Acids and Bases in
Organic Chemistry
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Chapter 1
Electronic Structure and Bonding
Acids and Bases

Models of Acids and Bases

- Arrhenius: Acids produce H\(^+\) & bases produce OH\(^-\) in aqueous solutions.
- Brønsted-Lowry: Acids are H\(^+\) donors & bases are proton acceptors.

\[
\text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+
\]
acids bases

Acid-Base Equilibrium
Conjugate Acid/Base Pairs

- HA(aq) + H\(_2\)O(l) \(\rightarrow\) H\(_3\)O\(^+(aq)\) + A\(^-(aq)\)

\(\text{acid} 1 \quad \text{base} 2 \quad \text{conj} \quad \text{conj} \quad \text{acid} 2 \quad \text{base} 1\)

- conjugate acid: formed when the proton is transferred to the base.
- conjugate base: everything that remains of the acid molecule after a proton is lost.

Weak Acids

- Weak acids are only partially ionized in solution.

\[
\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)
\]

\[
\text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}
\]

- \(K_a\) is the acid dissociation constant.

Organic Acids & Bases

- Organic acids are weak acids, eg. Acetic acid.
- However, there can be substantial differences in their relative strengths. What could you use to compare relative acidities?

- Organic bases are weak bases and relate to ammonia.
- However, there can be substantial differences in their relative strengths. What could you use to compare relative basicity?

Conjugates

The equilibrium favors the weaker of the acid vs. its conjugate or base vs. its conjugate. Weak wins!

<table>
<thead>
<tr>
<th>Acid</th>
<th>(K_a)</th>
<th>Base</th>
<th>(K_b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO(_2)</td>
<td>(6.8 \times 10^{-2})</td>
<td>NO(_3^-)</td>
<td>(Negligibly basic)</td>
</tr>
<tr>
<td>HF</td>
<td>(5.6 \times 10^{-3})</td>
<td>F(^-)</td>
<td>(4.5 \times 10^{-10})</td>
</tr>
<tr>
<td>HC(_2)NO(_2)</td>
<td>(1.8 \times 10^{-3})</td>
<td>C(_2)H(_5)O(_2^-)</td>
<td>(5.0 \times 10^{-8})</td>
</tr>
<tr>
<td>H(_2)CO(_3)</td>
<td>(4.3 \times 10^{-3})</td>
<td>HCO(_3^-)</td>
<td>(2.3 \times 10^{-5})</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>(5.6 \times 10^{-5})</td>
<td>NH(_2^-)</td>
<td>(1.8 \times 10^{-5})</td>
</tr>
<tr>
<td>HO(_2^-)</td>
<td>(5.0 \times 10^{-9})</td>
<td>O(_2^-)</td>
<td>(Strong base)</td>
</tr>
</tbody>
</table>

\[
K_a \times K_b = ? \quad K_w
\]

What do \(pK_a\) and \(pK_b\) refer to? \(-\log K_a\) or \(-\log K_b\)

\[
pK_a + pK_b = ? \quad 14
\]

Remember: \(pH + pOH = pK_w\)
Which is the stronger acid?
- methanol

\[ \text{CH}_3\text{OH} \quad \text{CH}_3\text{NH}_2 \]
- \( pK_a = 15.5 \)
- \( pK_a = 40 \)

Which is the stronger base?
- methylamine

\[ \begin{align*}
\text{CH}_3\text{CO}_2\text{H} + \text{NH}_3 & \rightleftharpoons \text{CH}_3\text{CO}_2\text{NH}_3, \quad pK_a = 36 \\
\text{CH}_3\text{CH}_2\text{OH} + \text{NH}_3 & \rightleftharpoons \text{CH}_3\text{CH}_2\text{ONH}_3, \quad pK_a = 50 \\
\end{align*} \]

Strong vs. weak: Weak is favored!

Organic Acids & Bases
- Organic molecules in context can be considered as behaving relatively as weak acids or weak bases.
- Formal Charge is important in considering which.
- Knowing the Formal Charge allows a prediction.
- (+) positive atoms behave acid-like, (-) negative atoms behave base-like.

This can be used in predicting how molecules will react--- or don't react, and the products of reactions.
Formal Charge = \# of valence e\(^{-}\) - 
\[ \frac{1}{2}(\# \text{ of bonding e}\(^{-}\)) + \# \text{ of non-bonding e}\(^{-}\) \]

For N:
\( 5 - \frac{1}{2}(4) + 4 \)
\( = -1 \)

Base

For O:
\( 6 - \frac{1}{2}(6) + 2 \)
\( = +1 \)

Structure and Acid-Base Properties

Important factors that affect acidity in binary compounds, e.g., HCl (having only two elements):
- Bond Length (shorter = stronger; favors lower acidities)
- Bond Strength (weak bonds favor higher acidity: more protons [hydronium ions] in solution)
- Bond Polarity (smaller e.n. differences favor higher acidities)

Select & explain which is the stronger acid: HBr or HF.

Relative electronegativities:
- F > Cl > Br > I
- Most electronegative
- Largest

Relative acidities:
- HF < HCl < HBr < HI
- Strongest acid

Therefore HBr is a stronger acid than HF.

Strength of Oxyacids
(Three atoms: ternary vs. binary)

- Push-Pull electronic effects on the proton.

- Name and rank HBrO, HIO, and HClO: (1) in order of increasing pH and (2) in order of increasing acidity.
  - HBrO, \( K_a = 2.06 \times 10^{-8} \)
  - HIO, \( K_a = 2.3 \times 10^{-11} \)
  - HClO, \( K_a = 3.0 \times 10^{-8} \)
- HClO₄ is a stronger or weaker acid than HClO?
  - Will this help? HClO₂, \( K_a = 1.2 \times 10^{-2} \)
**Strength of Acids**

- Use the concept of push-pull. Rank the following organic acids in order of increasing acidity.

Br-CH₂COOH, I-CH₃COOH, CH₃COOH

- pKa= 2.69  pKa=3.12  pKa=4.75

Is chloroacetic acid more or less acidic than bromoacetic acid?

**Strength of Acids**

- Use the concept of push-pull. Rank the following acids in order of increasing acidity.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>pKₐ (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>CH₃COOH</td>
<td>1.8 × 10⁻⁵</td>
</tr>
<tr>
<td>Chloroacetic</td>
<td>CH₂ClCOOH</td>
<td>1.4 × 10⁻³</td>
</tr>
<tr>
<td>Dichloroacetic</td>
<td>CHCl₂COOH</td>
<td>3.3 × 10⁻²</td>
</tr>
<tr>
<td>Trichloroacetic</td>
<td>CCl₃COOH</td>
<td>2 × 10⁻¹</td>
</tr>
</tbody>
</table>

Which is the stronger acid? Cl₂CCOOH or F₃CCOOH

**An Organic Base in Context**

*Erythroxylon spp.*

- It is very valuable. The leaves are chewed by indigenous tribes in the Andes to boost their energy.
- It has been used as a psycho-therapeutic, an ophthalmic anesthetic and was purportedly used in a popular beverage that is at the heart of a $20 billion corporation.
- However, both its base and conjugate acid are currently controlled substances under U.S. Federal Regulations: Title 21 secs. 329.1 & 1308.12 (1987).
- Can you name the beverage and the base?

**The beverage reportedly produced using the extract of leaves of *Erythroxylon coca*:**

The compound: *cocaine*, is an organic base: Merck Index, #2450. 11th ed.: Caution: May be habit forming....

**Acid -Base Chemistry**

*(Physical Properties)*

"Crack" Cocaine

- m.p. 98 °C
- b.p. (very volatile > 90 °C)

Solvency:
- Water: 1.67 × 10⁻³ g/mL
- CHCl₃: 1.43 g/mL
- Ether: 0.29 g/mL

What structural feature makes cocaine a base? What simple compound can you relate it to?

**“Regular” Cocaine**

Conjugate Acid of Cocaine

*(Physical Properties)*

- m.p. >195 °C
- Solubility:
  - Water: 2.5 g/mL
  - CHCl₃: 0.08 g/mL
  - Ether: insoluble

What accounts for the differences in solubilities of the base and conjugate acid?
Acid-Base Reactions

\[
\text{CH}_3\text{N}-\text{CO}_2\text{CH}_3 + \text{HCl} \rightarrow \text{CH}_3\text{N}-\text{CO}_2\text{CH}_3 \cdot \text{H}^+ + \text{Cl}^-
\]

Cocaine Hydrochloride

Acid Base Reactions

\[
\text{CH}_3\text{N}-\text{CO}_2\text{CH}_3 \cdot \text{OH}^- \rightarrow \text{CH}_3\text{N}-\text{CO}_2\text{CH}_3 + \text{OH}^-
\]

“Crack” Cocaine

Which form, Acid or its Conjugate Base?

The pH of the solution (surroundings) determines it.

\[ pK_a = pH + \log \frac{[HA]}{[A^-]} \]

• A compound will exist primarily in its acidic form if the pH is < than its pK_a
• A compound will exist primarily in its basic form if the pH is > than its pK_a
• NOTE: A buffer solution maintains a nearly constant pH within certain parameters.

Lewis Acids and Bases

• Lewis Acid: electron pair acceptor
• Lewis Base: electron pair donor
• Example:

\[ \text{Al}^{3+} + 6\left(\text{O}^{2-}\right)^{\text{H}} \rightarrow \left[\text{Al}\left(\text{O}^{2-}\right)^{\text{H}}\right]^{3+} \]

the curved arrow indicates
where the pair of electrons
starts from and where it ends up

\[ \text{Cl} - \text{Al} - \text{Cl} + \text{CH}_3\text{OCH}_3 \rightarrow \text{Cl} - \text{Al} - \text{O}^=\text{CH}_3 \]

aluminum trichloride
dimethyl ether
a Lewis acid
a Lewis base

\[ \text{H-H} + \text{N-H} \rightarrow \text{H-B-N-H} \]

borane
ammonia
a Lewis acid
a Lewis base

99% 90% 80% 70% 60% 50% 40% 30% 20% 10% 0%

99% 90% 80% 70% 60% 50% 40% 30% 20% 10% 0%

A weak acid with a pKa = 5.2

pH = pK_a - 2
pH = pK_a
pH = pK_a + 2

pH = pK_a - 2
pH = pK_a
pH = pK_a + 2

pH

pH

pH

pH
Acid-Base Reactions

Predicting if reactions occur and the products if they do

Acid-Base Reactions

Predicting Products