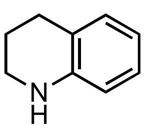
# Chemistry 30A Discussion – Week 5: Acids & Bases in Organic Chemistry – DCF

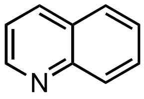
## I: Bronsted-Lowry Acids-Bases

1. In the two questions below you are asked to rank the relative strengths of the series of illustrated acids and bases. Use your knowledge of resonance and inductive effects to answer this question.

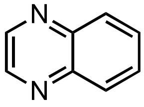
**Part A:** For the series of bases shown below, rank the set from strongest to weakest.



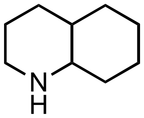
**A**



**B**

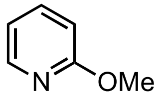


**C**

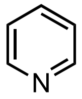


**D**

_D_ Strongest
_A_
_B_
_C_ Weakest



**A**



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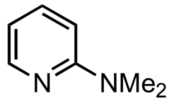
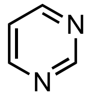


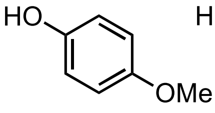
**C**



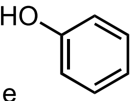
**D**

_C_ Strongest
_A_
_B_
_D_ Weakest

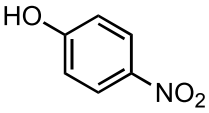
**Part B:** For the series of acids shown below, rank the set from strongest to weakest.



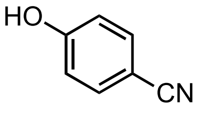
**A**



**B**

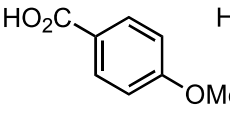


**C**

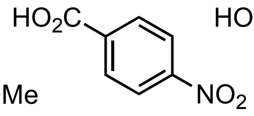


**D**

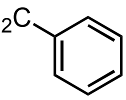
_C_ Strongest
_D_
_B_
_A_ Weakest



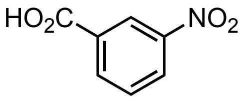
**A**



**B**



**C**



**D**

_B_ Strongest
_D_
_C_
_A_ Weakest

2. (i) Determine whether each species in the following equations is acting as a Bronsted acid or base, and label it. (ii) Indicate whether the equilibrium lies to the left or the right. (iii) Estimate *K* for each reaction if possible. **(Hint**: Use the Evan's pKa Table)†

Blue = Base
Red = Acid

K=

$H_2O + HCN \rightleftharpoons H_3O^+ + CN^-$ -1.3 x $10^{11}$

$CH_3O^- + NH_3 \rightleftharpoons CH_3OH + NH_2^-$ -3.2 x $10^{22}$

$HF + CH_3COO^- \rightleftharpoons F^- + CH_3COOH$ ~40

$CH_3^- + NH_3 \rightleftharpoons CH_4 + NH_2^-$ $10^{10}$

$H_3O^+ + Cl^- \rightleftharpoons H_2O + HCl$ 2 x $10^6$

$CH_3COOH + CH_3S^- \rightleftharpoons CH_3COO^- + CH_3SH$ 1.7 x $10^5$

3. Write the for the conjugate base of each of the following acids.[†]
**(a)** $H_2SO_3$; **(b)** $HClO_3$; **(c)** $H_2S$; **(d)** $(CH_3)_2OH^+$; **(e)** $HSO_4^-$
$HSO_3^-$ $ClO_3^-$ $HS^-$ $(CH_3)_2O$ $SO_4^{2-}$

4. Write the for the conjugate acid of each of the following bases.[†]
**(a)** $(CH_3)_2N^-$; **(b)** $S^{2-}$; **(c)** $NH_3$; **(d)** $(CH_3)_2C{=}O$; **(e)** $CF_3CH_2O^-$
$(CH_3)_2NH$ $HS^-$ $NH_4^+$ $(CH_3)_2C{=}OH^+$ $CF_3CH_2OH$

## II: Lewis Acids-Bases

5. Identify each of the following species as either a Lewis acid or Lewis, and write an equation illustrating a Lewis acid-base reaction for each one. Use curved arrows to depict electron-pair movement. Be sure that the product of each reaction is depicted by a complete, correct Lewis structure.[†]
**(a)** $CN^-$; **(b)** $CH_3OH$; **(c)** $MgBr_2$; **(d)** $(CH_3)_2OH^+$; **(e)** $CH_3BH_2$; **(f)** $CH_3S^-$

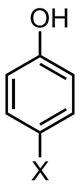
RED = Lewis Acid / Blue = Lewis Base

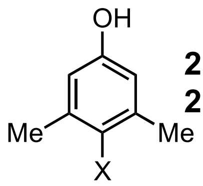
## III: Acid-Base / Resonance Theory

6. The acidity of **1a** and **2a** are the same; however, **1b** is a significantly stronger acid than **2b**.

Explain these observation. (Note: A picture is worth a thousand words) Answer on next page.

**1a**, X = CN
**1b**, X = $NO_2$



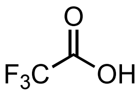


**2a**, X = CN
**2b**, X = $NO_2$

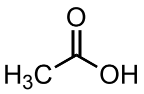
7. Compare the relative acidity of the following sets of organic compounds. Which is more acidic? Why? (be specific)

**(a)** $CH_3OH$ *vs.* $CH_3SH$

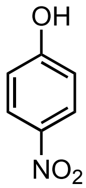
**(b)**


$CF_3COOH$

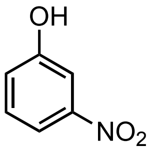
*vs.*


$CH_3COOH$

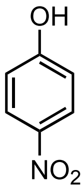
**(c)**



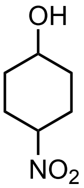
*vs.*



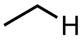
**(d)**



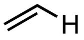
*vs.*



**(e)**

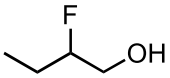


*vs.*

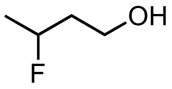


*vs.*

**(f)**



*vs.*



(a) $CH_3SH$ is more acidic because the atomic radius of sulfur is larger than that of oxygen.
(b) Trifluoroacetic acid is more acidic because of the inductive effect of the three fluorine atoms.
(c) The 4-nitrophenol is more acidic because the negatively charged conjugate base is able to delocalize its electrons into the nitro group, this is not possible in 3-nitrophenol.
(d) Again, 4-nitrophenol is more acidic. This is because the phenol is conjugated with the nitro group, this is not the case in 4-nitrocyclohexan-1-ol.
(e) Acetylene is the most acidic because the conjugate base has the most s-character.
(f) 2-fluorobutan-1-ol is more acidic because the fluorine atom is close to the acidic proton, therefore it better stabilizes the conjugate base.

[†] Adapted from Vollhardt & Shore

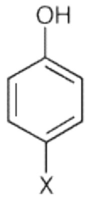
## Answer to Problem 6:

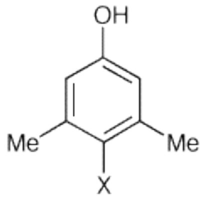
The acidity of **1a** and **2a** are the same; however, **1b** is a significantly stronger acid than **2b**.

Explain these observations.

**1a**, X = CN

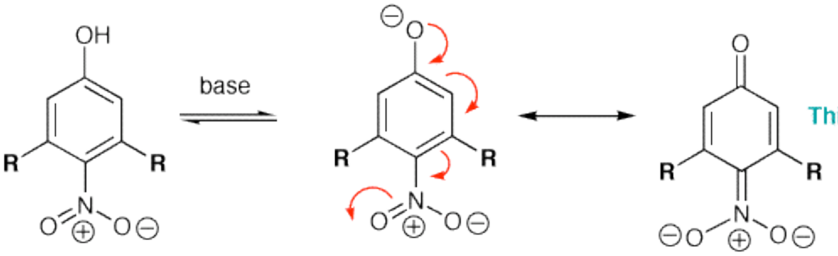
**1b**, X = $NO_2$





**2a**, X = CN

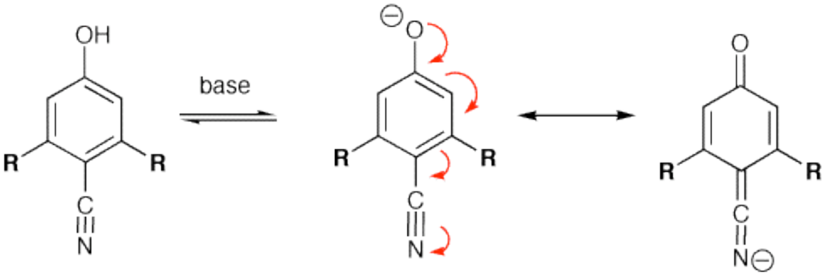
**2b**, X = $NO_2$



This is an important resonce structure for the stabilizatin of the phenoxide

When R = H, there will be no difficulties in achieving this resonance interaction. When R = Me, the nonbonding interactions between R and the nitronate function will destabilize this resonannce structure thus decreasing the acidity of 2b.

(Steric Inhibition to resonance)



The steric requirement of the cyano function are far less than those for $-NO_2$. Accordingly, methyl substitution as in 2a does not affect its pKa.