Solutions to Problem Assignment 5 (more bonding)

Zumdahl 67c, new version

CO has 10 valence electrons. Following figure 14.43, the electron configuration is \((\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2\), so the HOMO is \(\sigma_{2p}\) and the LUMO is the next one up in energy, \(\pi^*_{2p}\). Because the O atomic orbitals are lower in energy than the C ones (because O has larger \(Z_{\text{eff}}\)), the O and C AOs will make different contributions to the MOs, as discussed in class and in Figures 14.45-14.46 for HF. Here's what they look like:

![CO HOMO, \(\sigma_{2p}\)](image)

![CO LUMO, \(\pi^*_{2p}\)](image)

Because of the relative energies of the C and O AOs, a CO bonding MO, closer in energy to O, has a greater contribution from the O AO, while a CO antibonding MO, closer in energy to C, has a greater contribution from the C AO.

![M-CO \(\sigma\)-bonding MO](image)

![M-CO \(\pi\)-bonding MO](image)

Match these up with the metal d-orbitals: I have chosen the M-CO axis to be the z-axis and the paper to be the xz plane, so the metal \(d_{z^2}\) and \(d_{xz}\) orbitals have the right symmetry to interact with the CO HOMO and LUMO as shown.
1. $\text{H}_3\text{CCl}$, $\text{H}_2\text{CCl}_2$ and $\text{HCCl}_3$ have dipole moments. In $\text{CH}_4$ and $\text{CCl}_4$, the bond dipole moment vectors (which are of small magnitude anyway in $\text{CH}_4$) add to give a **ZERO NET SUM**. **Note** that there is **ONLY ONE** possible structure for $\text{H}_2\text{CCl}_2$. You might think you can draw more, but they can be rotated and superimposed to give the same structure.

2. Depending on the relative conformations of the $\text{CH}_2\text{Cl}$ fragment about the $\text{C-C}$ bond, many different structures are possible. Four of them are illustrated here, using a method you will see in organic chemistry, called a Newman projection. These are drawn so that you are looking down the $\text{C-C}$ bond. **[Note, using molecular models will be helpful to see these!]**

Of this set of conformations, **ONLY** the "STAGGERED" conformation with a Cl-C-C-Cl angle of 180° has a ZERO NET DIPOLE MOMENT, due to exact cancellation of its individual bond dipole moment vectors. A bulk sample of 1,2-dichloroethane will have some net dipole moment since not all the molecules will be in the staggered conformation. Actually the bulk dipole moment is expected to be quite small since the staggered conformation is the lowest energy conformation; it keeps the two bulky and partially negatively charged chlorines as far apart as possible.
3. Each molecule has only one reasonable Lewis structure

\[ \text{Ethylene; } \begin{array}{c}
\text{H} \\
C = C \\
\text{H} \\
\text{H}
\end{array} \quad \text{n=1} \]

\[ \text{Allene; } \begin{array}{c}
\text{H} \\
C = C \\
\text{H}
\end{array} \]

e etc.

In ethylene, each C is sp\(^2\) hybridized and trigonal planar. The C-H sigma bonds are formed from a C sp\(^2\) hybrid and a H 1s atomic orbital. The C-C \(\pi\)-bond is formed from the "leftover" C p-orbitals not used in making the sp\(^2\) hybrids. In allene, the CH\(_2\) carbons are again sp\(^2\) and trigonal planar. The central carbon is sp. Note that here the two CH\(_2\) fragments must be mutually perpendicular.

All the molecules in the series have LINEAR –C–(C)\(_n\)–C– axes and TRIGONAL PLANAR terminal CH\(_2\) groups; for n = 0, 2, 4, ... the molecules have overall PLANARITY; for n=1, 3, 5, ... the terminal CH\(_2\) planes are mutually PERPENDICULAR.

4. For C(CH\(_3\))\(_3\)+ there are 4x4+9x1−1=24 valence electrons. The structure is TRIGONAL PLANAR with an sp\(^2\) central carbon; the molecular geometry about each of the -CH\(_3\) group C atoms is TETRAHEDRAL. There is free rotation about the C-C bonds. Note that this does not satisfy the octet rule.

For the anion, # of valence electrons = 4x4+9x1+1=26. Use 24 valence electrons to satisfy the octet rule for each of the -CH\(_3\) group C atoms. Thus there are 4 electron pairs around the central C atom-- 3 \(\sigma\)-bonds and 1 unshared pair. The central C is sp\(^3\) hybridized. The electron pair geometry about the central C atom is now TETRAHEDRAL, giving rise to a PYRAMIDAL framework.
Again, the CH₃ groups are TETRAHEDRAL and there is FREE ROTATION about the C-C bonds.