Objectives

After completing this section, you should be able to

1. list a given series of carboxylic acids in order of increasing or decreasing acidity.
2. explain the difference in acidity between two or more given carboxylic acids.
3. arrange a series of substituted benzoic acids in order of increasing or decreasing acidity.
4. determine whether a given substituted benzoic acid will be more or less acidic than benzoic acid.
5. decide which of two or more substituted benzoic acids is the most acidic, and explain your decision on the basis of the electron-withdrawing or electron-releasing ability of the substituent.
6. use the $K_a$ (or $pK_a$) of a substituted benzoic acid to predict the effect that the substituent has on the susceptibility of the benzene ring to electrophilic attack.

Study Notes

You have already seen how the presence of an electron-withdrawing or electron-releasing group affects the stability of a positively charged carbocation. Now you see how these groups affect the stability of carboxylate anions, and in turn, determine the dissociation constant of a carboxylic acid.

The resonance effect described here is undoubtedly the major contributor to the exceptional acidity of carboxylic acids. However, inductive effects also play a role. For example, alcohols have $pK_a$'s of 16 or greater but their acidity is increased by electron withdrawing substituents on the alkyl group. The following diagram illustrates this factor for several simple inorganic and organic compounds (row #1), and shows how inductive electron withdrawal may also increase the acidity of carboxylic acids (rows #2 & 3). The acidic hydrogen is colored red in all examples.

Water is less acidic than hydrogen peroxide because hydrogen is less electronegative than oxygen, and the covalent bond joining these atoms is polarized in the manner shown. Alcohols are slightly less acidic than water, due to the poor electronegativity of carbon, but chloral hydrate, $\text{Cl}_3\text{CCH(OH)}_2$, and 2,2,2,-trifluoroethanol are significantly more acidic than water, due to inductive electron withdrawal by the electronegative halogens (and the second oxygen in chloral hydrate). In the case of carboxylic acids, if the electrophilic character of the carbonyl carbon is decreased the acidity of the carboxylic acid will also decrease. Similarly, an increase in its electrophilicity will increase the acidity of the acid.
Acetic acid is ten times weaker an acid than formic acid (first two entries in the second row), confirming the electron donating character of an alkyl group relative to hydrogen, as noted earlier in a discussion of carbocation stability. Electronegative substituents increase acidity by inductive electron withdrawal. As expected, the higher the electronegativity of the substituent the greater the increase in acidity (F > Cl > Br > I), and the closer the substituent is to the carboxyl group the greater is its effect (isomers in the 3rd row). Substituents also influence the acidity of benzoic acid derivatives, but resonance effects compete with inductive effects. The methoxy group is electron donating and the nitro group is electron withdrawing (last three entries in the table of pKₐ values).

**Acidity of Substituted Benzoic Acids**

**Electron-withdrawing groups**

The conjugate base of benzoic acid is stabilized by electron-withdrawing groups (EWG). This makes the acid more acidic by delocalizing the charge of the carboxylate ion.

Electron-withdrawing groups deactivate the benzene ring to electrophilic attack and make benzoic acids more acidic.
Electron-donating groups

The conjugate base of benzoic acid is destabilized by electron-donating groups (EDG). This makes the acid less acidic by pushing more electron density toward the negative charge in the carboxylate.

Electron-donating groups activate the benzene ring to electrophilic attack and make benzoic acids less acidic.

Contributors

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Notice the trend in the following table where electron donating substituents (X) at the para position lead to weaker acids while those having more electron withdrawing groups, further down the table, generate stronger acids.
Dissociation Constants of \( p \)-Substituted Benzoic Acid

<table>
<thead>
<tr>
<th>X</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -\text{N(CH}_3\text{)}_2 )</td>
<td>6.03</td>
</tr>
<tr>
<td>( -\text{NHCH}_3 )</td>
<td>5.04</td>
</tr>
<tr>
<td>( -\text{OH} )</td>
<td>4.57</td>
</tr>
<tr>
<td>( -\text{OCH}_3 )</td>
<td>4.50</td>
</tr>
<tr>
<td>( -\text{C(CH}_3\text{)}_3 )</td>
<td>4.38</td>
</tr>
<tr>
<td>( -\text{H} )</td>
<td>4.20</td>
</tr>
<tr>
<td>( -\text{Cl} )</td>
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<tr>
<td>( -\text{Br} )</td>
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</tr>
<tr>
<td>( -\text{CHO} )</td>
<td>3.77</td>
</tr>
<tr>
<td>( -\text{CN} )</td>
<td>3.55</td>
</tr>
<tr>
<td>( -\text{NO}_2 )</td>
<td>3.43</td>
</tr>
</tbody>
</table>
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