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1.3.3 The Effects of Heteroatoms—Formaldehyde

Rule 5 states that similar molecules have similar MO diagrams. This is true, but there can be important differences that one needs to consider.

Formaldehyde and ethylene are isoelectronic – they have the same number of valence electrons and the same type of valence orbitals. However the oxygen introduces some important perturbations to the system.

The primary consequence of introducing heteroatoms into a hydrocarbon system is to alter orbital energies.

The key to our understanding of this aspect of the problem is the fact that electronegative elements have relatively low-lying atomic orbitals.

Thus the atomic orbitals contributed by oxygen to the formaldehyde molecule start at much lower energies than those of C or H.
As a result, the mixings are no longer degenerate and one must consider the consequences of the second order perturbation rules for orbital mixing.

The mixing diagram for formaldehyde is shown in Figure 9, although the energies of the orbitals are not precisely placed. They are simply indicated as being lower than the respective orbitals of CH$_2$. 
Group Orbital Picture of Formaldehyde
Since the building blocks for $\pi$ and $\pi^*$ are isolated $p$-orbitals, there is no ambiguity about the relative energies of the two initial orbitals:

the oxygen orbital lies below the carbon orbital. As such, there is no ambiguity about the expected polarizations.

The lower energy MO, the $\pi$-orbital, must be polarized towards the oxygen. Similarly, the higher energy MO, the $\pi^*$, must be polarized towards the carbon.

Inserting the 12 electrons, an interesting feature emerges:

although the LUMO is $\pi^*$, as expected, the HOMO is not $\pi$, but rather is a lone pair, which we describe as $\pi$(CH$_2$) minus the oxygen $p_y$ orbital.

It is a $\pi$-type lone pair with significant out-of-phase mixture of the $\pi$(CH$_2$) orbital.
Figure 1.17. The orbital mixing diagram of $\text{CH}_2=\text{O}$ from $\text{CH}_2$ plus an oxygen atom
The MO diagram for this prototype carbonyl has significant implications for predicting/rationalizing reactivity patterns.

1. Polarization of the LUMO is towards carbon. Therefore nucleophiles will interact with the LUMO preferentially at the carbon atom (bearing the larger coefficient). This MO leans away from the bonding region, as is typical for antibonding orbitals (As depicted in the diagram below.)

2. The polarization of the HOMO towards oxygen also has implications. Protonation will occur on oxygen, not carbon, and will utilize a lone pair, not the $\pi$-bond.
All of this is totally compatible with what we learned using VB theory – recognizing electronegativity differences and resultant bond polarities, or invoking a resonance argument.

The group orbitals that we have developed for formaldehyde correspond very well with the important functional group orbitals of any simple aldehyde or ketone.
Although alkyl groups are often simply “spectators” when it comes to organic reactivity, when a CH$_3$ group is substituted adjacent to a conventional $\pi$-system, such as an alkene, a carbocation, or a carbonyl, important interactions between the methyl (alkyl) group may occur.

For example, Figure 10 shows an orbital mixing diagram for propene, concentrating one’s attention on the interaction (perturbation) of the pertinent methyl (CH bonding) group orbitals with the $\pi$-system of ethylene.
As can be seen, the in-phase and out-of-phase mixing of the lower-lying methyl $\pi$(CH$_3$) orbital with the $\pi$ orbital of the double bond gives rise to two new orbitals, both filled, one lower and one higher in energy than the original unmixed orbitals. The new HOMO for the molecule is thus the orbital resulting from the out-of-phase interaction.

Mixing diagram for propene, showing the perturbation of ethylene by a methyl substituent.
The predicted elevation in orbital energy is fully supported by the photoelectron spectrum of propene which exhibits a band at 9.75 eV, compared to ethylene’s value of 10.51 eV.

The fact that the orbital resulting from in-phase interaction is lowered turns out to have little impact on understanding the reactivity of propene.

A similar mixing can be done with the $\pi^*$ orbital, and you should examine this yourself and consider its repercussions regarding reactivity.
Propene

\[ \sigma(\text{out}) \]

\[ \pi(\text{CH}_3) \]

\[ \sigma(\text{CH}_3) \]

\[ \text{H} - \text{O} - \text{H} \]

\[ \text{H} - \text{O} - \text{H} \]

\[ \text{H} - \text{O} - \text{H} \]

\[ \text{H} - \text{O} - \text{H} \]