Topics
- Inductive Effect
- Resonance Effect
- Predicting Acid/Base Equilibria
- Hybridization Effects
- Thermodynamics of Organic Reactions

Inductive Effect
The tendency of the more electronegative atom in a polar covalent bond to pull electron density toward itself resulting in a partial positive charge ($S^+$) on the atom it is bonded to.

Dashed bond structure of ethanol:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} - \text{C} - \text{O} - \text{H} \\
\text{F} & \quad \downarrow \\
\text{F} & \quad \text{C} - \text{C} - \text{O} - \text{H}
\end{align*}
\]

$\text{PK}_a = 16.00$ [higher $\text{PK}_a \Rightarrow$ weaker acid!!]

Bromstead def. of acid is a proton donor !! The more the $H$ begins to look like $H^+$, the more acidic it is!!

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} - \text{C} - \text{C} - \text{O} - \text{H} \\
\text{H} & \quad \text{H} \\
\text{F} & \quad \downarrow \\
\text{F} & \quad \text{C} - \text{C} - \text{O} - \text{H}
\end{align*}
\]

$\text{PK}_a = 18.00$ $C$ is more electronegative than $H$!! Overall effect is a ($S^-$) charge on the central $C$.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{F} & \quad \downarrow \\
\text{F} & \quad \text{C} - \text{C} - \text{O} - \text{H}
\end{align*}
\]

$\text{PK}_a = 5.4$ $F$ is more electronegative than $C$!!

[acetic acid $\text{PK}_a = 4.75$]
\[ CH_3-CH_2-OH + H_2O \rightarrow H_3O^+ + CH_3-CH_2-O^- \]

\[ pK_a = 16.00 \]

Ethanol has no possible resonance structures!!

\[ CH_3-C=O + H_2O \rightarrow H_3O^+ + CH_3-CO^- \]

\[ pK_a = 4.75 \]

Acetic acid is stabilized by resonance; this explains its acidity.

[Diagrams of resonance structures]

\[ CH_3-C(OH) \leftrightarrow CH_3-C=O^- \]

Resonance of parent compound

[Diagrams of resonance structures]

\[ CH_3-C(OH) \leftrightarrow CH_3-C=O^- \]

Resonance of anionic compound

\begin{align*}
\text{Acid} & & \text{pk}_a & & \text{As pk}_a \text{ approaches 0, we begin to approach the strong acid range!!} \\
CH_3-C-OH & & 4.75 & & \\
ClCH_2-C-OH & & 2.85 & & \text{Adding electronegative atoms to acetic acid combines inductive & resonance effects!!} \\
Cl_2CH-C-OH & & 1.48 & & \\
Cl_3C-C-OH & & 0.23 & & 
\end{align*}

Note: **DO NOT** use (\(\equiv\)) to denote resonance structures. These arrows are for acid/base equilibria only!
Hybrid Orbital Effect (Hybridization)

\[ \text{CH}_3-\text{CH}_3 \quad \text{sp}^3 \quad \frac{\text{PK}_a}{50} \]
\[ \text{H}_2\text{C}==\text{CH}_2 \quad \text{sp}^2 \quad 44 \quad \text{Why? More of the electron density is centered around the pi bond in the alkene.} \]
\[ \text{H}_2\text{C}==\text{CH} \quad \text{sp} \quad 25 \]

When you hybridize carbon to sp, you put more electrons in a non-hybridized orbital. Result:
AS THE \( \text{(S) CHARACTER OF A C-C BOND INCREASES,} \)
SO DOES ITS ACIDITY!! \( \{\% \text{S}(\ddagger) \Rightarrow \text{Acidity}(\ddagger)\} \)

\[ \text{CH}_3-\text{CH}_2-\dddot{\text{O}}\dddot{\text{H}} + \text{NH}_3 \xrightarrow{\text{equilibrium right}} \text{CH}_3-\text{CH}_2-\dddot{\text{O}}^+ + \text{NH}_4^+ \]

Is this equilibrium favored? \( \square \)

1. Identify the acids/bases in the reaction.
   \[ \text{PK}_a = 16.00 \quad \text{of ethanol \leftarrow stronger acid} \]
   \[ \text{PK}_a = 38 \quad \text{of ammonia} \]

2. The stronger acid will protonate the conjugate base of the weaker acid!

\[ \text{CH}_3-\cdots\text{C}-\text{CH}_3 + \text{NH}_3 \xrightarrow{\text{Right}} \text{CH}_3-\cdots\text{C}-\text{CH}_2^+ + \text{NH}_4^+ \]
\[ \text{PK}_a = 19.2 \quad \text{PK}_a = 3.8 \]

\[ \text{CH}_3-\cdots\text{C}-\text{CH}_3 + \text{NH}_3 \xrightarrow{\text{Left \downarrow}} \text{CH}_3-\cdots\text{C}-\text{CH}_2 + \text{NH}_4^+ \]
\[ \text{PK}_a = 19.2 \quad \text{PK}_a = 9.2 \]

[These \text{PK}_a \text{ values are based on aqueous conditions!} \]
Thermodynamics of Org. Reactions

Energy \( E \) = heat gained or lost when a chemical reaction occurs at constant volume

\* Normally reactions are carried out in open containers on the bench; therefore, volume changes, but pressure remains constant.

Enthalpy \( H \) = heat gained or lost when chem. rxn. occurs @ constant pressure.

\[ \Delta H = \mp \text{ endothermic} \]

\[ \Delta H = \mp \text{ exothermic} \]

Entropy \( S \) = change in randomness or disorder in going from reactants to products

\[ A + B + C \rightarrow D \quad \Delta S = \pm \quad A \rightarrow B + C + D \quad \Delta S = \pm \]

\[ (H) \& (S) \text{ are important to consider when making/breaking bonds in a reaction!} \]

Generally, a more (\( S \)) \( \Delta S \) is favored. More disordered (or degrees of freedom) is desired.

Free Energy \( G \) = \( \Delta G = \Delta H - T \Delta S \)

\( \text{If } \Delta G < 0 \), \( \Delta G \) is a measure of whether or not a reaction will go forward.

Relationship between \( \Delta G \) & \( K \):

\[ A \oplus \Delta G \] means rxn. is not spontaneous in forward direction

\[ \Delta G = -RT \ln K \]

[Given \( pK_a \), one can calculate \( K_a \) & predict \( \Delta G \) or vice versa!]

\[ \Delta G = 2.303RT \log K \]
Weak acid (\( \leq 10\% \) ionized) \( \Delta G \geq 3 \) endergonic

Moderately strong (60\% - 90\% dissociated) 0 - 3 \( \approx \) 0 equilibrium

Strong acid \( \geq 90\% \) ionized \( \leq 0 \) exergonic

Energy Run Coordinate Diagram

If reaction is favored, energy of products \( \downarrow \) than energy of reactants

Reaction Coordinate (progress of reaction)