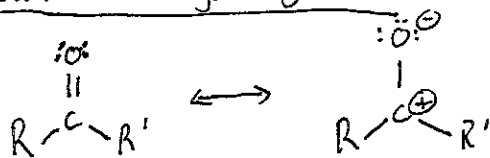


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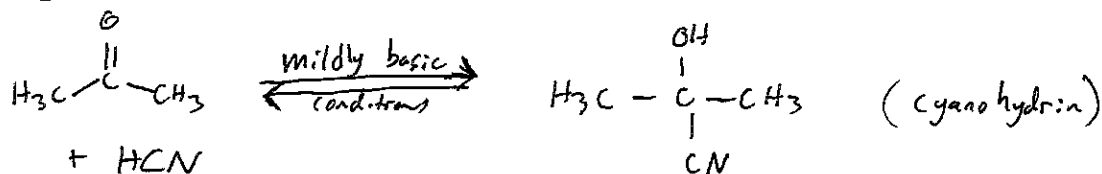
Recall: Aldehydes & Ketones



(minor, but important)

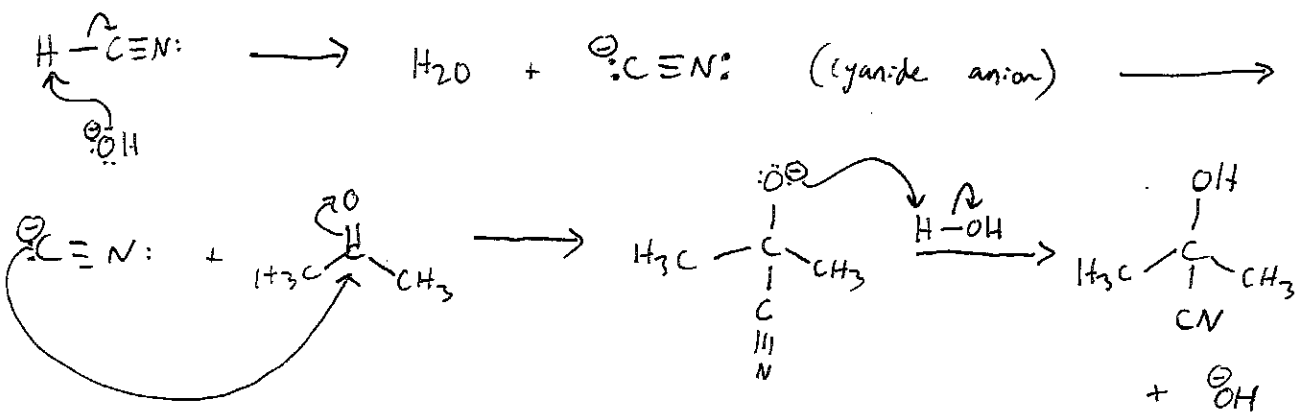
Reversible addition reactions to C=O

Ex.

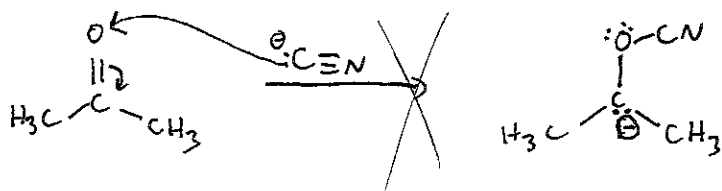


Mechanism:

[Note: the pKa of HCN \approx 9]



Note: Seemingly comparable mechanisms for nucleophile + π -bond reactivity are not reasonable

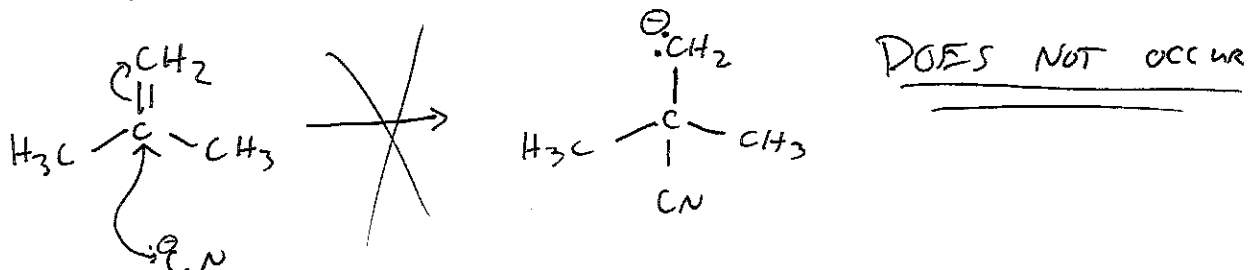


DOES NOT OCCUR

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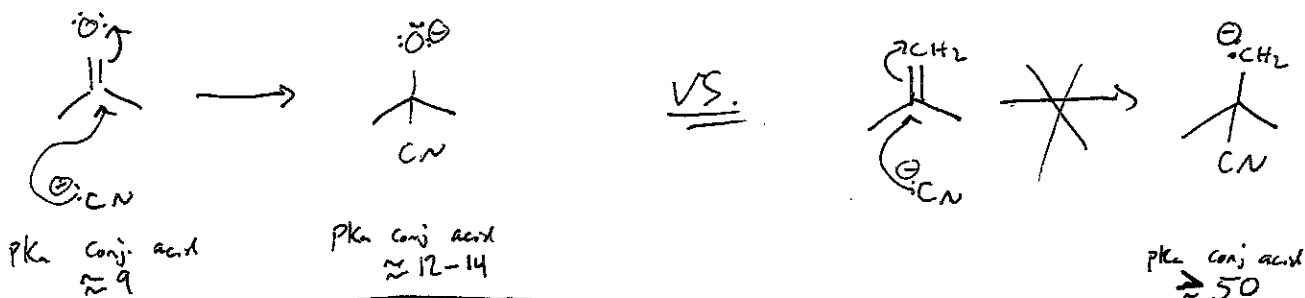
Why is this unreasonable? Charge (-) ends up on the less electronegative atom (C, rather than O)

What about:

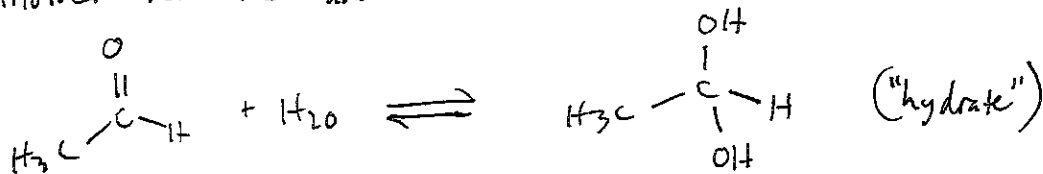


Again, carbon is a much less stable place for a negative charge, as it is less electronegative than oxygen.

We can also make a pK_a argument. pK_a considerations help us understand why some reactions are reasonable and others are not.



Another reversible addition reaction



Note: No change in carbon oxidation state. Both structures have a C (+2) oxidation state at the central carbon.

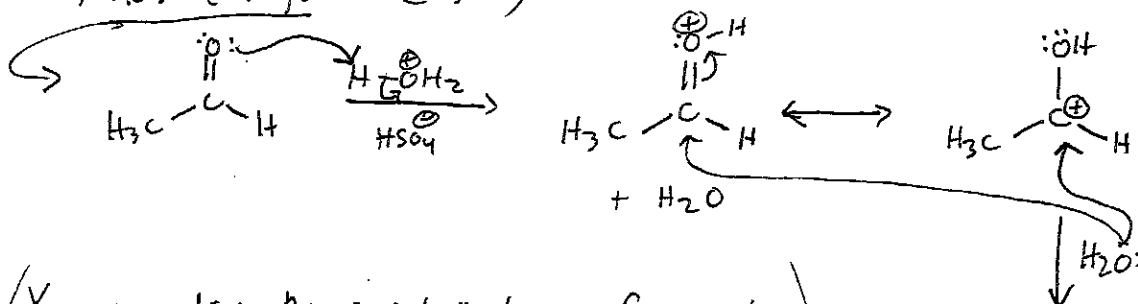
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Two mechanisms...

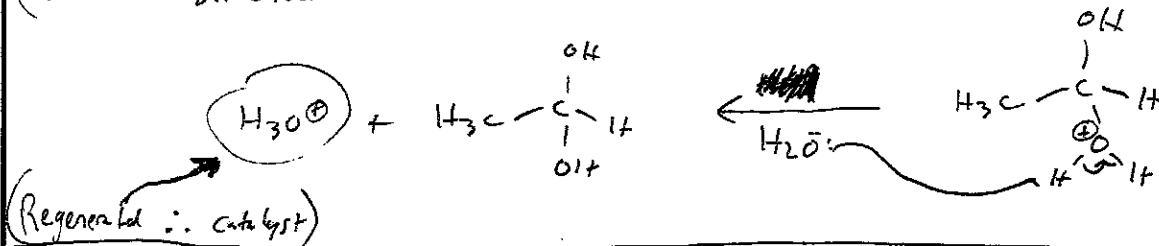
1) Base-catalyzed (OH^-), analogous to addition of HCN

[You fill in]

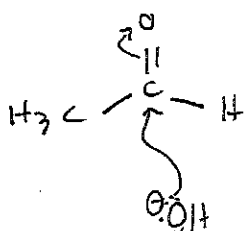
2) Acid-catalyzed (H_3O^+)



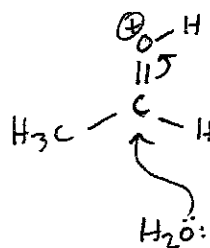
(You can draw the correct mechanism from either resonance structure)



Compare key steps from each mechanism



vs.



Stronger nucleophile ($\text{OH}^- > \text{H}_2\text{O}$)
 weaker electrophile (non-protonated)

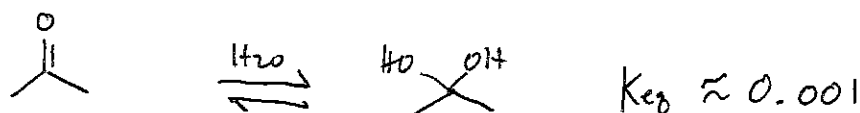
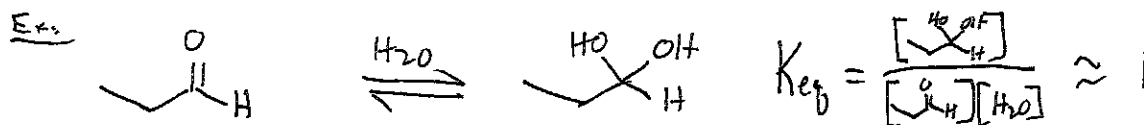
Stronger electrophile ($\text{C}=\text{O}^+$)
 weaker nucleophile (H_2O)

Note: You can't have both, because it would involve a strong acid and strong base simultaneously. The OH^- would simply deprotonate the protonated carbonyl.

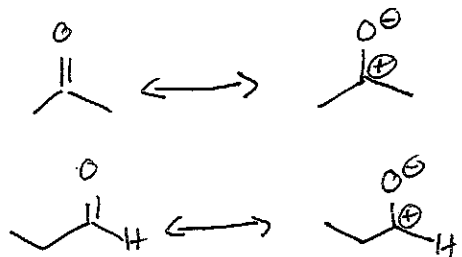
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The position of hydrate formation ~~is~~ equilibria provides insight on carbonyl reactivity.

① Aldehyde hydrates are generally much more stable than ketone hydrates.



Rationale: consider the charge-separated resonance structures



Recall that alkyl groups stabilize carbocations ($3^\circ > 2^\circ > 1^\circ$).

⇒ Expect ketone isomer to be more stable than aldehyde isomer.

Difference in heats of formation (ΔH_f°) favors the ketone by $\approx 7 \text{ kcal/mol}$.
 However, there is no C^\oplus character for the hydrate carbon. ~~At the~~
 Thus, hydrates from aldehyde and ketone are nearly identical in ΔH_f° .

In general, aldehydes are much more reactive towards nucleophiles than are ketones (incipient C^\oplus , also steric factors).

This incipient C^\oplus consideration allows other predictions regarding relative hydrate stabilities.

For Example:

1) Electronegative atoms near $\text{C}=\text{O}$ favor the hydrate

Course Chem 345

Instructor Gellman

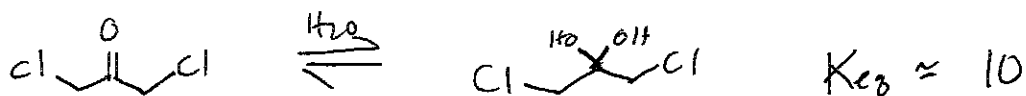
Day Monday

Date 3 March 2014

Notes Taken By Kar Skabi

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(vs. acetone, $K_{\text{eq}} \approx 0.001$)

2) Adjacent π -systems have strong influence \rightarrow destabilize the hydrate because they stabilize the ketone/aldehyde

