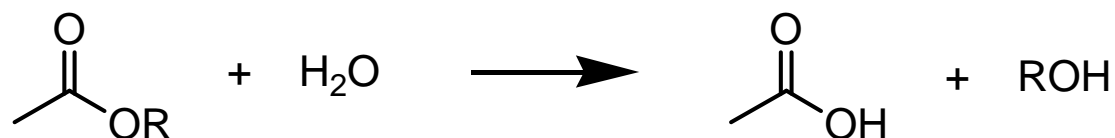


Chemical Reactions Involve Changing Electronic Configuration

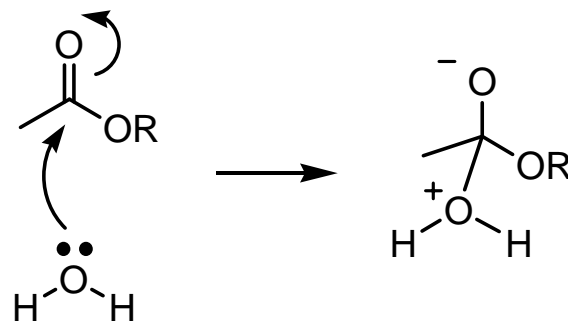
- Electrons move (many orders of magnitude) faster than atoms.
- So, as atoms move, electrons & orbitals are constantly responding.
- One method for tracking/illustrating this: “Electron Pushing”
- Not just useful for accounting; also shows intermediates along reaction path

“Electron Pushing”

Simple but effective example:
Base-catalyzed hydrolysis of acetyl ester.



A tempting beginning...



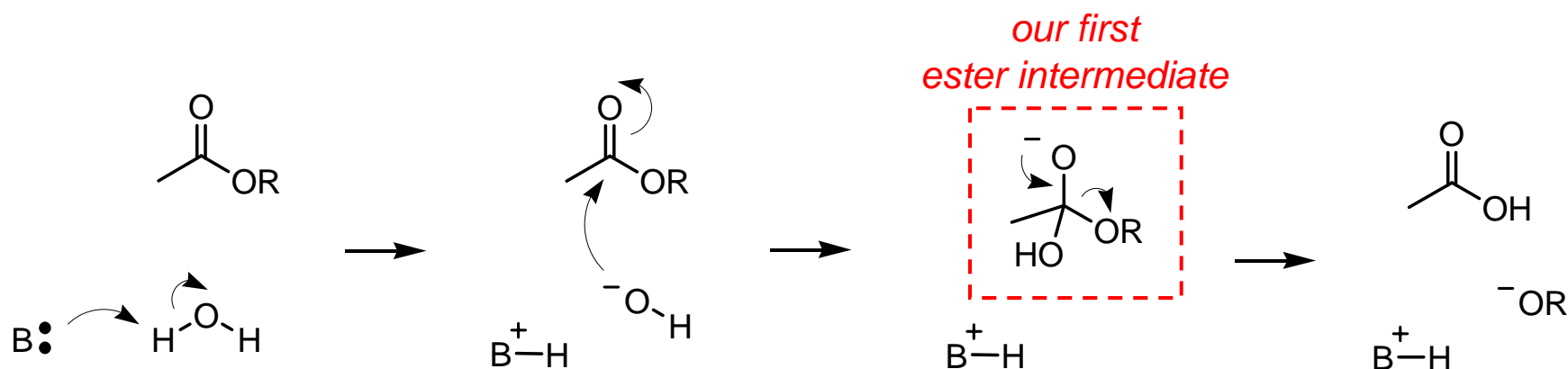
*This does happen,
but intermediate is very unstable.*

Some electron-pushing rules of thumb:

- Retain all atoms, electrons, and charge
- Avoid zwitterions (especially when related by proton transfer)
- Avoid multiple charges on same molecule
- Don't take shortcuts; show all steps

“Electron Pushing”

Simple but effective example:
Base-catalyzed hydrolysis of acetyl ester.

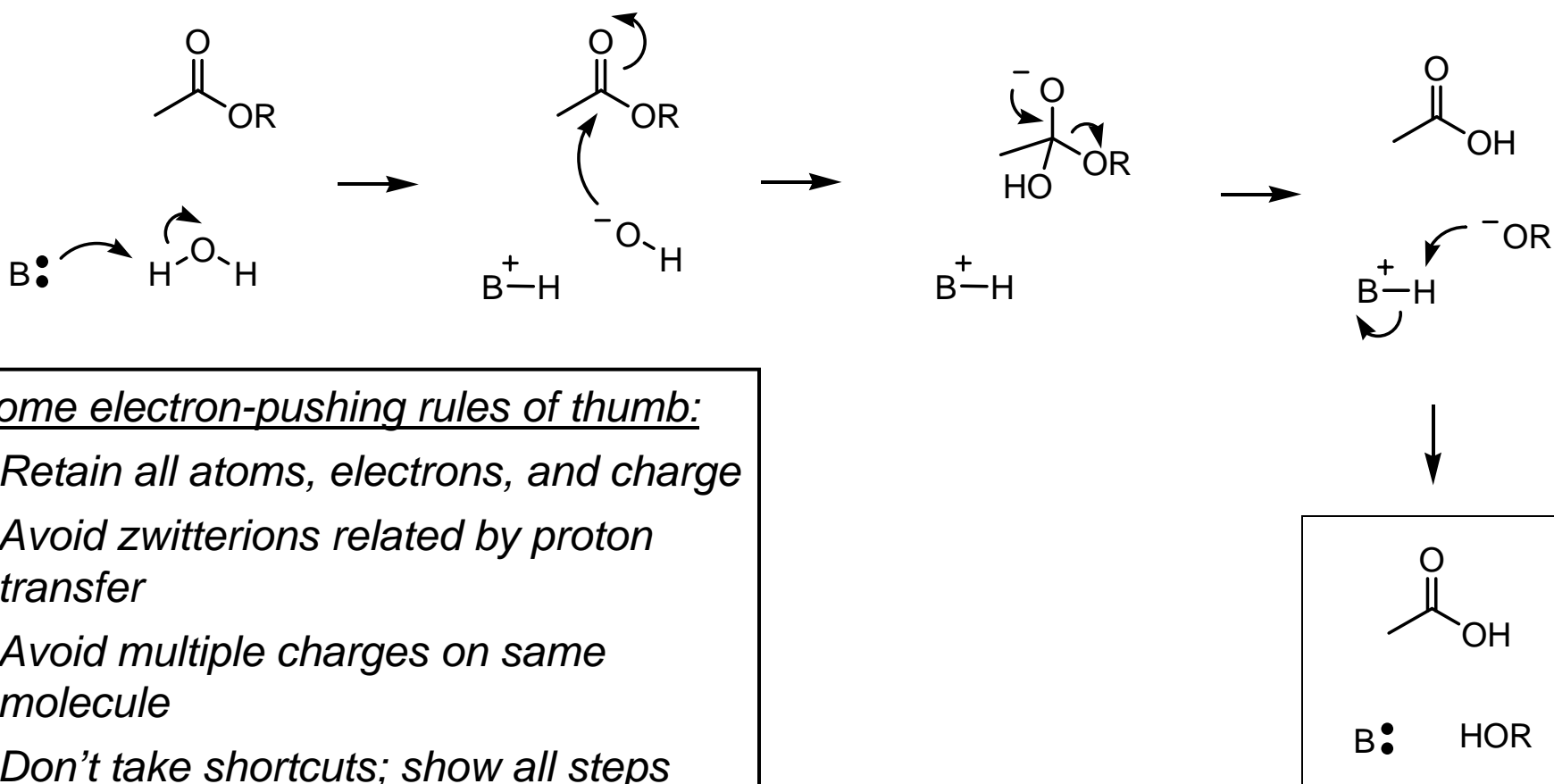


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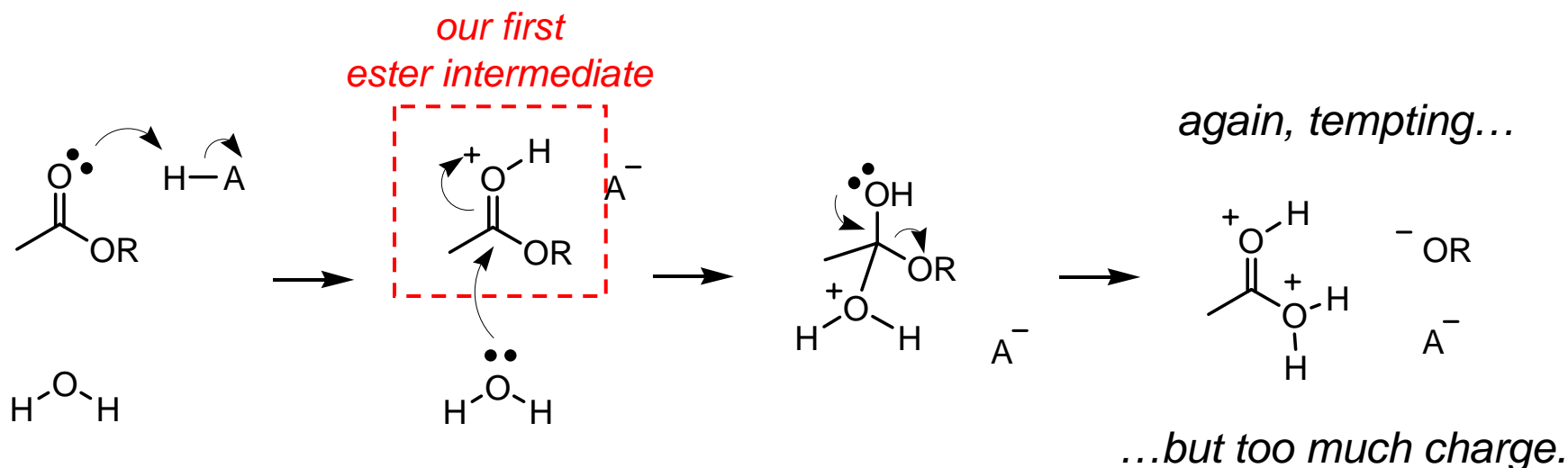
“Electron Pushing”

Simple but effective example:
Base-catalyzed hydrolysis of acetyl ester.



“Electron Pushing”

Acid-catalyzed hydrolysis of acetyl ester:

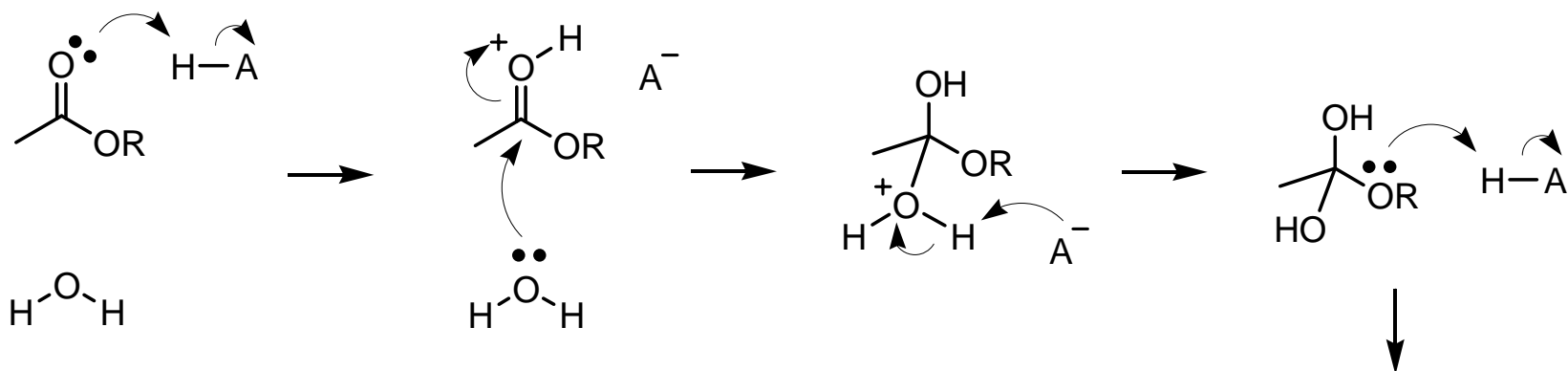


Some electron-pushing rules of thumb:

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- Avoid multiple charges on same molecule
- Don't take shortcuts; show all steps

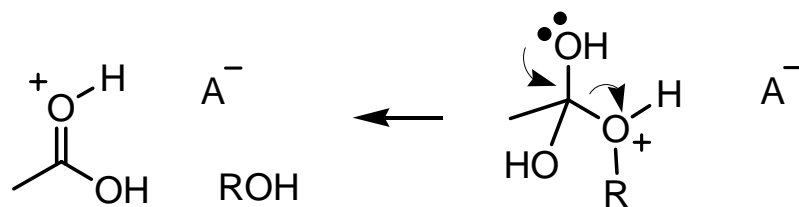
“Electron Pushing”

Acid-catalyzed hydrolysis of acetyl ester:



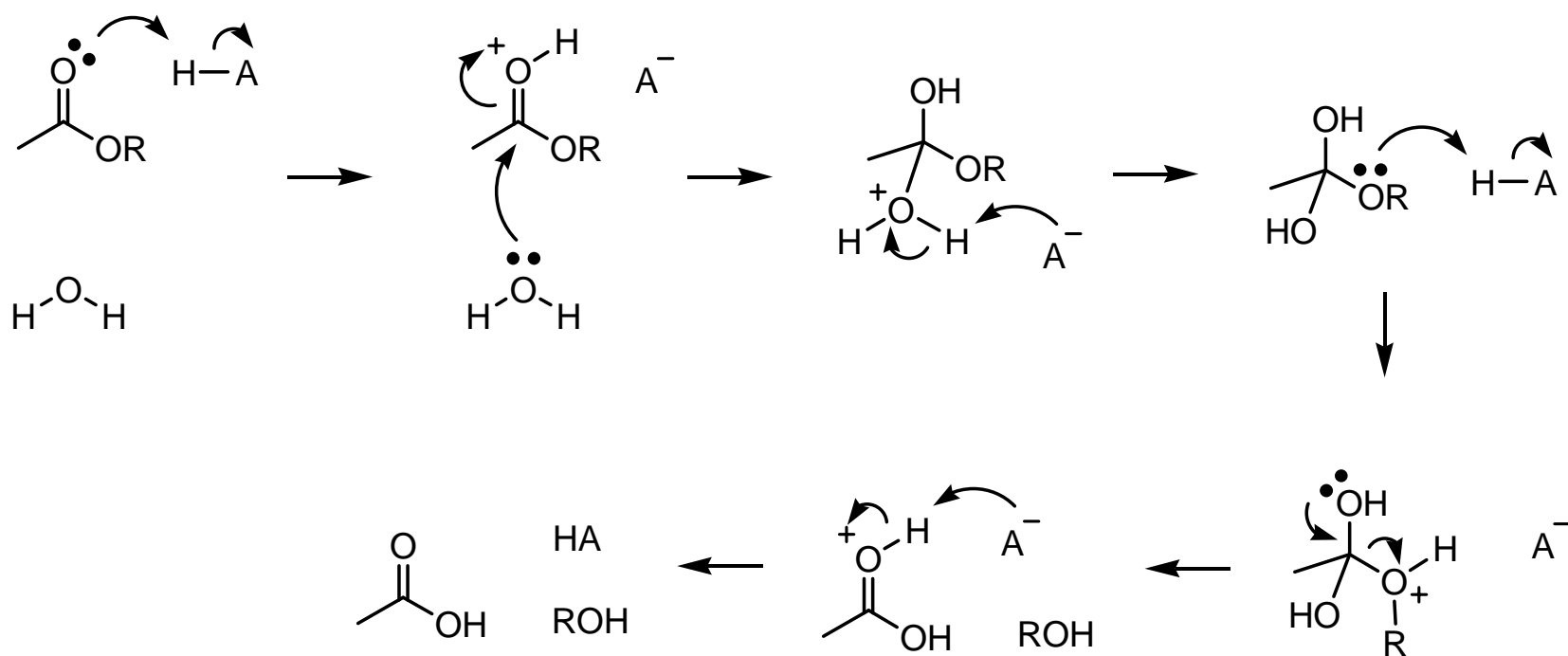
Some electron-pushing rules of thumb:

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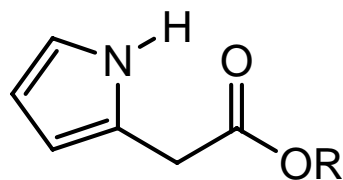
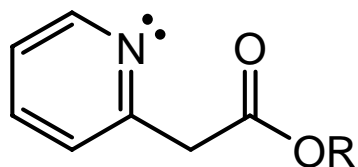
“Electron Pushing”

Acid-catalyzed hydrolysis of acetyl ester:



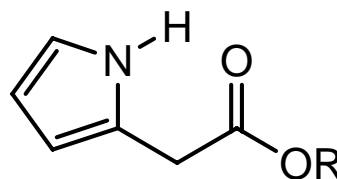
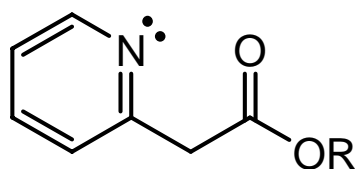
Discussion Question

If catalyzed rate is determined, in part, by stability of the initial ester intermediate, for which of these reactants would hydrolysis be more susceptible to catalysis by added acid? Which would be more susceptible to added base?

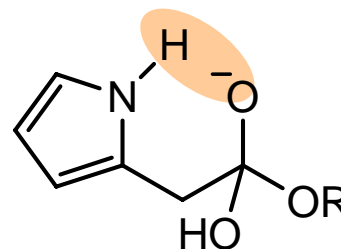
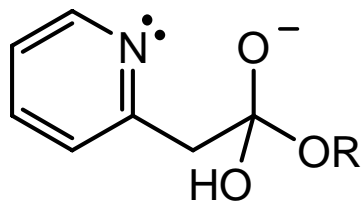


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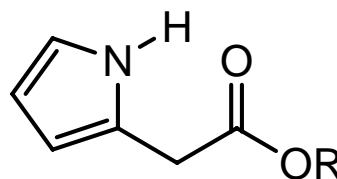
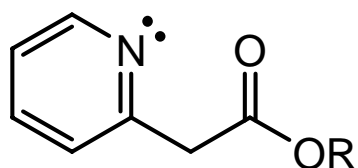
In **base**, ester intermediate looks like:



*hydrogen bonding
stabilizes anion;
facilitates base
catalysis*

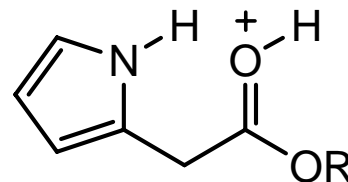
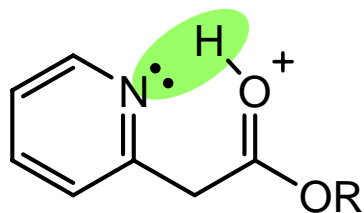
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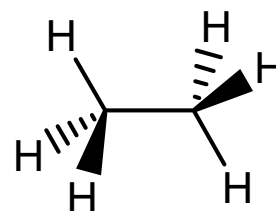


*(no H-bonding
that isn't already
present in
unprotonated
state)*

Molecular Orbital (MO) Theory

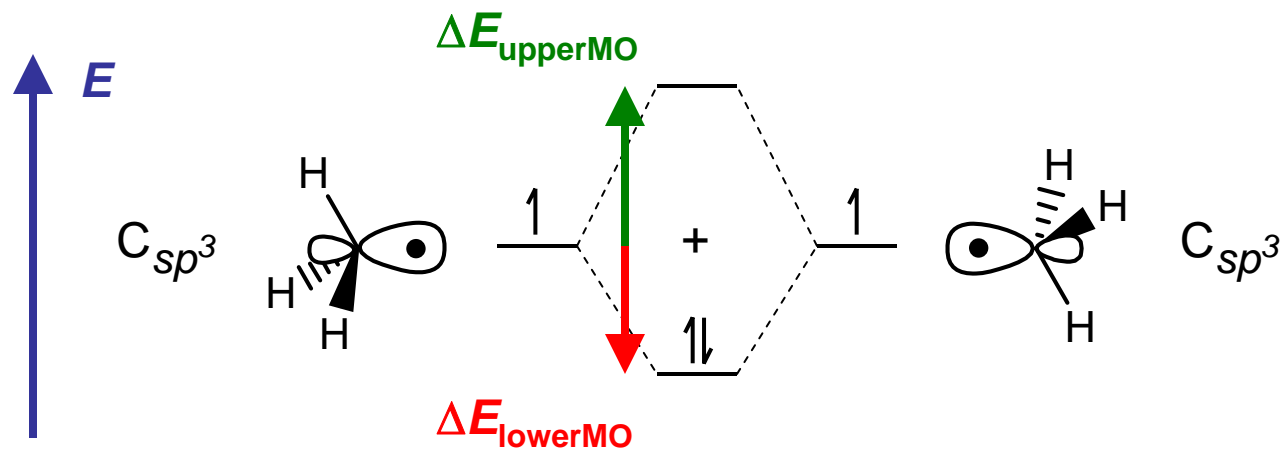
MO Theory explains energy of bonding in terms of “orbital mixing”.

C-C bond in ethane built from component atomic orbitals.



equals

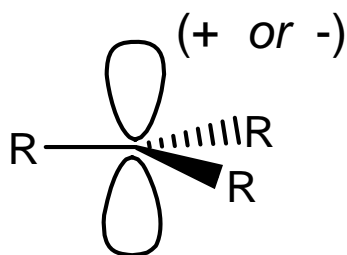
Because energetics of system are determined by energies of *electrons*, orbital mixing stabilizes this bond.



Typically, $\Delta E_{\text{upperMO}} > -\Delta E_{\text{lowerMO}}$

Molecular Orbital (MO) Theory

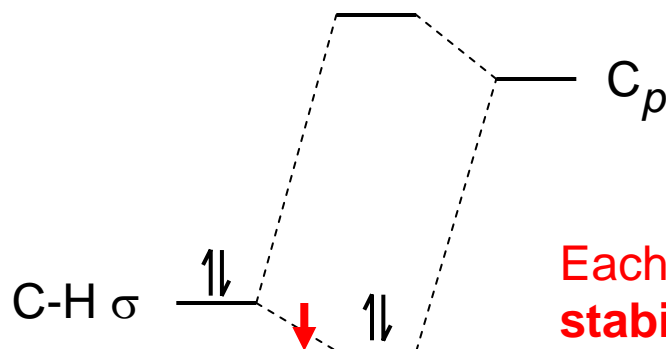
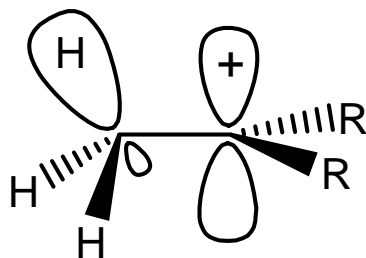
MO Theory explains difference in effect of substitution on carbocation and carbanion stability.



stability for R_3C^+ : $3^\circ > 2^\circ > 1^\circ > CH_3$

stability for R_3C^- : $3^\circ < 2^\circ < 1^\circ < CH_3$

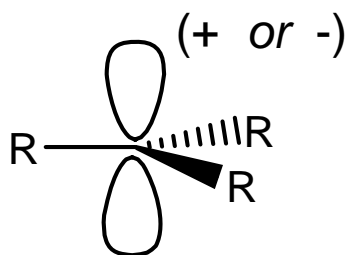
For each neighboring C-H bond in R_3C^+ ,



Each neighboring C-H σ stabilizes empty C_p orbital ($\Delta E_{\text{lowerMO}}$) in cation

Molecular Orbital (MO) Theory

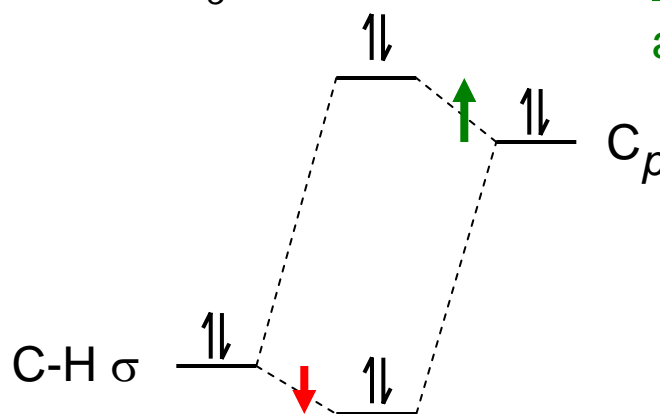
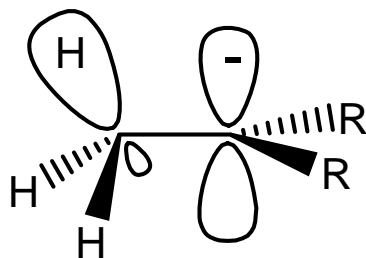
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stability for R_3C^- : $3^\circ < 2^\circ < 1^\circ < CH_3$

For each neighboring C-H bond in R_3C^- ,



Because

$\Delta E_{\text{upperMO}} > \Delta E_{\text{lowerMO}}$,
anion is **destabilized**