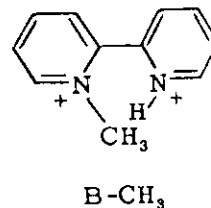
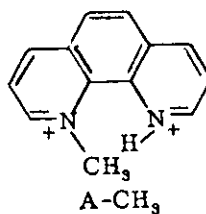
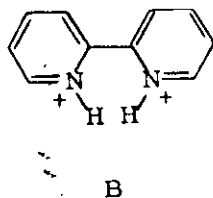
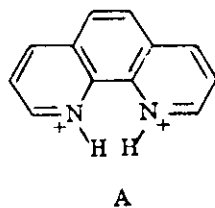


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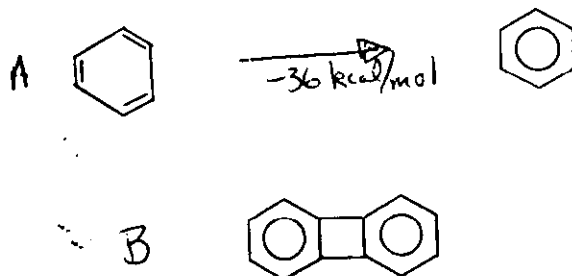
Chem 313
Final Exam, June 24, 1997
Prof D. Naud

1) The K_a (solvent is sulfuric acid) for removal of the first proton in 1,10-phenanthroline- $2H^+$ (A) is 35.5, but that for 2,2'-dipyridine- $2H^+$ (B) is 3.3. The K_a for removal of the proton in the N-methyl analogue of A is 129, for the N-methyl analogue of B, 0.49. Why does K_a go up for A (ratio is 3.6) but down for B (ratio is 0.15)?



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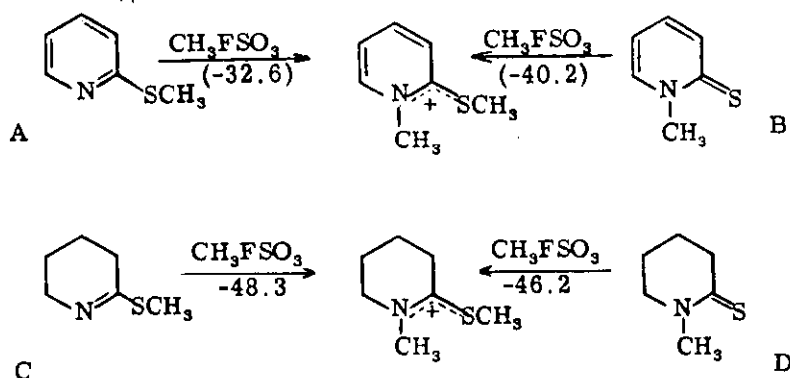
2) The empirical resonance energy (ERE) of benzene is -36 kcal/mol. (The ERE of benzene is calculated from the hypothetical cyclohexa-1,3,5-triene (A) with alternating bond lengths and localized double bonds. The heat of hydrogenation of A should be three times that of cyclohexene. The difference between this value and the heat of hydrogenation of benzene is the ERE.) What should the ERE of biphenylene (B) be? The observed ERE of B is -10 kcal/mole. Explain why there is a discrepancy between the observed and the expected.



3) In order for $\Delta\Delta G^\circ$ (or $\Delta\Delta G^\ddagger$) of a series of reactants to be linearly proportional to the $\Delta\Delta G^\circ$ of another series of reactants, one of three conditions must be met. What are these three conditions?

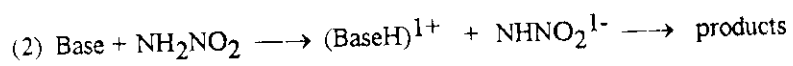
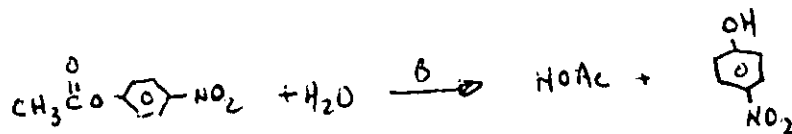
4) Measurement of the heats of methylation of two compounds that give a common product is a useful procedure for determining relative stabilities. Consider the following data (kcal/mole) for reactions conducted in the vapor phase.

- Which is the more stable compound of the isomer pair, A-B, and by how much? For C-D?
- The pair C-D can be used as a model for the localized bond version of A-B. Calculate the difference in ERE between A and B. Which (A or B) is more stabilized according to this criterion? Give an energy level diagram to help out with your answers.



5) A chemist wants to study the nucleophilic catalysis of an ester (1) and the base-catalyzed decomposition of nitramide (2) with a variety of bases. His studies will generate a Brønsted plot for each reaction. What would you advise him?

Reactions
(1)



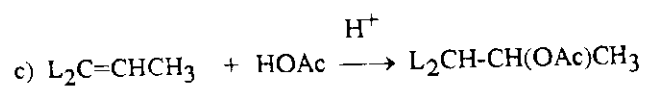
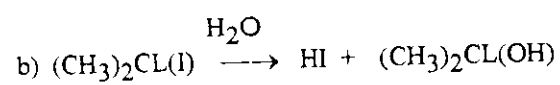
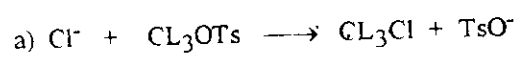
Proposed bases: para-substituted N-methyl-anilines; para-substituted pyridines and various 2-halo acetates and propanoates.

6) Pyridinium ion, pyr-H^+ , has similar acidities in water and methanol. Acetic acid is three times more acidic than pyr-H^+ when in water, but is 10,000 times less acidic when in methanol. Explain this observation.

<u>Acid</u>	<u>Solvent</u>	<u>K_a</u>
Acetic Acid	water	1.8×10^{-5}
	methanol	2.2×10^{-10}
pyr-H^+	water	6.2×10^{-6}
	methanol	2.8×10^{-6}

7) The halogenation of acetone is general acid and base catalyzed. Write the rate law expression for the bromination of acetone buffered by acetate and acetic acid. Include the Dawson-Spivey third-order term in the rate law and describe its mechanism of reaction.

8) What kinetic isotope effects would one expect for these reactions?

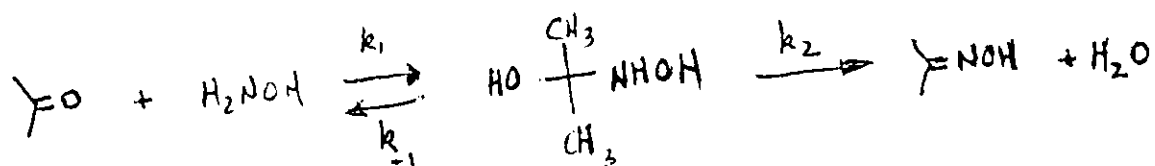


9. For the free radical reactions of substrate ZH with A, B, and C, the following data were obtained:

		k_H/k_D	ΔH_r
Z-H + A	Z + AH	1.2	very exothermic
Z-H + B	Z + BH	7.1	moderately exothermic
Z-H + C	Z + CH		little exothermicity

- a) Describe the transition state for each reaction (i.e., early, late, etc.)
- b) Predict the kinetic isotope effect for the third reaction and state reason why!

10 The formation of acetone oxime has the following generalized mechanism:



The plot below is $\log k_{\text{obs}}$ of oxime formation versus pH. Give mechanistic reasons why k_{obs} decreases from acidic to neutral conditions, and increases from neutral to basic conditions. At high pH, do you believe the reaction is specific or general acid (and/or base) catalyzed?

