

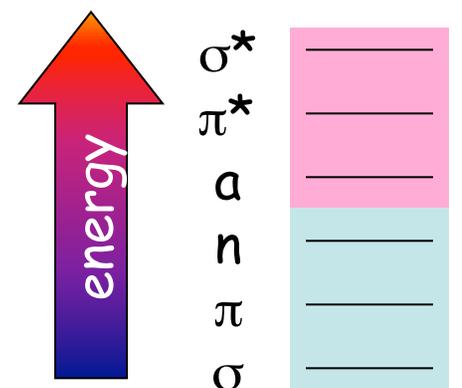
Recognizing Electrophiles and Acids

Electrophiles accept electrons into their lowest unoccupied MO

The usual order of energy levels

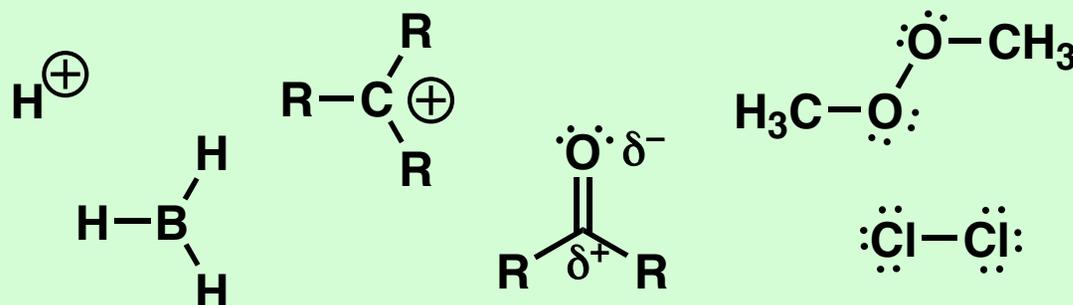
The signatures of electrophiles and acids

- an electron deficient atom especially as revealed by an incomplete octet (duet for H) of electrons (e.g., carbocation, boron, H^+)
- a partial positive charge owing to a polarized H-X or C-X bond (polarization results when H or C is bound to electronegative atom "X" or an atom X^+ that bears a positive formal charge such as $[H-NH_3]^+$)
- a partial positive charge revealed via resonance contributor(s)
- a weak bond usually involving a pair of heteroatoms e.g., X-Y bonds like Br-Br, I-Cl, -O-O-
- strong acids tend to be strong electrophiles
- any species with a low lying LUMO



empty / filled	σ^*	a	π^*
σ	$\sigma \rightarrow \sigma^*$	$\sigma \rightarrow a$	$\sigma \rightarrow \pi^*$
n	$n \rightarrow \sigma^*$	$n \rightarrow a$	$n \rightarrow \pi^*$
π	$\pi \rightarrow \sigma^*$	$\pi \rightarrow a$	$\pi \rightarrow \pi^*$

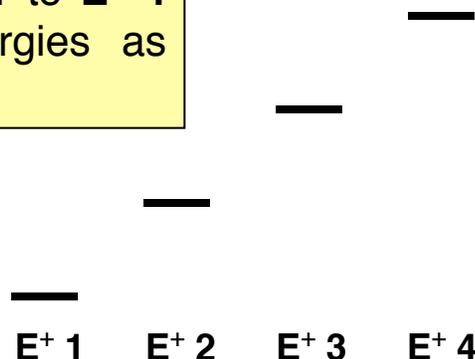
Typical electrophiles



Electrophilicity and LUMO Energy Level

There's a good analogy between electrophiles and acids. Just as some acids are stronger than others, some electrophiles are stronger than others. Whereas we speak of acidity to describe the strength of acids, we speak of **electrophilicity** to describe the strength of electrophiles.

Consider the series of electrophiles $E^+ 1$ to $E^+ 4$ with LUMO energies as shown



HOMO Energy of Nu



Given the HOMO energy level of Nu as indicated:

Which frontier orbital interaction will be the strongest?

Which empty orbital is most easily accessed?

Which electrophile has the highest electrophilicity?

REACTIVITY CONCISELY SUMMARIZED: Continuing the acid/base analogy further, strong nucleophiles will generally react with strong electrophiles just as strong acids and strong bases always react. Such favorable reactions are expected from small frontier orbital HOMO-LUMO **energy gaps**. Weak nucleophiles and weak electrophiles are not likely to react at all; the frontier orbital gap is too wide in this case. A weak electrophile is likely to react only if it encounters a strong nucleophile; a weak nucleophile is likely to react only if it encounters a strong electrophile.