Acidity of Phenols

most characteristic property of phenols is their acidity
Compare

\[ \text{苯酚: } K_a = 10^{-10} \]

\[ \text{乙醇: } K_a = 10^{-16} \]
Delocalized negative charge in phenoxide ion
Delocalized negative charge in phenoxide ion
Delocalized negative charge in phenoxide ion
Delocalized negative charge in phenoxide ion

\[ \text{Phenoxide ion} \]

\[ \text{Delocalized negative charge} \]
Delocalized negative charge in phenoxide ion
Delocalized negative charge in phenoxide ion
Phenols are converted to phenoxide ions in aqueous base.

Stronger acid: 

\[
\text{Phenol} + \text{HO}^- \rightarrow \text{Phenoxide ion} + \text{H}_2\text{O}
\]

Weaker acid:
24.5 Substituent Effects on the Acidity of Phenols
Electron-releasing groups have little or no effect

$K_a: \quad 1 \times 10^{-10}$

$5 \times 10^{-11}$

$6 \times 10^{-11}$
Electron-withdrawing groups increase acidity

Electron-withdrawing groups increase acidity

\[ \text{OH} \]
\[ \text{Cl} \]
\[ \text{NO}_2 \]

\[ K_a: \ 1 \times 10^{-10} \]
\[ 4 \times 10^{-9} \]
\[ 7 \times 10^{-8} \]
Effect of electron-withdrawing groups is most pronounced at ortho and para positions.

$$K_a: \quad 6 \times 10^{-8} \quad 4 \times 10^{-9} \quad 7 \times 10^{-8}$$
Effect of strong electron-withdrawing groups is cumulative

\[
\begin{align*}
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{NO}_2 & \quad \text{NO}_2 & \quad \text{O}_2\text{N} \\
\text{Ka} & : \quad 7 \times 10^{-8} & \quad 1 \times 10^{-4} & \quad 4 \times 10^{-1}
\end{align*}
\]
Resonance Depiction