

Key F10

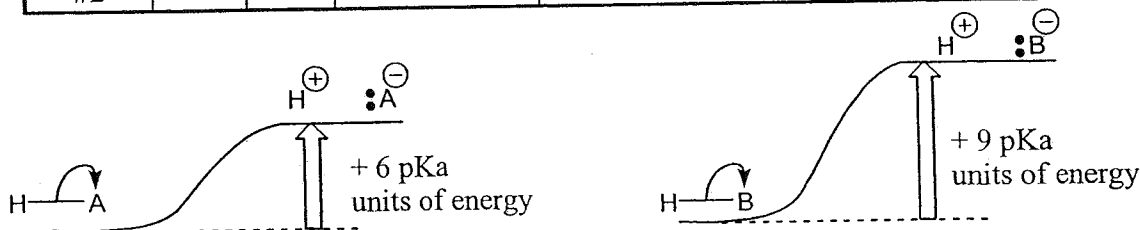
ChemActivity 38

CB[⊖] = conjugate basePart A: pK_a of Phenols(What can you tell about a molecule and its conjugate base from its pK_a?)Model 1: Review of pK_a

Consider the hypothetical acids H-A and H-B...

Table 1: Information Contained in a pK_a Value

	Acid	pK _a	Conjugate Base	pH when [HX] = [X ⁻]	Energy Required to Break H-X Bond
Acid #1	H-A	6	A ⁻	6	6 pK _a units of energy
Acid #2	H-B	9	B ⁻	9	9 pK _a units of energy



Acid base reactions are very fast, and usually come to equilibrium within seconds.

Critical Thinking Questions

- According to the pK_a data, which is a stronger acid, **HA** or **HB** [circle one]?
- According to Model 1, which acid requires **more** energy to remove the H⁺? (Is this consistent with your answer to CTQ 1?) **HB**
- The pK_a of an acid can tell you how difficult it is to remove an H⁺ from that acid. Explain. *The lower the pKa the easier to remove H⁺ (the stronger the acid).*
- A **buffer** "sets" the pH of a solution and keeps it at that pH. In the lab, you can choose a buffer to "set" your solution to almost any pH between pH 2 and 12.
 - To what pH would you "set" your solution of HA in water if you want [HA]=[A⁻] (the concentration of HA = the concentration of A⁻)? *pH = pK_a = 6*
← occurs when pH = pKa

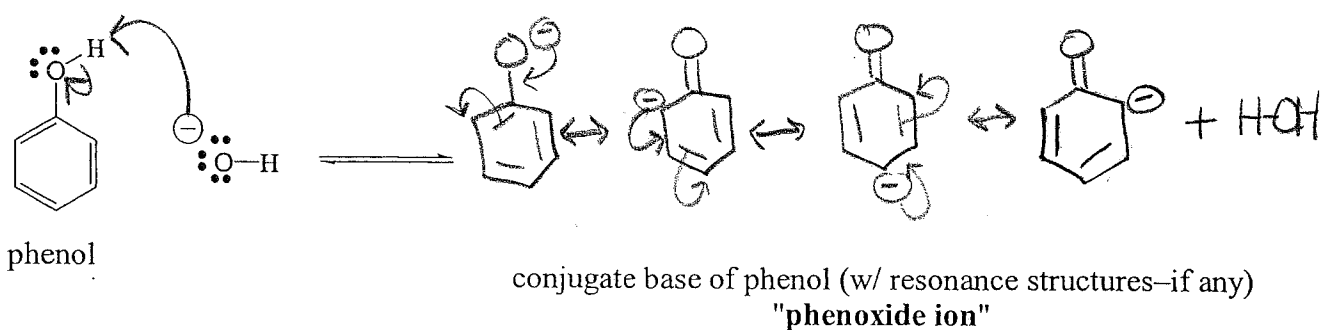
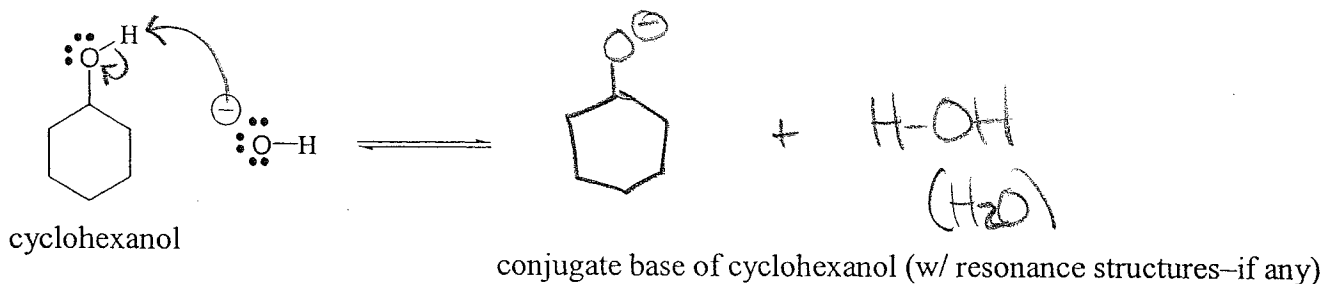
Information:

- At **higher pH** there is a **higher [OH⁻]** and lower [H⁺] in solution
- At **lower pH** there is a **higher [H⁺]** and a lower [OH⁻] in solution. (recall that for all solutions [H⁺] × [OH⁻] = a constant = 10⁻¹⁴)

- You put a sample of HA into water buffered to pH 7, which is greater when the solution comes to equilibrium (in a few seconds): [HA] or **[A⁻]**? Explain.

pH > pKa ∴ basic environment so loss of H⁺ is favored

Model 2: Acidity of Cyclohexanol vs. Phenol



Critical Thinking Questions

5. Show the most likely acid-base reaction between each pair of reactants in Model 2, and draw the conjugate base that results from the reaction, including all important resonance structures (if any). *see above*

- a) Which conjugate base do you expect to be lower in potential energy? Explain your reasoning.



- b) Sketch an energy diagram showing these two reactions. Assume phenol and cyclohexanol have about the same energy.



- c) Predict which alcohol (cyclohexanol or phenol) is more acidic. (More acidic = easier to remove an H⁺.) **phenol**

6. The pKa of phenol is 10. The pKa of cyclohexanol is 17. Is this consistent with your conclusions on the previous page? *yes*

a) You put phenol in water buffered to pH 11. A minute later, which do you expect to be greater: **[phenol]** or **[phenoxide ion]** [circle one]?
pH > pKa *basic environ.* *so lose H+ favored*

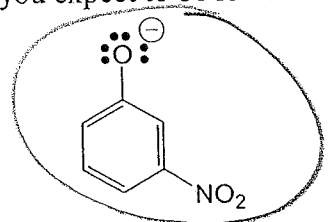
b) Shifting the pH by 1 changes the ratio of [H-A]/[A⁻] by a factor of 10. What is the following ratio at pH 14?
 (Hint: first think, which dominates at pH 14.)

pKa = 10
pH = 14

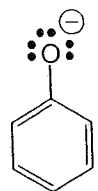
$$\frac{[\text{phenoxide}]}{[\text{phenol}]} = \frac{10^4}{1}$$

c) At what pH do you expect a buffered solution to be ≈99% phenol (and ≈1% phenoxide)?
1 phenoxide / 100 phenol *pH = 8* **2 pH units below pKa*

7. A nitro group (abbreviated —NO₂) is an electron withdrawing group. Circle the ion you expect to be lower in potential energy?



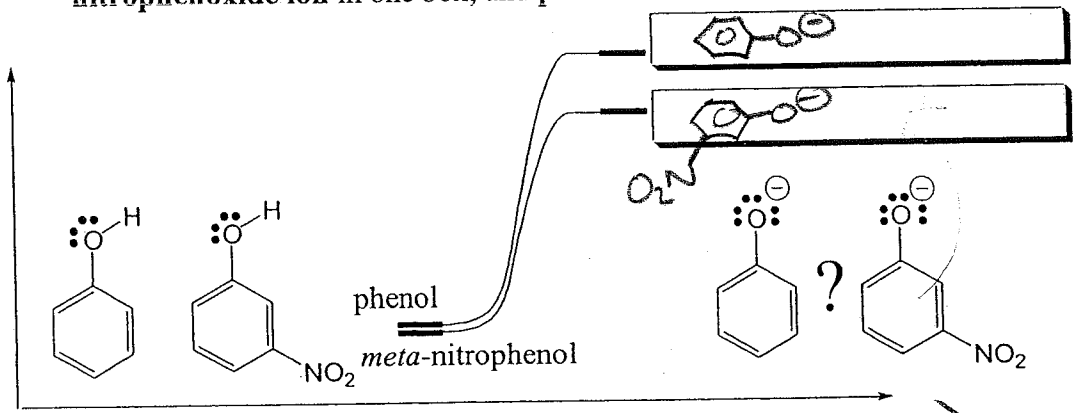
meta-nitrophenoxide ion
 (one of several resonance structures)



phenoxide ion
 (one of several resonance structures)

Explain your reasoning.
The e- withdrawing of the nitro group (-NO2) helps to stabilize the - charge by lowering the e- density

8. Below is an energy diagram for removal of an H⁺ from two different acids. Assume the two acids have about the same starting energy. Write the name *meta-nitrophenoxide ion* in one box, and *phenoxide ion* in the other box.

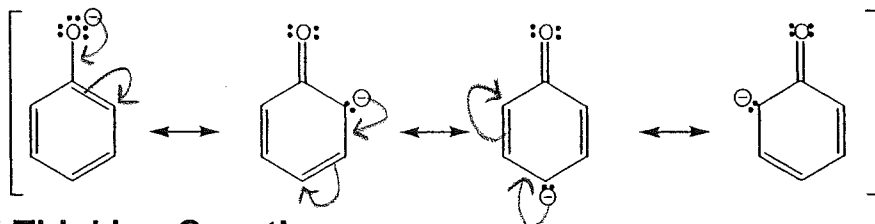


9. Predict which acid has a lower p*K*_a (is more acidic) ***meta-nitrophenol*** or phenol. ***

Part B: pK_a's of Substituted Phenols

(How does the position of an electron withdrawing or donating group affect pK_a?)

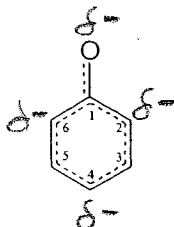
Model 3: Resonance Description of Phenoxide Ion



Critical Thinking Questions

10. Use curved arrows to show generation of the set of resonance structures in Model 3. *see above*
11. Based on the description of phenoxide ion above, complete the composite structure below. Place δ^- where appropriate. Lone pairs not shown. Ion has overall -1 charge.

Composite Structure of Phenoxide Ion (*please complete*)



12. At which positions on the phenyl ring do you expect an **electron withdrawing group** to have the greatest impact on the potential energy of the phenoxide ion?

2(ortho)

3(meta)

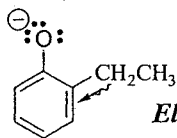
4(para)

5(meta)

6(ortho)

[circle all that apply]

13. Do you expect an **electron donating group** (such as an alkyl group) to stabilize (lower the P.E. of) or **destabilize** (raise the P.E. of) a phenoxide ion? Explain.



Electron Donating Group

"e⁻DG"

e⁻DG increases e⁻ density which destabilizes the anion.

14. At what position/s on the ring would you expect such an electron donating group to have the greatest impact?

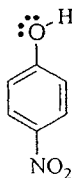
ortho & para

15. Number the following phenols from most acidic to least acidic and explain your reasoning. (1 = most acidic...4 = least acidic).

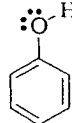
1 = most acidic

or most stable

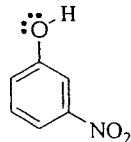
CB[⊖] (lowest e⁻ density)



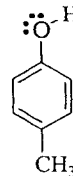
1



3

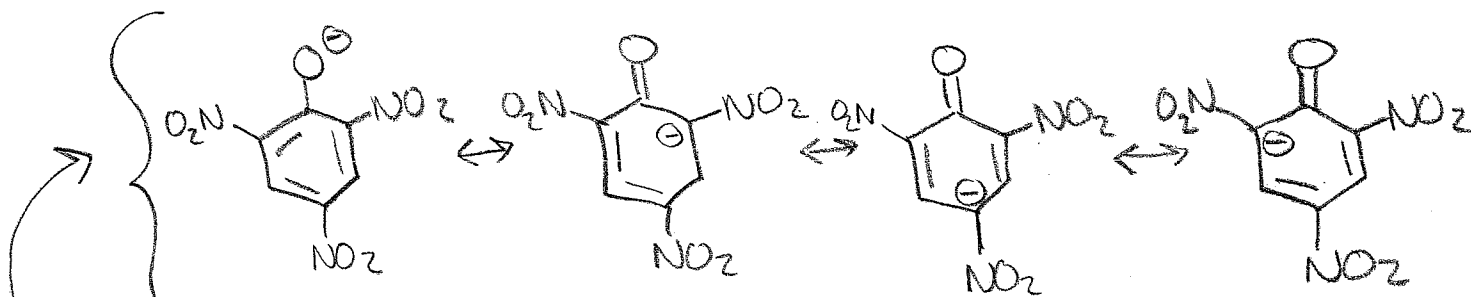
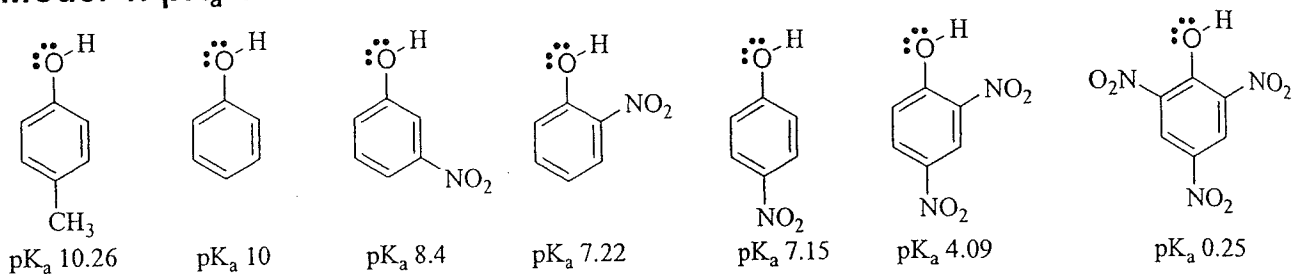


2



4

Model 4: pK_a Values for Various Substituted Phenols



Critical Thinking Questions

16. Are your predictions in the previous question consistent with the pK_a data above? *yes!*

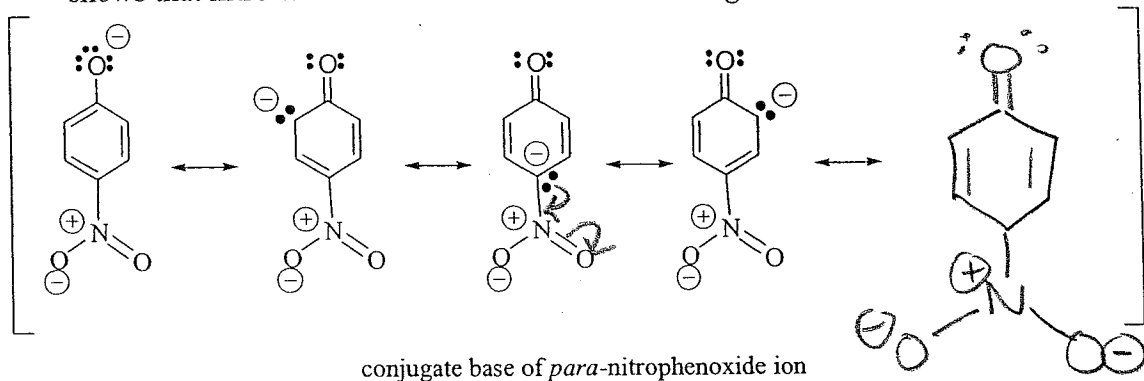
17. Below the tri-nitro phenol, draw its conjugate base.

a) Is this conjugate base the highest P.E. or the lowest P.E. among the conjugate bases of structures in Model 4? the lowest P.E.

b) Explain your reasoning.

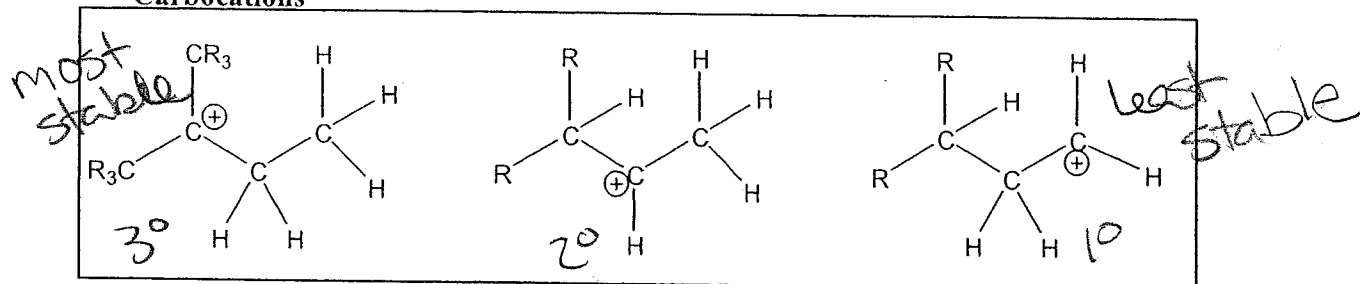
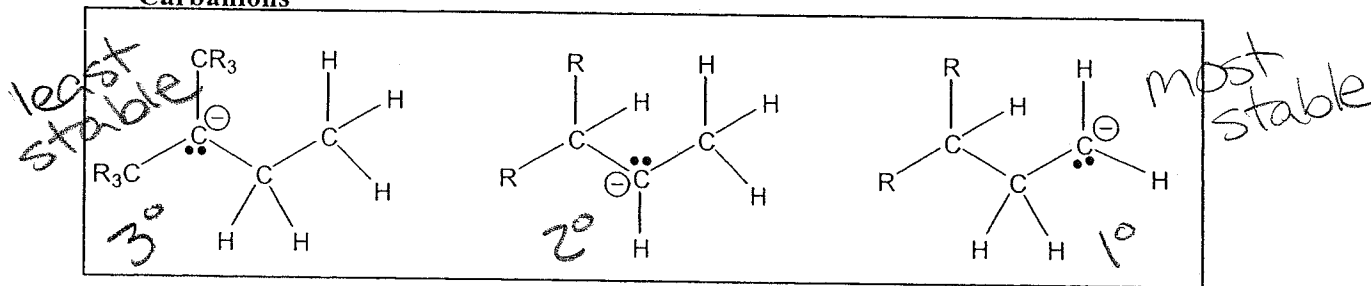
The e⁻ withdrawing groups create add'n e⁻ delocalization which stabilizes the base

18. Below are four resonance structures of the conjugate base of *para*-nitrophenol, with the nitro group drawn as a full Lewis structure. Draw a fifth resonance structure that shows that nitro **withdraws electrons from the ring via resonance effects**.



Model 5: Carbanions (Opposite of Carbocations)

- A carbanion is a structure with a negative charge on carbon.
- In many ways, carbanions are the opposite of carbocations.

Carbocations**Carbanions****Critical Thinking Questions**

19. Label each carbocation and each carbanion in Model 5 as being primary (1°), secondary (2°), or tertiary (3°). *see above*

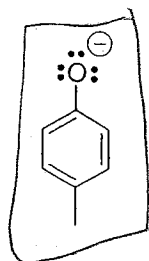
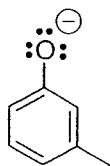
20. Label one of the carbocations “most stable” and another “least stable,” and explain your reasoning.

The R groups on the 3°C^\oplus help stabilize the \oplus charge via inductive e^- donation.

21. Label one of the carbanions “most stable” and another “least stable,” and explain your reasoning.

The R groups on the 3°C^\ominus destabilize the \ominus charge via inductive e^- donation.

22. Which of the following is higher in potential energy and therefore a stronger base?
(Hint: consider which carbons on each structure hold a partial negative charge.)



Methyl group creates the most destabilization b/c it is inductively donating at the para position which already exhibits δ^- charge via resonance

HB pKa = 9

Exercises for Part A

1. You put 1 mole of acid #2 (from Model 1) into an aqueous solution and exactly 1/2 of it (0.5 mole) dissociate into H₃O⁺ and B⁻, and the other half of it stays as H-B. What is the pH of this solution?

$pH = -\log [H^+] = -\log \left(\frac{0.5 \text{ mol}}{1L} \right) = 1L$

2. It is useful to memorize the following approximate pKa's:

	Conj. Acid	Approx. pKa	Conj. Base
<i>strongest acid</i>	Carboxylic Acid 	5	Carboxylate Ion
	Ammonium Ion 	9	Amine
	Phenol 	10	Phenoxide Ion
	Alcohol (or water) 	16	Alkoxide Ion
	Amine 	35	
<i>weakest acid</i>		50	

weakest base (next to Carboxylate Ion)
strongest base (next to R3C^-)

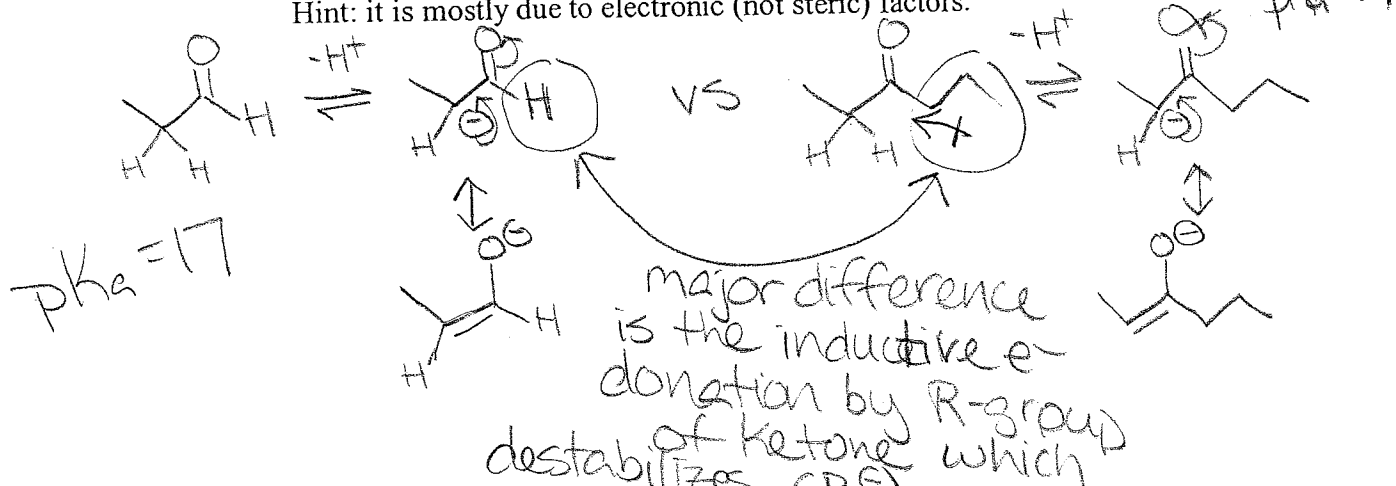
3. For the species in the table above, label the strongest base, strongest acid, weakest base and weakest acid. *see above*

4. What is the ratio of [carboxylic acid]/[carboxylate] in a solution buffered to pH 8?

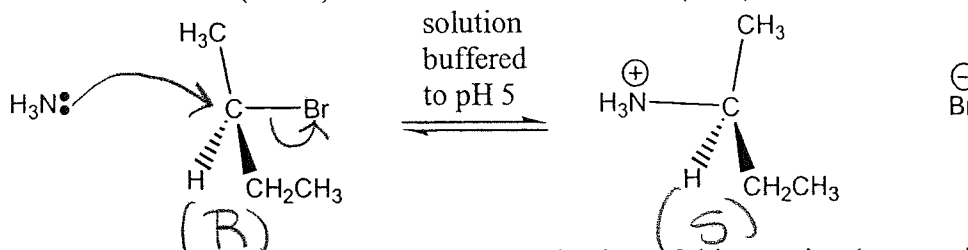
basic environ: 3 pH units above pKa
 $\frac{[HA]}{[A^-]} = \frac{1}{10^3} = \frac{1}{1000}$

5. A typical aldehyde such as propanal has a pKa of 17, while a typical ketone such as 3-hexanone has a pKa of 19.

- a) Draw the conjugate bases of propanal and 3-hexanone. (*ionize alpha-carbon*)
 b) According to the pKa's which compound is more acidic?
 c) Construct an explanation for why this compound is more acidic?
 Hint: it is mostly due to electronic (not steric) factors.



6. It is recommended that the following nucleophilic substitution reaction be run with at least a 0.001 M (molar) concentration of ammonia (NH₃).



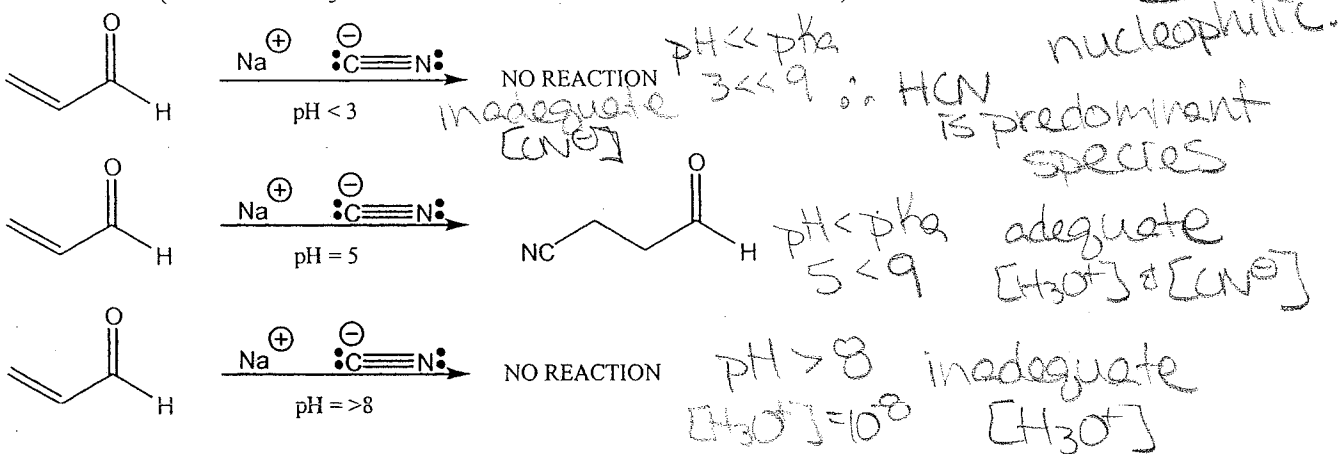
\oplus
RNH₃
pK=9

@ pH=5
acidic env
NH₄⁺ = 10⁴
NH₃ = 1

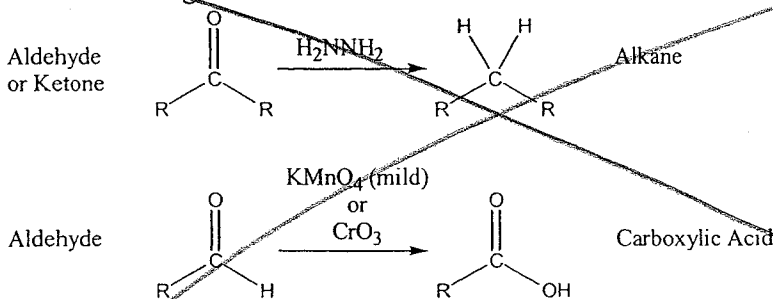
- Use curved arrows to show the mechanism of this reaction (assume it is a one-step reaction). *see above*
- What is the name of this type of reaction mechanism? *SN²*
- Label the reactants and products with their absolute configuration (R or S). *see above*
- You place 1 mole of NH₄Cl into a 1 L solution buffered to pH 5. Is the reaction within the recommended NH₃ concentration? *NO*
- What is the minimum pH at which this reaction can be run? *pH 8*
- What is the problem with running the reaction below this pH?

The ammonia will exist primarily as ammonium

7. Cyanide ion has a pKa of 9. For each of the following reactions, sodium cyanide (NaCN) is added to a solution containing an α,β -unsaturated aldehyde. The solution is buffered to the pH given below the arrow. Explain the results of each reaction below. (Hint: both H₃O⁺ and NC⁻ are needed for the reaction.)



8. Review the reactions on Reaction Sheets R1 and R4. You may want to add the following reactions to R4.

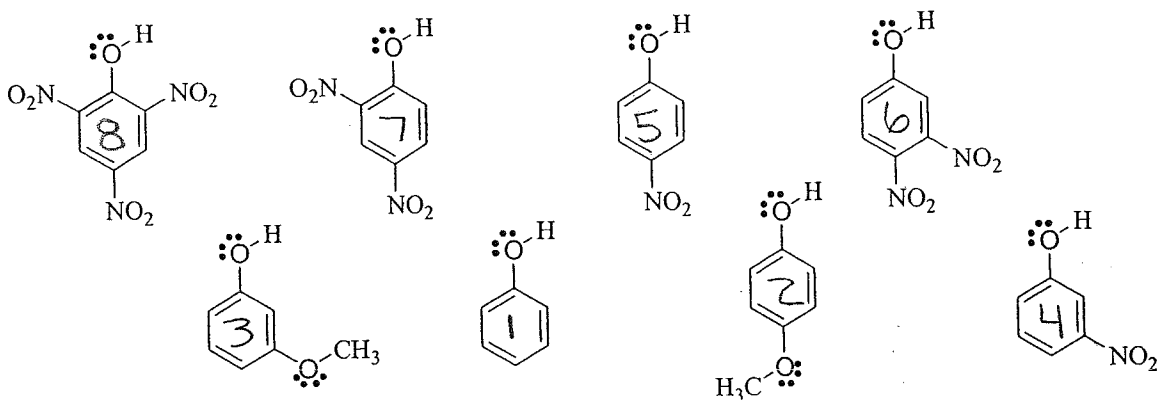


9. Read the assigned pages in your text and do the assigned problems.

Exercises for Part B

10. Number the following molecules from **least acidic (1)** to **most acidic (8)**.

(Note: an —OR group is a strong electron donating group.)



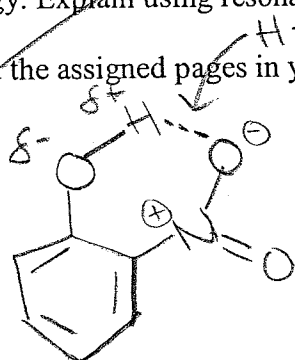
11. 2-nitrophenol is slightly less acidic than 4-nitrophenol. This is because the ortho-nitro group can form a hydrogen bond to the alcohol H.

- Draw the full Lewis structure of 2-nitrophenol showing this hydrogen bond as a ---- (dotted line).
- Explain how this hydrogen bond can increase the pKa of 2-nitrophenol relative to 4-nitrophenol.

~~12. Draw all four resonance structures of the conjugate base of *para*-methylphenol, circle the **least important (least favorable) resonance structure** and explain your reasoning.~~

~~13. Carbocations and carbanions follow the opposite trend in terms of the energy of primary, secondary and tertiary. However, an allyl (allyl) carbanion is much lower energy than a primary carbanion, and a benzyl (benzyl) carbanion is even lower in energy. Explain using resonance structures.~~

14. Read the assigned pages in your text and do the assigned problems.



H-bonding helps to decrease the \ominus formal charge of the oxygen which increases the \oplus formal charge on the Nitrogen increasing the e^- withdrawing effect.