### Acidity of alcohols continued ...



What is the influence of substituents?

#### **Inductive & Resonance:**

- Inductive Effect: through single bonds, can be electron donating or withdrawing.
- Resonance Effect: through π (double bonds) systems; can be electron donation or withdrawing. Usually stronger than inductive effects.

Resonance form of phenol:



Phenol has a  $pK_a$  value of 10 (given this information, you should immediately recognize that it is more much acidic (about 6 orders of magnitude) than water ( $pK_a$  15.7) and methanol ( $pK_a$  16) since it has lower  $pK_a$  value). As phenol is more acidic, this means

that its conjugate anion is more stable. The phenoxide anion is stabilized through resonance (shown above). It has 4 resonance forms, and therefore, more ability to spread the negative charge and be stabilized.

## *Where does the equilibrium lie for ionization of phenol to phenoxide and a proton* $(H^+)$ *?*

Answer: It lies far to the left (not ionized). Even though phenol is  $10^6$  more acidic than water, its pK<sub>a</sub> of 10 tells you that the acidity constant is  $10^{-10}$  or that only one part in  $10^{10}$  is ionized, the rest exists as phenol with H attached to oxygen. Example: Chlorophenol (Above)



Is the anion more or less stabilized compared to phenol?

Answer: more stabilized. The chlorine atom is electron withdrawing, and stabilizes the negative charge at the *para* position through the inductive withdrawing effect. However, it also has a weak resonance donating effect. The inductive effect of chlorine wins over resonance effect in this case (contrast this with electrophilic aromatic substitution where the resonance donating effect wins out against the inductive effect).

Example:



*m*-nitrophenol has a  $pK_a$  value of 9.3, whereas the *p*-nitrophenol has  $pK_a$  value is 7.2. *Which one is more acidic?* 

# Answer: *p*-nitrophenol

Why? (Think about conjugate anion stabilization and resonance forms).

Resonance forms for *m*-nitrophenoxide anion:



Resonance forms for *p*-nitrophenoxide anion:



The nitro group offers an additional resonance form for *p*-nitrophenol that is not possible for *m*-nitrophenol (we are able to drive electrons all the way in to the nitro group for the *para*- substituted nitrophenol). Since there is one more reasonable resonance form, the *p*nitrophenol pK<sub>a</sub> 7.2 is about 100 times (10<sup>2</sup>) more acidic than the *m*-nitrophenol with pK<sub>a</sub> 9.3 (pK<sub>a</sub> 9.3-7.2 = 2.1 pK<sub>a</sub> units)

If there are two nitro groups in the *ortho* and *para* positions of the phenoxide anion, the  $pK_a$  of the phenol (2,4-dinitrophenol) drops to 4.5. If three nitro groups are attached, the  $pK_a$  of the phenol becomes even lower (2,4,6-trinitrophenol has a  $pK_a$  of approximately 0.5). This is because *ortho* and *para* positions are where the negative charge of the resonance form can be located, and addition of a nitro group is able to offer more stabilization. This phenomenon is not observed for the *meta* position.

# Preparation of Alcohols and Ethers from Alkanes



**Examples:** 





E.g. 2)

