Homework due Wed.

Last time:
- Lewis acids
- K_eq, K_a pKa
- Predicting acid/base strength
  a. Polarizability
  b. Electronegativity

Today:
- c. Hybridization
- d. Inductive Effects
- e. Resonance
- f. Solvation
- Energy issues

Review:
Lewis Acids - acidity extends beyond proton donation
- lone pair donors/acceptors.

As pKa ↑, acidity ↓
pKa ↓ as you go ↓ halogen series because of stabilization on iodide anion (I⁻ larger, less e⁻-e⁻ repulsion than F⁻) + polarizability

Hybridization:
- Pulling a proton off sp³ vs sp² vs sp.

\[
\text{H}_3\text{C}-\text{CH}_3 \quad \text{H}_2\text{C}≡\text{CH}_2 \quad \text{HC}≡\text{CH}
\]

pKa 50 44 25
hybridization sp³ sp² sp

Why is it easier to pull a proton off of acetylene?

s character: 25% 33% 50%
How does 's-character' affect the acidities of these compounds?

\[ \text{sp} \quad \text{sp}^3 \quad \text{sp}^2 \quad \text{p} \quad \text{p} \]

\[ \text{O:} \quad \text{O:} \quad \text{O:} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \]

O, p orbitals \quad \text{for pi bonding, pi bonding}

The boxed electrons are those that would form the anion. The sp electrons are lowest in energy and would therefore be the most stable.

\[ R_3C-H + H_2O \rightarrow R_3C^O + H_3O^+ \]

Anion stabilization with respect to hybridization: \( \text{sp} > \text{sp}^2 > \text{sp}^3 \).

D. Inductive Effects: "thru bond" effects

- Electron withdrawing groups (electronegative elements) → stabilize anionic charge
- Electron donating groups (alkyl groups) → destabilize anionic charge
E. Resonance Effects:

\[
\text{CH}_3-\overset{\circ}{\text{C}}\overset{\circ}{\overset{\circ}{\text{H}}}=\overset{\circ}{\overset{\circ}{\text{H}}}_2 \quad \rightleftharpoons \quad \text{CH}_3-\overset{\circ}{\text{C}}=\overset{\circ}{\text{O}}+\overset{\circ}{\overset{\circ}{\text{H}}}_3^+\]

\[
\text{CH}_3\text{CH}_2\text{OH} \quad \text{CH}_3\overset{\circ}{\text{C}}\overset{\circ}{\text{OH}}
\]

\[\text{pka} \ 11.6 \quad 4.75\]

The charge is delocalized over 2 oxygens. This is more stable than the \(\overset{\circ}{\text{C}}\) on just one oxygen (localized charge).
dipoles:

It has also been said that this

partial positive charge stabilizes
anion by inductive effects.

in pKa/acidity is due to inductive effects:

It is not known whether inductive effects or resonance effects give a higher effect on pKa/acidity.

F. Solvation

(F/c protons)

1. Polar Protic Solvents

* stabilize anion (conjugate base) thru H-bonding and proton by dipole-ion interactions

H-bonding: CH₃-C=O⁻ H⁺ OH⁻ H

Hydronium ion surrounded by more than 1 H₂O:

H⁺ O⁻ H O⁻ H

2. Polar Aprotic Solvents

* stabilize H⁺ thru dipole-ion interactions (only weak stabilization of the anion)

ex. diethyl ether

Et⁻ H⁺ O⁻ Et⁻
iii Non polar solvent

V. little ability to stabilize ionized species.

MeOH in H₂O (polar/protic) MeOH in DMSO (polar/aprotic) MeOH in Hexane

\[ \text{pK}_a = 15.5 \]

\[ \downarrow 13 \text{ log units} \]

\[ 10^{13} \text{ less ionized} \]

\[ \text{can't even dissolve!} \]

\[ \text{No ability to stabilize } +/− \text{ charges.} \]

All of these effects we have looked at stabilize/desstabilize charges!

Energetic Issues:

\[ \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ \]

\[ \Delta G = -RT \ln K_{eq} \]

\[ R = 8.314 \text{ J/mol} \cdot \text{K} \]

\[ T = \text{absolute temp.} \]

\[ \text{(in Kelvin)} \]

\[ +\Delta G^\circ \rightarrow \text{rxn lies to left (non spontaneous)} \]

\[ -\Delta G^\circ \rightarrow \text{rxn lies to right (spontaneous rxn)} \]

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]

\[ \Delta H^\circ \rightarrow \text{enthalpy} \]

\[ \Delta S^\circ \rightarrow \text{entropy} \]

Potential energy in bonding (stability of species) As disorder ↑, rxn becomes more spontaneous, \( \Delta G \) becomes more negative
CH$_3$CO$_2$H  CICH$_2$CO$_2$H

Will the chlorine favor or disfavor the ionization of acetic acid? Why?

Favors formation of $\Theta$ bc of inductive effects

pK$_a$ 4.75  2.86