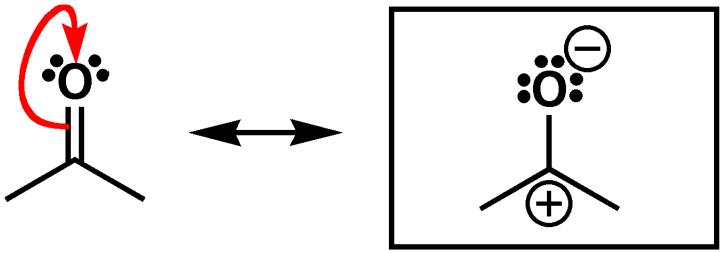
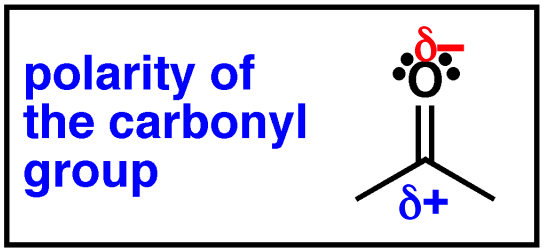
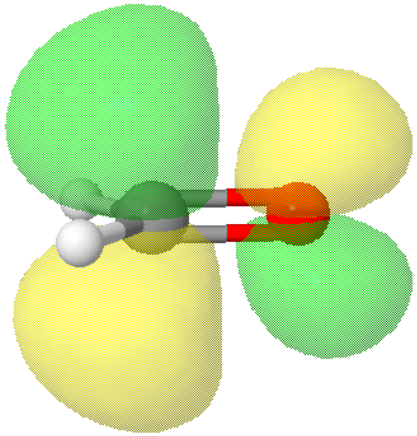
Resonance Contributors and the LUMO Reveal a Consistent Picture of Carbonyl Polarity

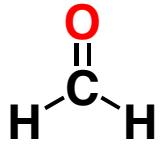


2nd best resonance contributor



The molecular orbital model is consistent with the above resonance picture. The LUMO (π*) of formaldehyde is shown; the π* lobe on carbon is much larger than on oxygen. In other words, carbon contributes more to π* than does oxygen. Nucleophiles will be attracted to the largest lobe of the LUMO. Conclusion: Carbon (not oxygen) is the electrophilic site in carbonyl groups.

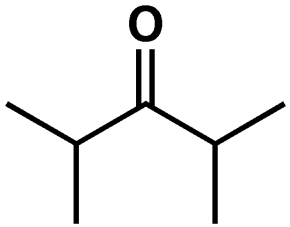




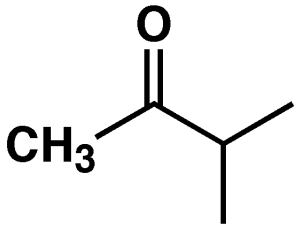
formaldehyde

Structure-Reactivity and the Carbonyl Group

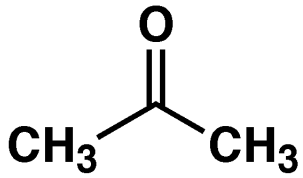
Aldehydes are more reactive than ketones.



A



B

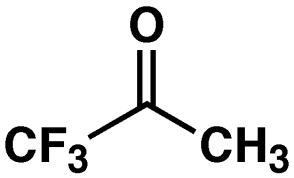


C

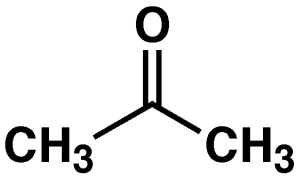
Reason:

Steric factors

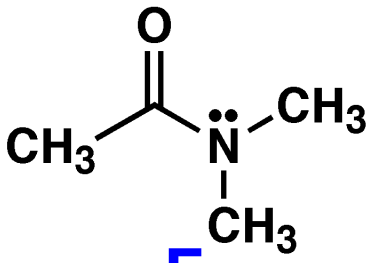
Better electrophile



D



E



F

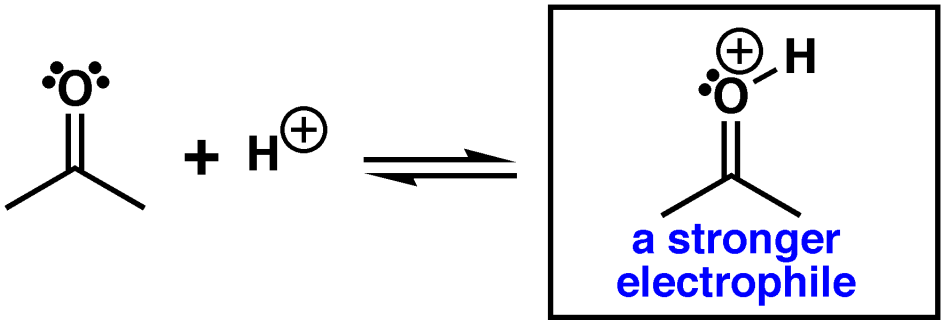
Reason:

Electronic factors;

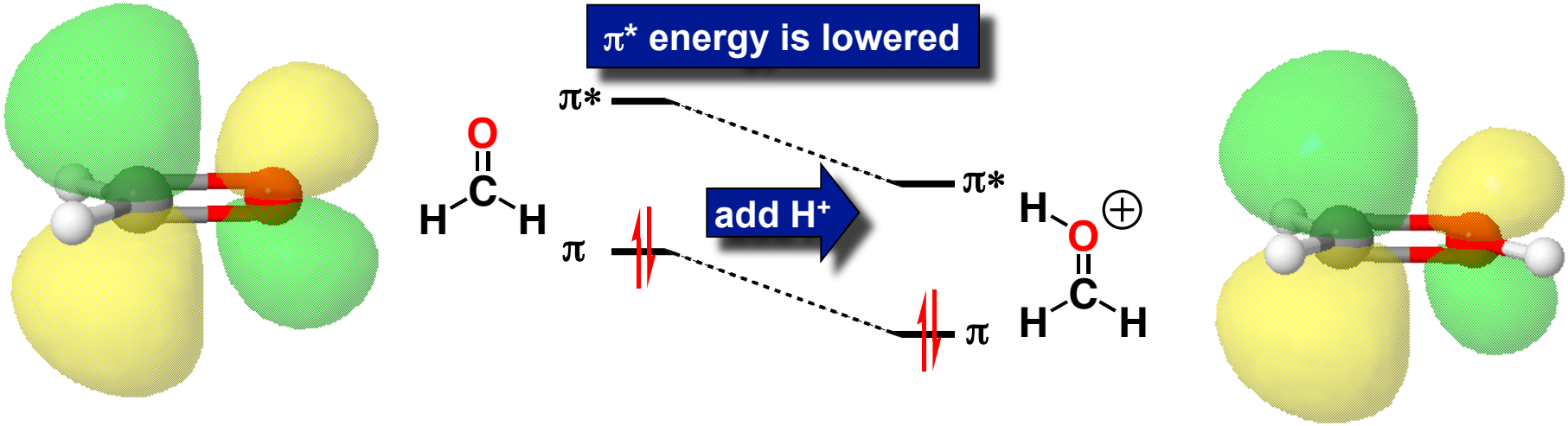
LUMO energy level

better electrophile

The Carbonyl Oxygen is Protonated Under Acidic Conditions



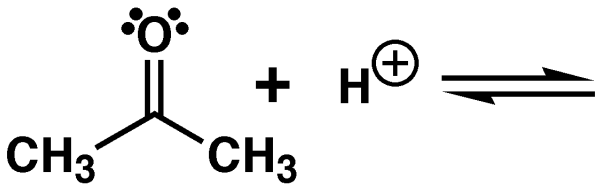
The carbonyl is converted into a more powerful electrophile by protonating the carbonyl oxygen.

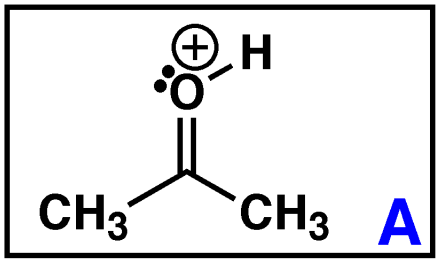


Characteristic of a more powerful electrophile, the protonated carbonyl has a lower lying π* (LUMO) energy than the neutral carbonyl.

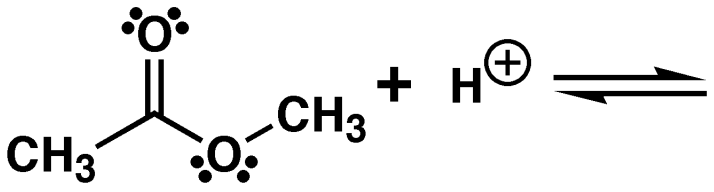
On the Bascisity of Carbonyl Oxygen

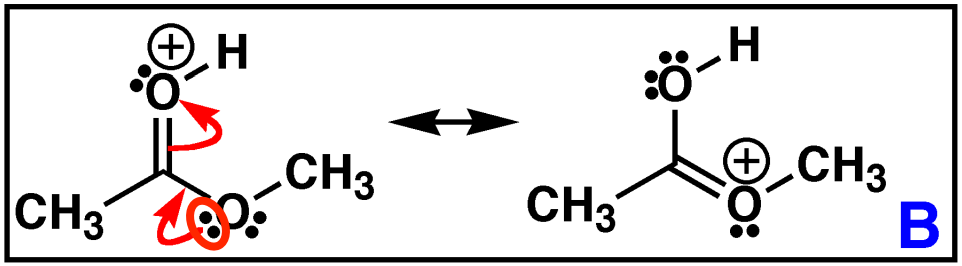
Which carbonyl is the stronger base?

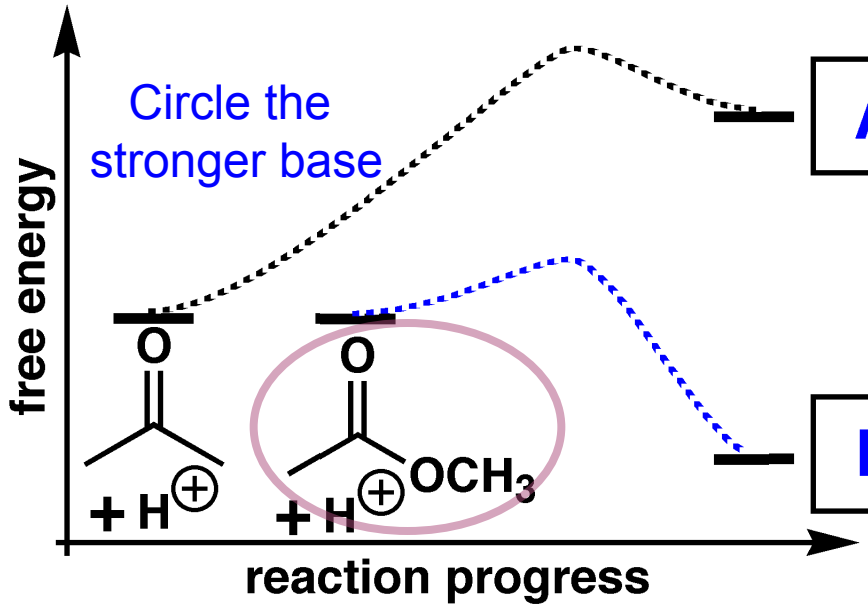




Which of these protonated forms (**A** or **B**) is more stable? Why?
delocalized charge







A pK_a = -7.2
(stronger acid)

B pK_a = -6.5
(weaker acid)