Carbon Acid Strengths: Stability of Carbanions

The term carbon acid refers to the atom to which the proton is attached. Loss of a proton produces a carbanion.

Simple Alkanes

Simple alkanes are the least acidic of organic compounds as shown by the estimated value of the pKa of methane.

Aryl Substitution Enhances Acidity

pKa values:
- CH₃ pKa ~ 41
- CH₂ pKa = 33
- CH pKa = 31
Enhanced Stability of Delocalized Carbanions: Increased Acidity

The enhanced acidity of the carbon acids with aryl substitution is due to increased stability of the carbanion (conjugate base) because of $\pi$-delocalization as illustrated by the resonance structures below.

\[
\begin{align*}
\text{H-C-H} & \quad \text{H-C-H} & \quad \text{H-C-H} & \quad \text{H-C-H} \\
\text{etc.} & & & \\
\end{align*}
\]
The Inductive Effect

A second important mechanism for dispersing and stabilizing the negative charge is the **inductive effect** of the aryl ring which is **electron-withdrawing**.

![Inductive Effect Diagram]

Note sp² carbon withdraws electrons.

Orbital Hybridization Influences

Electrons are stabilized by interaction with the positive nuclear charge. The s-orbital has finite probability, while the p-orbital has zero probability, at the nucleus. The greater the amount of s-character in a hybrid orbital, the more the electrons in that orbital are stabilized by interaction with the positive charge in the nucleus.

<table>
<thead>
<tr>
<th></th>
<th>CH₃CH₂-H</th>
<th>H₂C=CH-H</th>
<th>HC≡C-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKa</td>
<td>&gt; 50</td>
<td>44</td>
<td>24</td>
</tr>
<tr>
<td>hybridization at C</td>
<td>sp³</td>
<td>sp²</td>
<td>sp</td>
</tr>
</tbody>
</table>

**stabilization of electrons in hybrid orbital**
A Special Electronic Effect: Cyclopentadiene

Cyclopentadiene is extraordinarily acidic for a hydrocarbon. It has an acidity comparable to water or an alcohol.

\[
\text{H} \quad \text{H} \quad \text{pKa} = 16 \\
\text{cyclopentadiene}
\]

This acidity is not adequately explained by resonance theory, even though a series of resonance structure may be drawn for the anion.

\[
\text{H} \quad \text{H} \quad \text{pKa} = 36 \\
\text{cycloheptatriene}
\]

The pKa of cycloheptatriene, for which even a greater number of resonance structures may be drawn for the anion, is 36.

Hückel Molecular Orbital Theory: The 4n + 2 Rule

The cyclopentadienyl anion is a 6 \( \pi \)-electron system and is, therefore, aromatic with special stability. The cycloheptatrienyl anion is an 8 \( \pi \)-electron system and is not aromatic.
Quiz 17.02

Rank the following hydrocarbons in order of their carbon acid strengths, strongest to weakest.

$I \quad \text{CH}_3\text{C}≡\text{CH} \quad \text{II} \quad \text{III} \quad \text{IV}$

$\text{III} \quad > \quad \text{II} \quad > \quad \text{I} \quad > \quad \text{IV}$