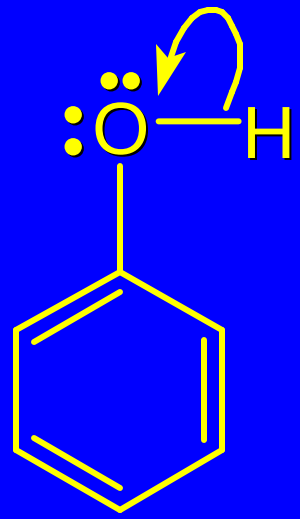
24.4

Acidity of Phenols

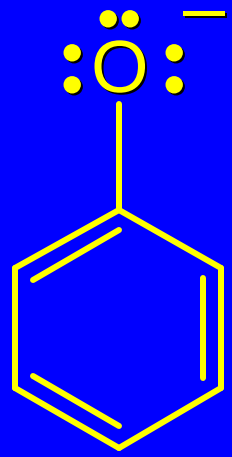
most characteristic property of phenols is their acidity

Compare



$K_a = 10^{-10}$

$H^+ +$

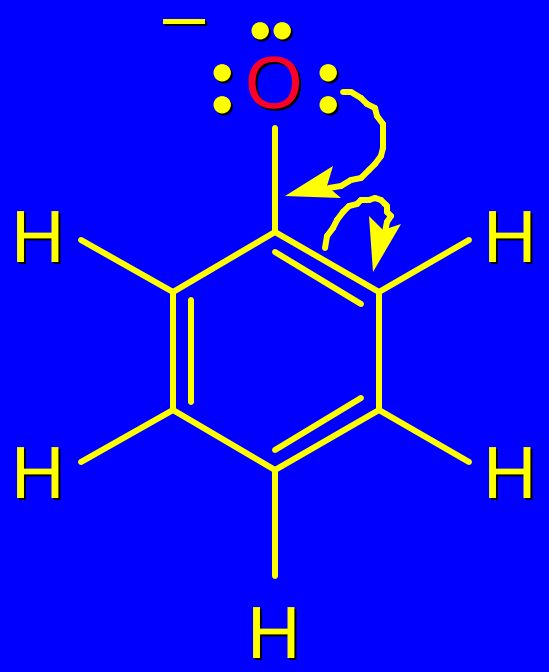


$K_a = 10^{-16}$

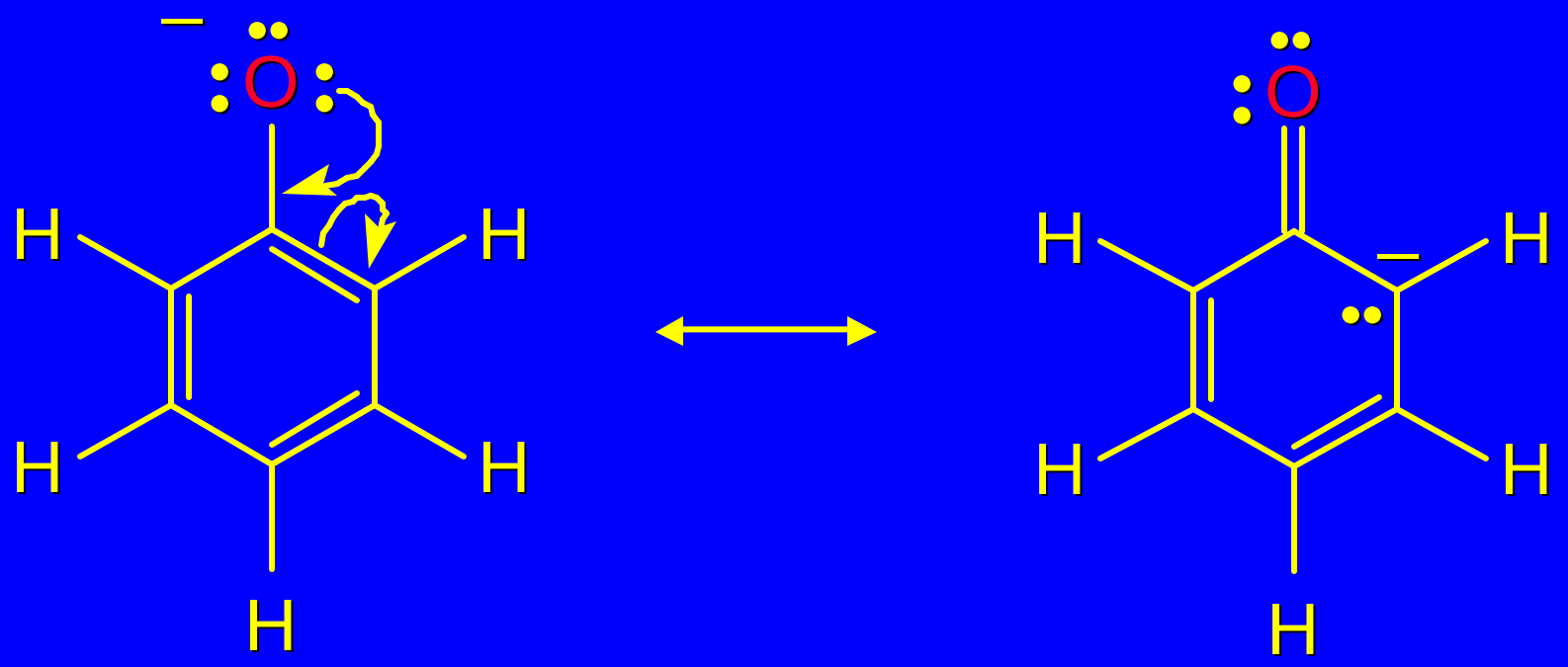
CH_3CH_2O-H

$H^+ + CH_3CH_2O^-$

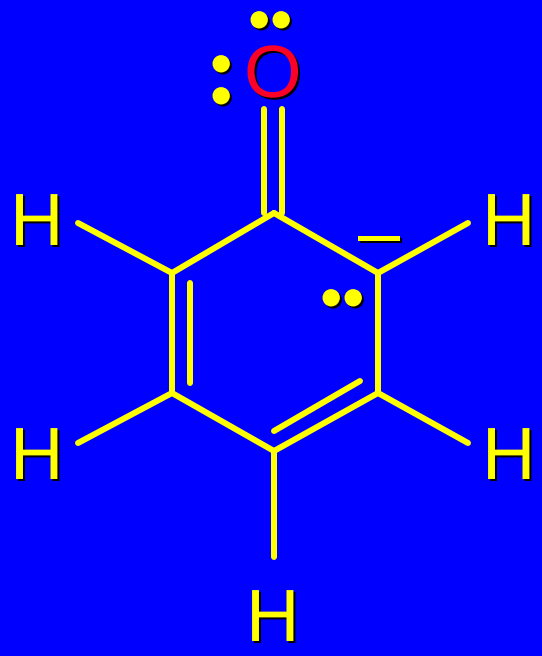
Delocalized negative charge in phenoxide ion



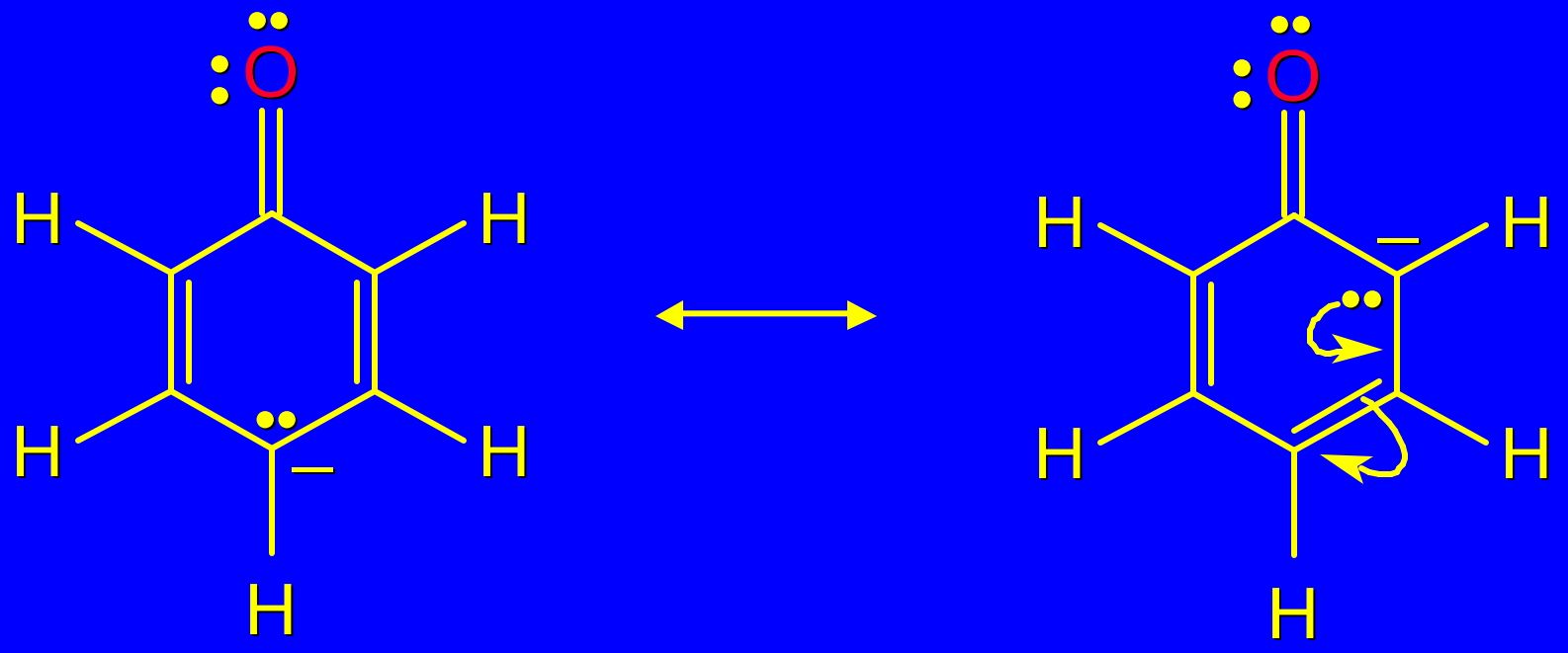
Delocalized negative charge in phenoxide ion



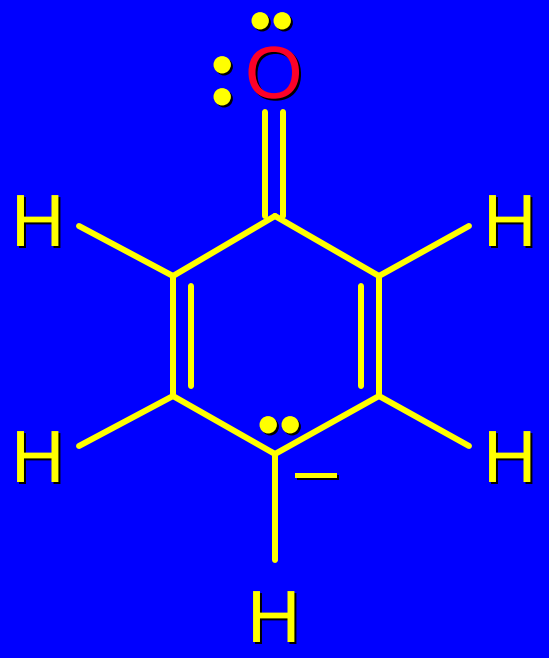
Delocalized negative charge in phenoxide ion



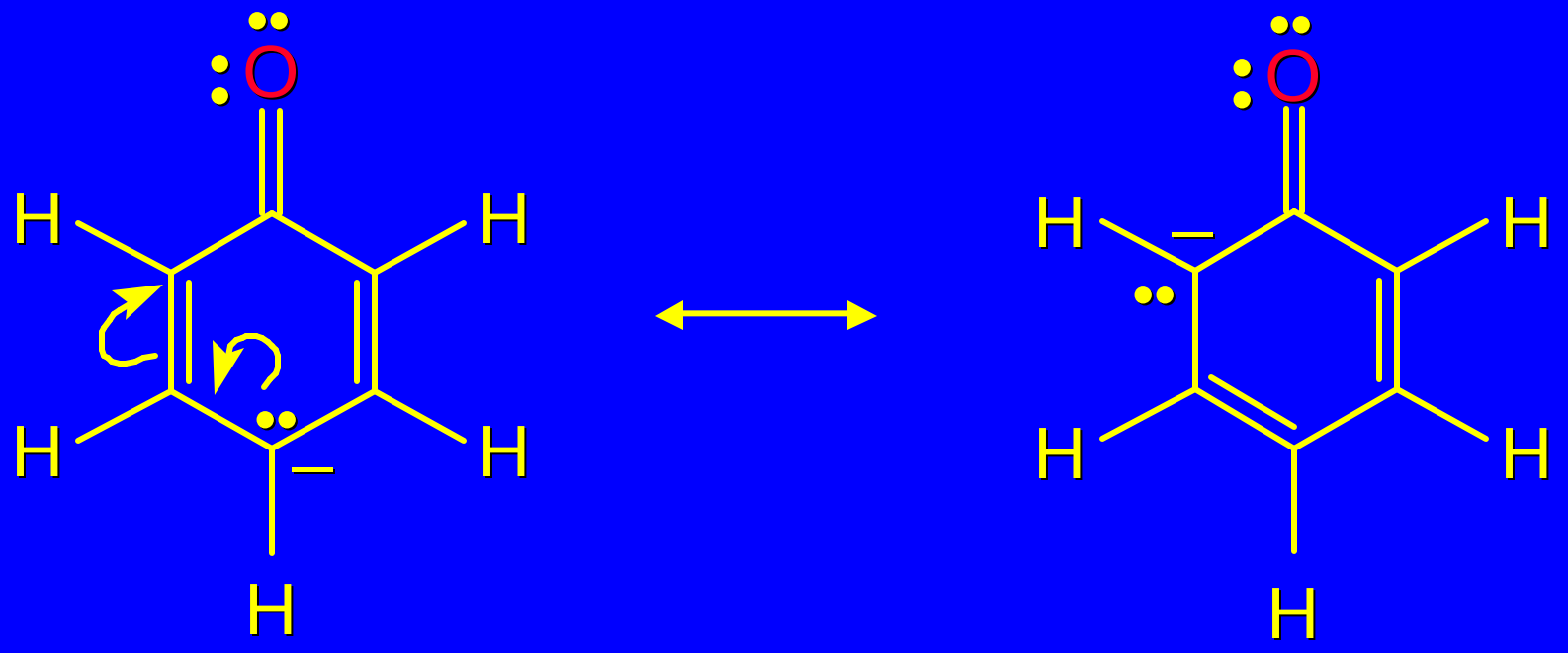
Delocalized negative charge in phenoxide ion



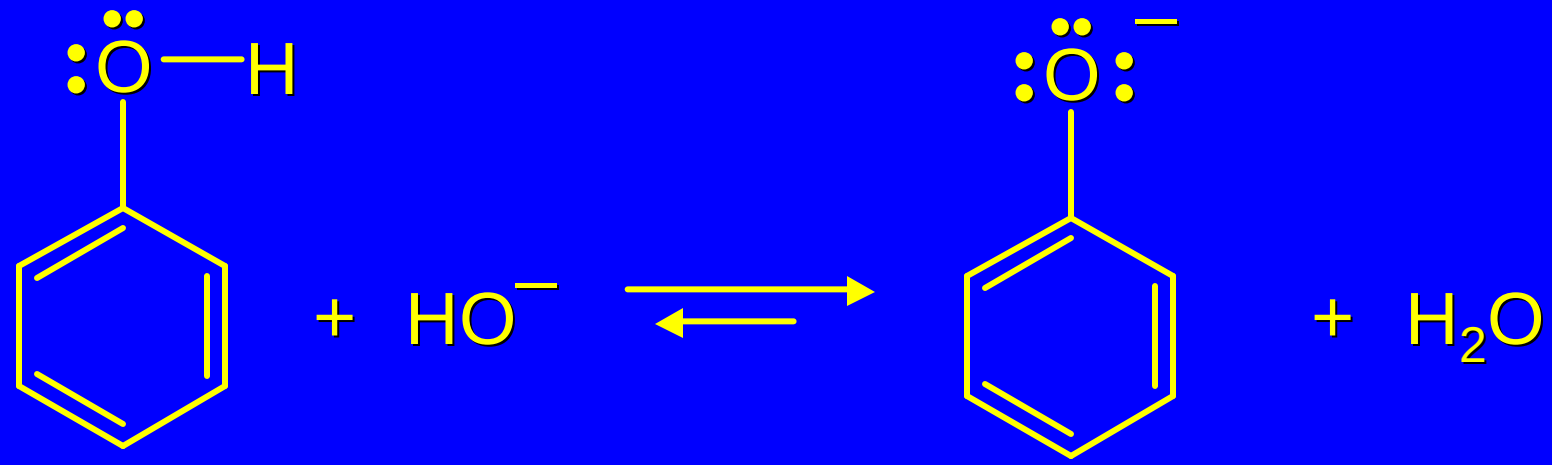
Delocalized negative charge in phenoxide ion



Delocalized negative charge in phenoxide ion



Phenols are converted to phenoxide ions in aqueous base

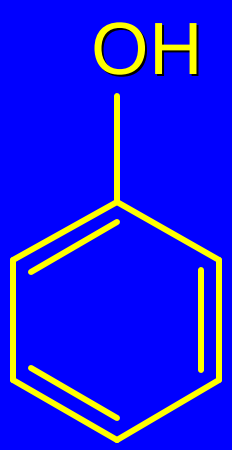


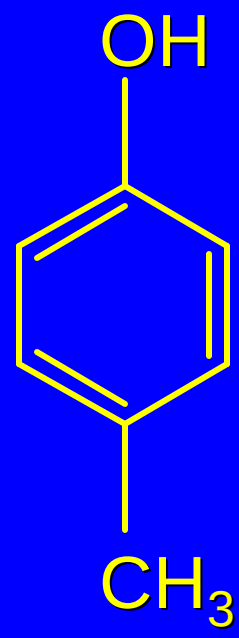
stronger acid

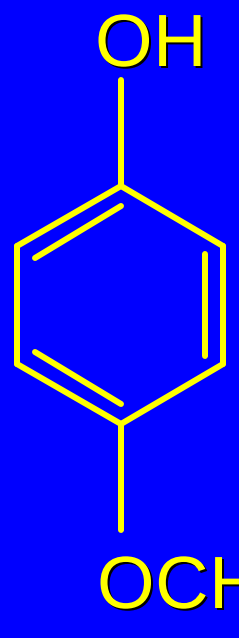
weaker acid

24.5
Substituent Effects on the Acidity of Phenols

Electron-releasing groups have little or no effect

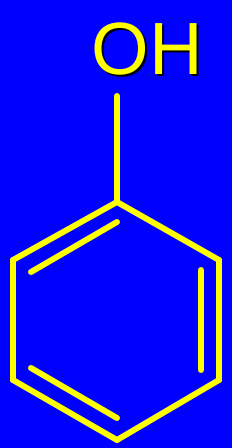


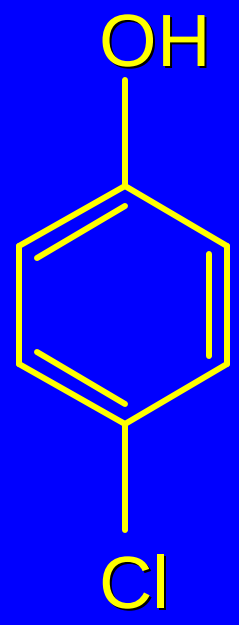


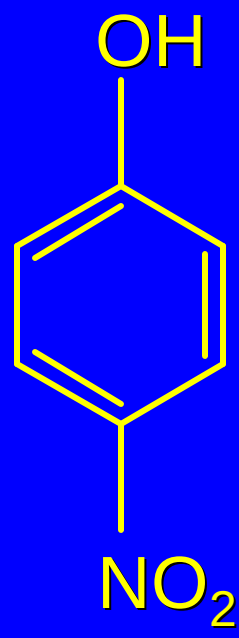


K_a: 1×10^{-10} 5×10^{-11} 6×10^{-11}

Electron-withdrawing groups increase acidity

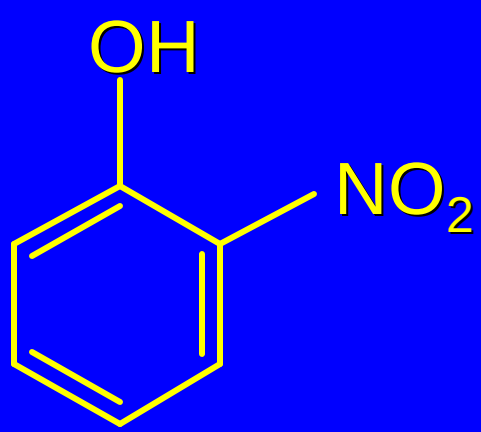


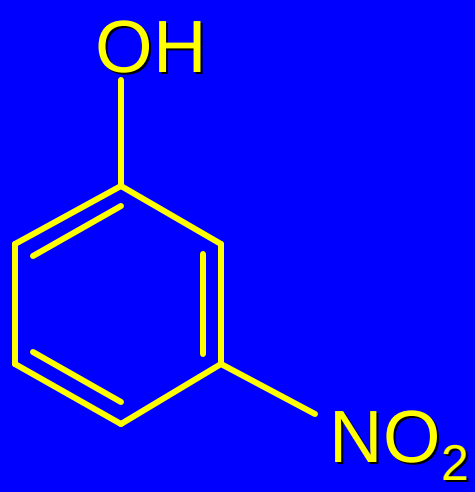


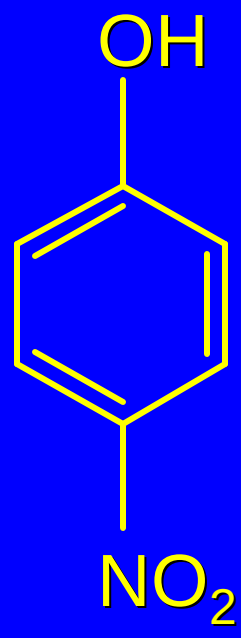


K_a: 1×10^{-10} 4×10^{-9} 7×10^{-8}

Effect of electron-withdrawing groups is most pronounced at ortho and para positions

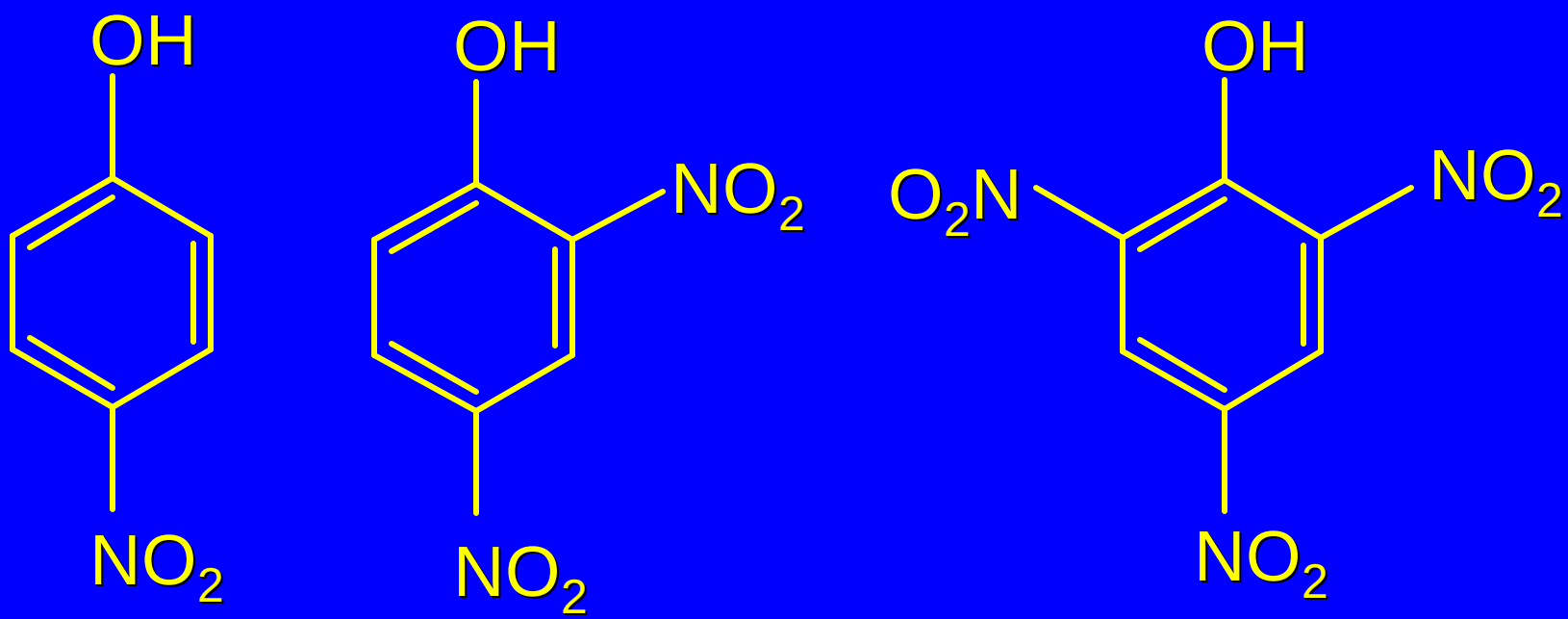






K_a: 6×10^{-8} 4×10^{-9} 7×10^{-8}

Effect of strong electron-withdrawing groups is cumulative



K_a: 7×10^{-8} 1×10^{-4} 4×10^{-1}

Resonance Depiction