MOLECULAR ORBITAL PICTURE OF CARBONYLS

Often it is useful to look at the molecular orbital picture of a molecule to learn something about its reactivity.

In the case of carbonyls, frontier orbital ideas tell us to look at the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO).

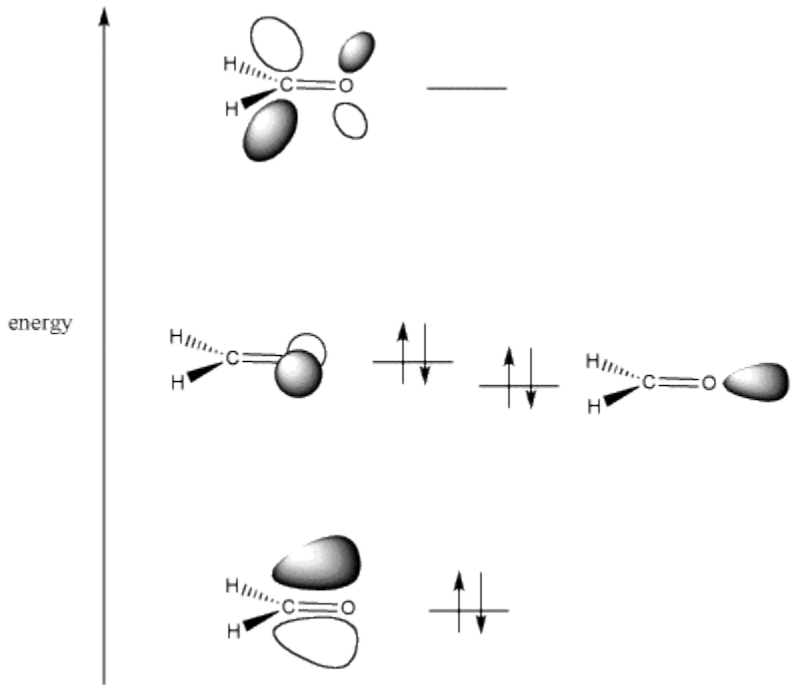

Figure CO3.1. Frontier orbitals in a carbonyl compound.

When two different atoms bond together, the molecular orbitals that they form are not evenly distributed between the atoms. Instead, the new molecular orbital is closest in space to the atom to which it is closest in energy.

In the case of carbon and oxygen, oxygen is more electronegative than carbon. That means its electrons are more tightly held than carbon's. That means its electrons are lower in energy than carbon's.

When carbon and oxygen combine, a bonding orbital and an antibonding orbital result. The bonding orbital is lower in energy than the orbitals on either carbon or oxygen. However, it is closer in energy to oxygen. Thus, the orbital itself is more centered on oxygen. In other words, the electrons in the bond are closer to oxygen than to carbon.

The antibonding orbital, on the other hand, is closer to carbon in energy, although it is higher in energy than either carbon or oxygen. It is more centered on the carbon than the oxygen. That means the "target" for the electron donation is mostly found on the carbon. The carbonyl carbon is the electrophilic position.

If electrons are going to be donated to the molecule, the lowest energy position available for electrons in the molecule is described by the LUMO. The LUMO in this case is the C=O pi* or pi antibonding orbital.

If the carbonyl is going to donate electrons, the electrons will come from the HOMO. In this case, that refers to the non-bonding electrons. These electrons are found on the oxygen, and are equivalent to the lone pairs in the Lewis structure.

Source : http://employees.csbsju.edu/cschaller/Reactivity/carbonyl/COMO.htm