Frontier MOs: An Acid-Base Theory

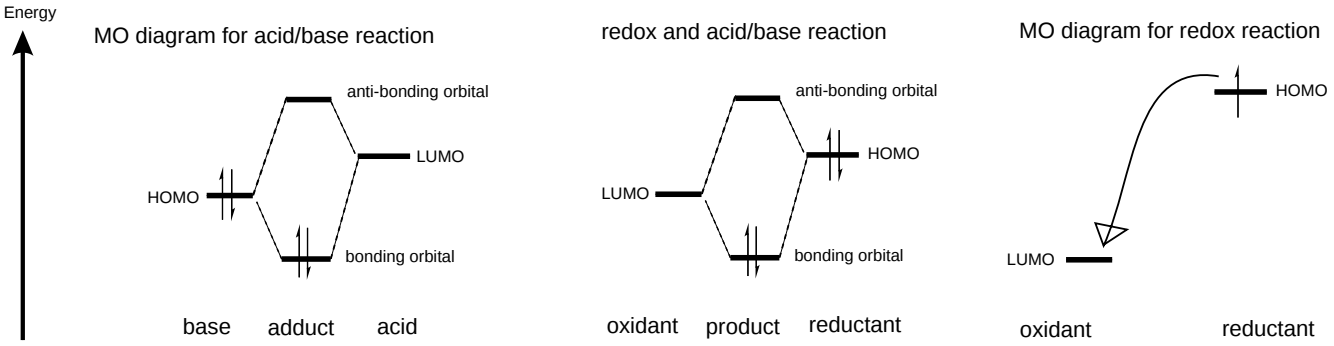
Skills to Develop

- Distinguish and describe the significance of frontier MOs

Frontier means a border area, between two things (often, between 2 countries). In this case, we are interested in the MOs at the border between occupied and empty. The **frontier MOs** are called the HOMO and the LUMO. HOMO is Highest Occupied MO, the highest-energy MO that has electrons in it. LUMO is Lowest Unoccupied MO, the lowest-energy MO that doesn't have any electrons in it.

Frontier MOs are very important for reactivity. Earlier, we said that most reactions can be called either Lewis acid/base or redox. In a Lewis acid/base reaction, an electron pair from the base is shared with the acid. What this really means is that the base has a HOMO that is pretty high-energy (a lone pair), and the acid has a LUMO that is pretty low energy. (A lone pair in MO theory is an electron pair in a non-bonding MO. A low LUMO usually means an empty valence orbital, like on B or on a cation.) We can make a bonding and anti-bonding combination of the base HOMO and acid LUMO, and that will stabilize the electrons from the base's HOMO, lowering the total energy. This creates a bond between the acid and base.

In a redox reaction, the oxidant has a low LUMO, and the reductant has a high HOMO, but this time the oxidant LUMO is lower than the reductant HOMO, so that the electrons in the reductant HOMO move completely to the oxidant LUMO. Often the energy match is bad, so that no covalent bond forms, just the electron moves. Sometimes a covalent bond forms also. This depends on the AO energies, which depends on the electronegativity, just like you would expect. You can still predict covalent/ionic bonding based on electronegativity.

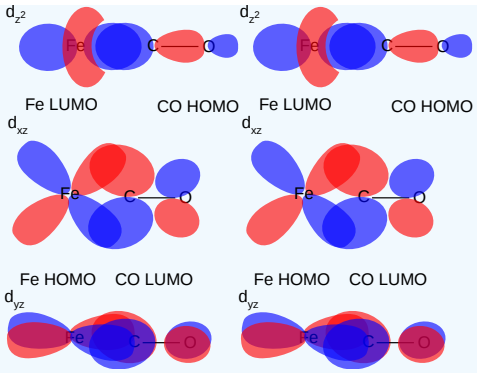


Diagrams of acid/base, redox, and both reactions.

Molecules with low HOMO and high LUMO, a big HOMO-LUMO gap, are not very reactive! Hydrocarbons are a good example (like oil, etc). They do burn easily, but you have to get them hot first. At room temperature, they don't react. This is why if you want to store something reactive like K metal, you probably keep it in a bottle of oil.

Example $FrontierMOs.1$: CO Toxicity

You probably know that CO is toxic (which is why you shouldn't stay in a garage with a car running, because the CO from incomplete combustion can kill you). The reason CO is toxic is because it binds metal ions really tightly. You use Fe(II) ions in your blood to bind O_2 and carry it to your cells. CO binds to the Fe(II) more tightly than O_2, so if you breathe too much CO, your cells won't get any oxygen, because all the Fe(II) in your blood bound CO instead. We can understand how and why CO binds Fe(II) using MO theory. Go back and look at the MO diagram for CO. The HOMO is a slightly-bonding orbital that is mostly on carbon. It is pretty high-energy. The LUMO is a π* orbital that is also mostly on carbon, and it is kind of low-energy because the splitting of π MOs is smaller than σ MOs (because of less overlap). CO has a small gap between the HOMO and LUMO. Fe(II) also has a small gap between HOMO and LUMO, because it has 6 electrons in 3d orbitals. The HOMO is high, because 3d is not so stable, and the LUMO is low, because it is also 3d and not much higher than the HOMO (there is a gap because the other atoms around the Fe(II) in hemoglobin make the d orbitals different energies). So what can happen is that the HOMO on CO makes a σ bond with the LUMO on Fe(II), and the HOMO on Fe(II) makes a π bond with the LUMO on CO. This "multiple bond" between CO and Fe(II) makes CO toxic. And because the HOMO and LUMO of CO are big on carbon, you won't be surprised that the bond is Fe-C=O, not Fe-O=C.



MO interactions between Fe and CO frontier MOs. Top: σ interaction. Bottom: π interactions (2 CO LUMOs, 2 Fe HOMOs, related by 90° rotation)

Contributors and Attributions

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