Reading: Chapter 7
Practice problems: those in text and 22-36, 38

Delocalized Electrons and Their Effect on Stability, Reactivity, and $pK_a$:
Ultraviolet and Visible Spectroscopy

Delocalized Electrons

- When it is possible to draw more than one valid Lewis diagram for a molecule or ion, that species is said to have resonance (electrons are delocalized).

- The molecule or ion is said to be a RESONANCE HYBRID of the structures drawn.

- For species with resonance, no single Lewis diagram will suffice to describe them correctly.
There are three alternative ways to draw the structure.

For any of the individual structures drawn we should expect:

- two different C-O bond lengths (single, double)
- two differently charged O atoms (neutral, negative).

**Expected:**
- C=O 122 pm **short**
- C-O 143 pm **long**
Delocalized Electrons

Experiments show bond length to be equal, which means none of the structures are a good representation.

Using the “average” of the three structures leads to averaged bond lengths, and also to averaged charges.

We need three Lewis representations to describe the real molecule.

Delocalized Electrons

The overall two negative charges are distributed over three oxygens. All have the same bond length and charge.

Structures are linked via $\leftrightarrow$ to indicate that they are resonance contributors.
Delocalized Electrons

Overall, the structure can be represented as above; however, this is not a Lewis representation.

Benzene

The Lewis representation of benzene suggests that we deal with a six-membered ring of carbon atoms that are held together by alternating single and double bonds.

C: $6 \cdot 4 = 24$ valence electrons
H: $6 \cdot 1 = 6$ valence electrons

Total $= 30$ electrons $= 15$ bonds
Benzene

This implies that we should observe alternating short (133 pm) and long (154 pm) bond lengths.

Measurements indicate that all bond lengths are the same (139 pm). Again, we need to draw resonance structures.

Benzene

Since both representations are equal, in average each C-C bond has a bond character in between a single and a double bond.

Measured bond length is: 139 pm
Benzene

This also explains why replacing two of the six hydrogens produces only three isomers. In case of alternating double and single bonds, A and B should be different and we should have four isomers.

Resonance

Alternating double bonds and single bonds in a ring system does not in all cases lead to resonance.

Cyclooctatetraene clearly exists as a nonresonating structure.

Measured bond lengths are typical for alternating single (146 pm) and double (133 pm) bonds.
Resonance

The ring atoms are not in one plane as in benzene.

In benzene there is overlap between all neighboring $p$ orbitals

In cyclo-octatetraene there is only pairwise overlap between neighboring $p$ orbitals

Resonance

DRAWING RESONANCE CONTRIBUTORS

- Only electrons move.
- The only electrons that move are $p$ electrons or lone pairs.
- The total number of electrons doesn’t change.
- Electrons can be moved only between $p$ orbitals.
- And only if they can be aligned properly.
Resonance

We move only the electrons

All atoms are $sp^2$ hybridized

Resonance distributes charge
Resonance shortens and lengthens bonds

\[ \text{butadiene} \quad 132.2 \text{ pm} \quad 147 \text{ pm} \quad \text{1-butene} \quad 151 \text{ pm} \quad \text{butane} \quad 153 \text{ pm} \]

Resonance

**REAL MOLECULE**

the real molecule has lower energy than any contributing structure would suggest

**RESONANCE CONTRIBUTORS**

\[ \text{O} \begin{array}{c} \text{C}=\text{O} \\ \text{O} \end{array} \quad \text{O} \begin{array}{c} \text{C}=\text{O}^- \\ \text{O}^= \end{array} \quad \text{O} \begin{array}{c} \text{O} \\ \text{C}=\text{O}^- \end{array} \]

**ENERGY**
Resonance and Acidity

The O-H bond is weakened, $O^+$ more electronegative

Negative charge distributed $\rightarrow$ stabilized

Resonance and Acidity

The equilibrium is shifted towards the right.
Resonance and Acidity

**Effect of electronegativity**

\[ \text{H}_3\text{C} - \text{CH}_2 - \text{H} \quad pK_a = 60 \]

\[ \text{H}_3\text{C} - \text{CH}_2 - \text{O} - \text{H} \quad pK_a = 16 \]

\[ \text{H}_3\text{C} - \text{C} - \text{O} - \text{O} - \text{H} \quad pK_a = 4.8 \]

**Effect of electronegativity and resonance**

Phenols behave differently than alcohols, they are acidic

\[ \text{Ph} \quad pK_a = 10 \]

\[ \text{Cyclohexanol} \quad pK_a = 16 \]
Resonance Stabilization of Phenolate Ion

Is again easily explained by resonance stabilization.

Resonance and Acidity

Protonated aniline is a stronger acid than protonated cyclohexylamine.
Resonance and Stability

1,3-cyclohexadiene is more stable than 1,4-cyclohexadiene

Conjugated polyenes are more stable because of resonance
Resonance and Stability

There are three resonance contributors for the diene.
Contribution of structures with charges is less important, however.

Stabilization of Charges

Stability of cations can be dramatically changed
Stabilization of Charges

Note: all carbons are $sp^2$ hybridized. All carbons are in one plane.

Effect in a Reaction

According to Markovnikov we should obtain products in a 50/50 ratio. The only product detected, however, is (1-bromoethyl)benzene.
Effect in a Reaction

This can best be explained by resonance stabilization of the carbocation intermediate.

Stability of Carbocations

Both resonance and higher order of substitution contribute to the stability of cations.
Stability of Carbocations

The more resonance, the better

Effect in a Reaction

Not IUPAC numbering

1,2-addition

1,4-addition
Effect in a Reaction

Resonance stabilization of the intermediate leads to two products.

THE ELECTROMAGNETIC SPECTRUM

\[ E = h\nu = hc/\lambda \]
Types of Energy Transitions in Each Region of the Electromagnetic Spectrum

<table>
<thead>
<tr>
<th>REGION</th>
<th>ENERGY TRANSITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>Bond-breaking</td>
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<tr>
<td>UV/Visible</td>
<td>Electronic</td>
</tr>
<tr>
<td>Infrared</td>
<td>Vibrational</td>
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<tr>
<td>Microwave</td>
<td>Rotational</td>
</tr>
<tr>
<td>Radio Frequency (NMR)</td>
<td>Nuclear and Electronic Spin</td>
</tr>
</tbody>
</table>

**EFFECT OF CONJUGATION**

<table>
<thead>
<tr>
<th>compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$C=CH$_2$</td>
<td>165</td>
<td>15,000</td>
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<tr>
<td></td>
<td>217</td>
<td>21,000</td>
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<tr>
<td></td>
<td>256</td>
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<td></td>
<td>290</td>
<td>85,000</td>
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<tr>
<td></td>
<td>334</td>
<td>125,000</td>
</tr>
<tr>
<td></td>
<td>364</td>
<td>138,000</td>
</tr>
</tbody>
</table>
Color of Objects

The principle photoreceptor in green plant photosynthesis is chlorophyll.

- Chlorophyll has two strong absorption bands one in the red and one in the blue wavelengths of visible light.
  - the peak molar absorption coefficient is higher than $10^5 \text{ M}^{-1}\text{cm}^{-1}$
  - chlorophyll a absorbs both lower and higher wavelength light than b
  - the formyl group on chlorophyll b shifts its absorption bands such that it efficiently absorbs light with wavelengths between 450 and 500 nm.
Carotenoids

- Carotenoids are extended polyenes that absorb light between 400 and 500 nm
  - Carotenoids are responsible for most of the yellow and red colors of fruits and flowers
  - Carotenoids serve at least two functions:
    - Light harvesting antennas
    - Through electronic interactions, they prevent light-excited chlorophyll molecules from transferring energy directly to O₂ to prevent formation of highly reactive O₂ species
      - Plants lacking carotenoids are quickly killed on exposure to light and O₂

Fall colors of deciduous trees

- Carotenoid accessory pigments (lycopene, carotene...) are largely responsible for fall colors in deciduous trees
  - In fall, chlorophyll molecules are degraded to reveal carotenoids before leaves fall