemistryNotes.com)