Announcements

Prof. Reisman Office Hours This Week:

Tuesday from 3-5 pm

If you have questions about the material we're covering, this is your opportunity to ask me directly

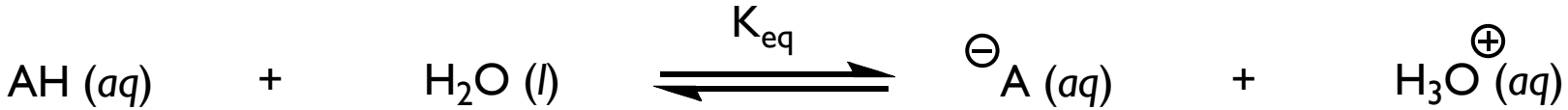
Some useful websites:
http://www.organicdivision.org/?nd=p_organic_web_links
http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/intro1.htm#contnt

Specific to today's lecture:
http://research.cm.utexas.edu/nbauld/teach/acidsbases.html#blacids

Useful reading from BPOC: Chapter 8, section 1 (pages 208-211)

The pK_a System

- pK_a values tell us how acidic a given hydrogen atom is
- pK_a values are useful for estimating reactivity in organic chemistry
- most pK_a values are determined in H_2O or DMSO (dimethylsulfoxide)



$$K_{eq} = \frac{[H_3O^+][A^-]}{[AH][H_2O]} \qquad K_a = \frac{[H_3O^+][A^-]}{[AH]} \qquad pK_a = -\log K_a$$

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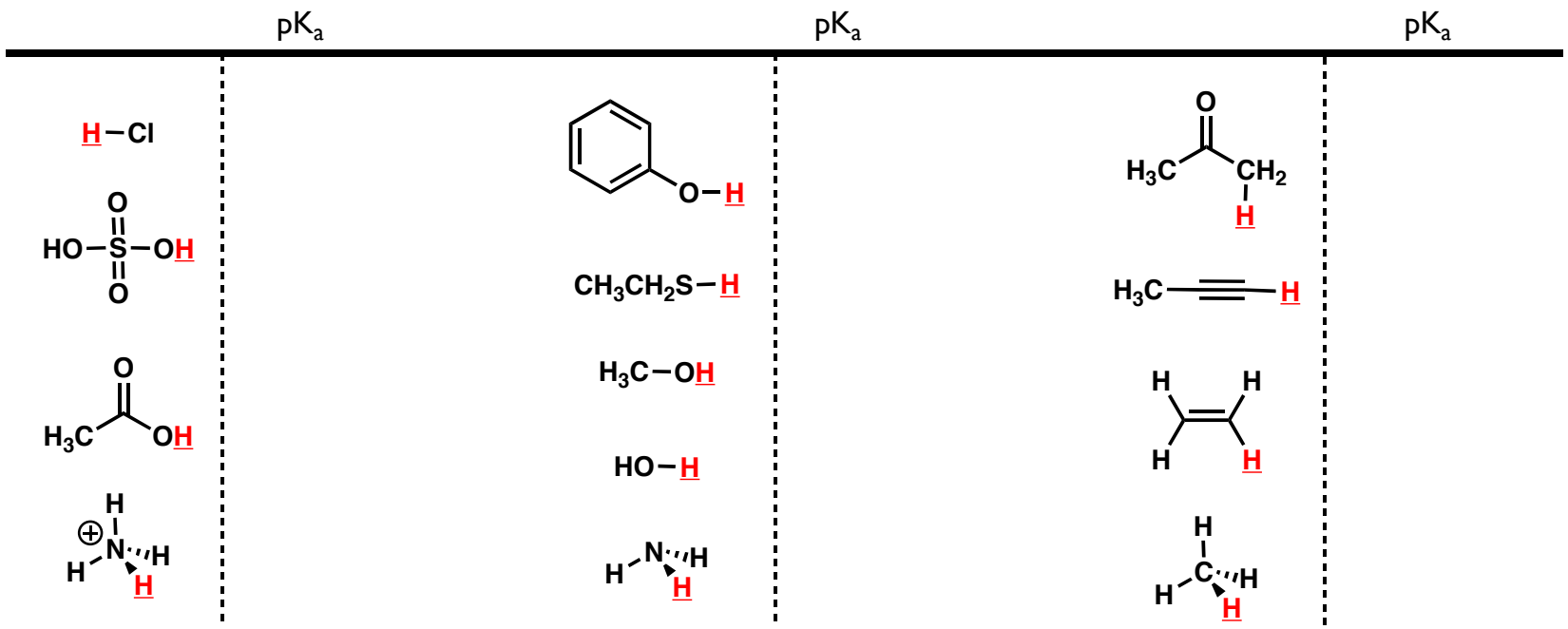
$$AH\ (aq) + H_2O\ (l) \underset{}{\overset{K_{eq}}{\rightleftharpoons}} {}^{\ominus}A\ (aq) + H_3O^{\oplus}\ (aq)$$

$$K_{eq} = \frac{[H_3O^+][A^-]}{[AH][H_2O]} \qquad K_a = \frac{[H_3O^+][A^-]}{[AH]} \qquad pK_a = -\log K_a$$

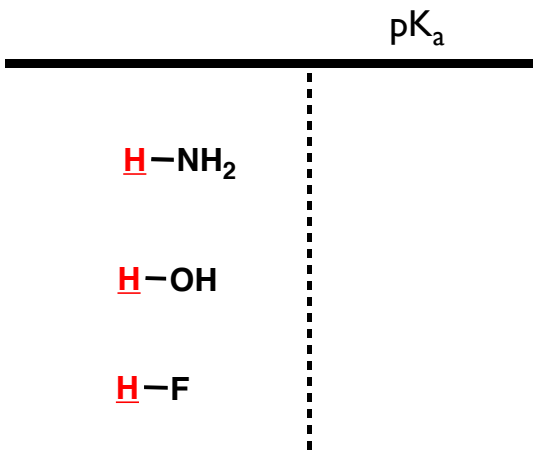


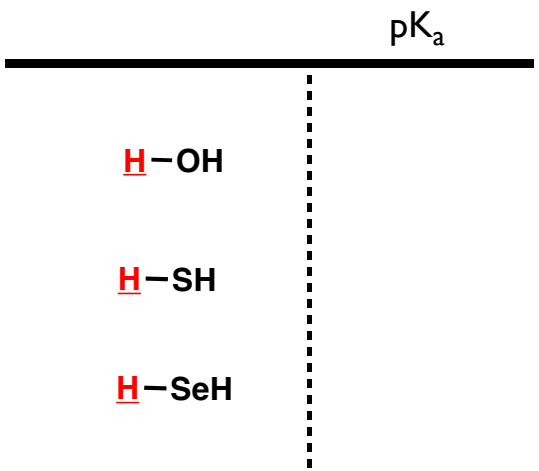
Periodic Trends and Acidity

the stability of the conjugate base is correlated to the pK_a of the acid

- stable conjugate bases lead to low pK_a values

compare the following:





Electronegative Atoms Stabilize Anions Inductively

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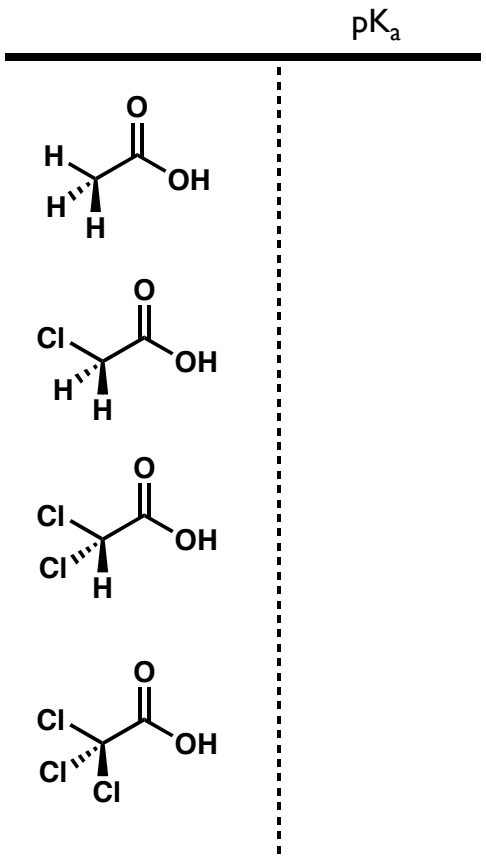

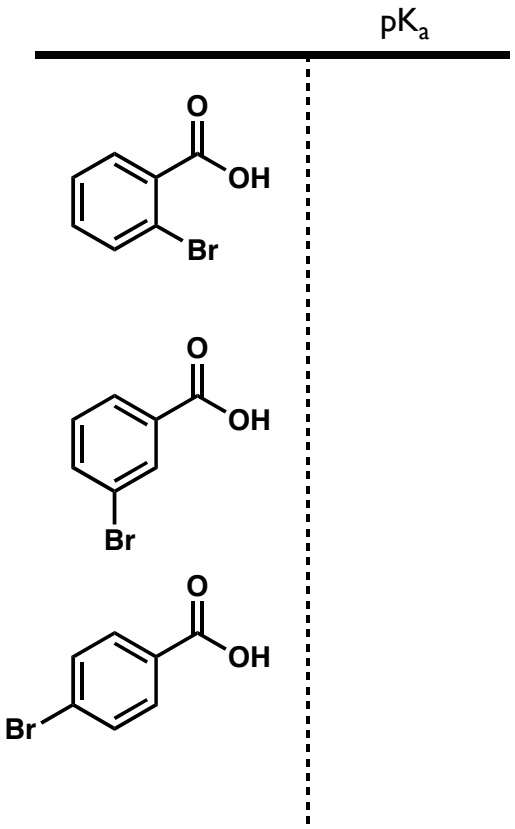

Hybridization Influences Acidity

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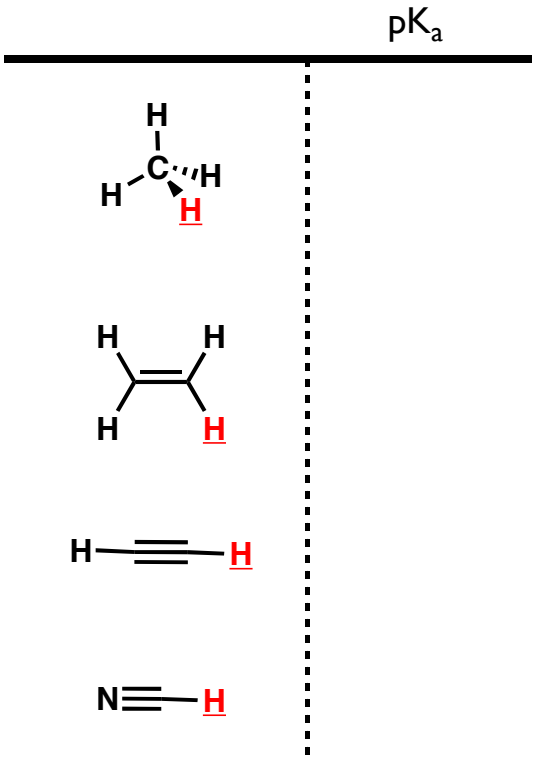
compare the following:



Delocalization Stabilizes Anions

The stability of the conjugate base is correlated to the pK_a of the acid

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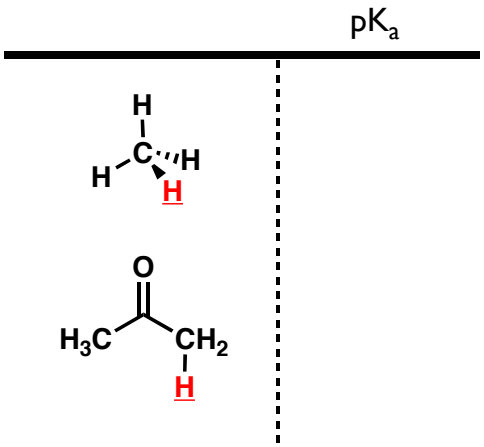
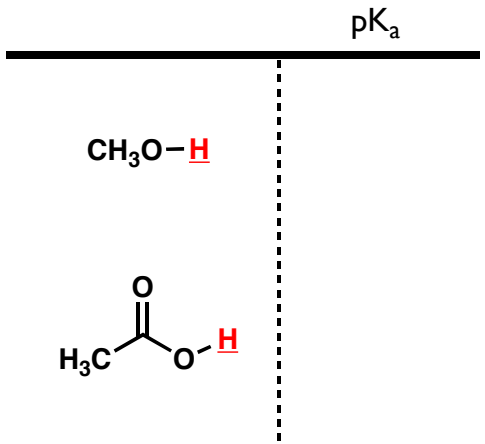
compare the following:

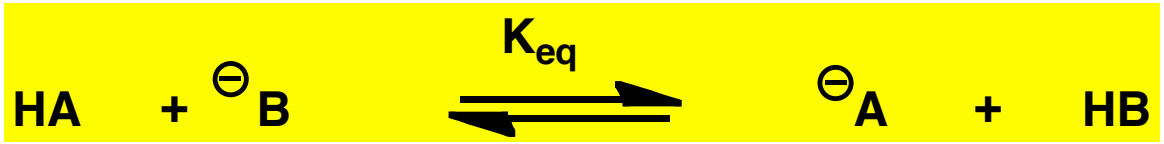




Take Home Messages:

When intuiting the relative pK_a of a proton, consider the stability of the conjugate base

- the more stable the conjugate base, the lower the pK_a of the acid, the stronger the acid
- electronegative atoms can stabilize the conjugate base inductively
- delocalization of negative charge can stabilize the conjugate base
- hybridization affects pK_a: orbitals with more s-character better stabilize negative charge



- the equilibrium will favor the more stable conjugate base
- if the difference between pK_{aHA} and pK_{aHB} is >3, typically the acid-base reaction is considered irreversible

The Same Rationale Applies to Basicity

Weaker acids have stronger conjugate bases.

- high pK_a values indicate strong conjugate bases

The higher the HOMO, the more accessible the unpaired electrons, the stronger the base

- negatively charged species are more basic relative to neutral species

- lone pair basicity increases from sp to sp^2 to sp^3

Amides are Weak Bases that Protonate on Oxygen

remember

- amide nitrogens are sp^2 hybridized to allow delocalization
- delocalization lowers the energy of the HOMO, makes lone pair less available

- positive charge from protonation on oxygen is stabilized by resonance