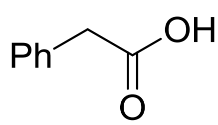
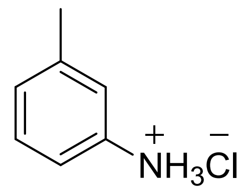
CHEM 344 Fall 2013 Midterm Quiz A **100 pts**

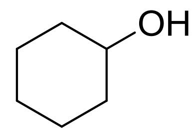
Name:

TA Name:

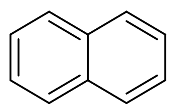
1) Circle each molecule that reacts with aq. NaOH solution to form water-soluble organic products (6 pts).







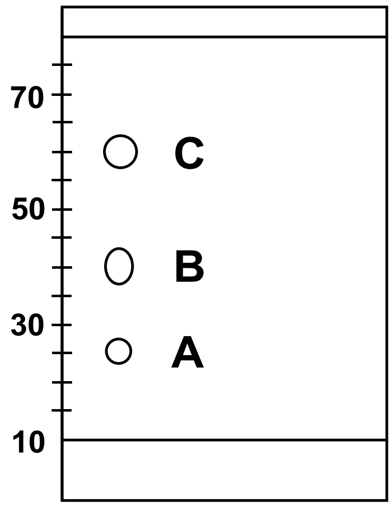
2) Draw a bullet point list to describe the most efficient way to separate a 1:1 mixture of solid potassium carbonate (K_2CO_3) and solid naphthalene ($C_{10}H_8$, shown below) into its individual solid components (6 pts).



Naphthalene

3) A reaction mixture was analyzed by TLC. The resultant TLC plate is shown below.

a) Showing all work, calculate the R_f values (as decimals) for compounds A, B and C (6 pts).



b) The reaction mixture analyzed by TLC contained an ester, a carboxylic acid, and an aromatic hydrocarbon. Assign each of the spots as one of these three compounds and explain your reasoning (5 pts).

4) 1,4-Dimethylbenzene (C_8H_{10}, *p*-xylene) was to be used as a solvent for a reaction. The ^{1}H-NMR spectrum of 1,4-dimethylbenzene (next page), taken in $CDCl_3$, shows that it is contaminated with another organic molecule. The formula of the contaminant is C_4H_8O, IHD = 1.

On the ^{1}H-NMR spectrum:

a) Draw a circle around the signals due to 1,4-dimethylbenzene;

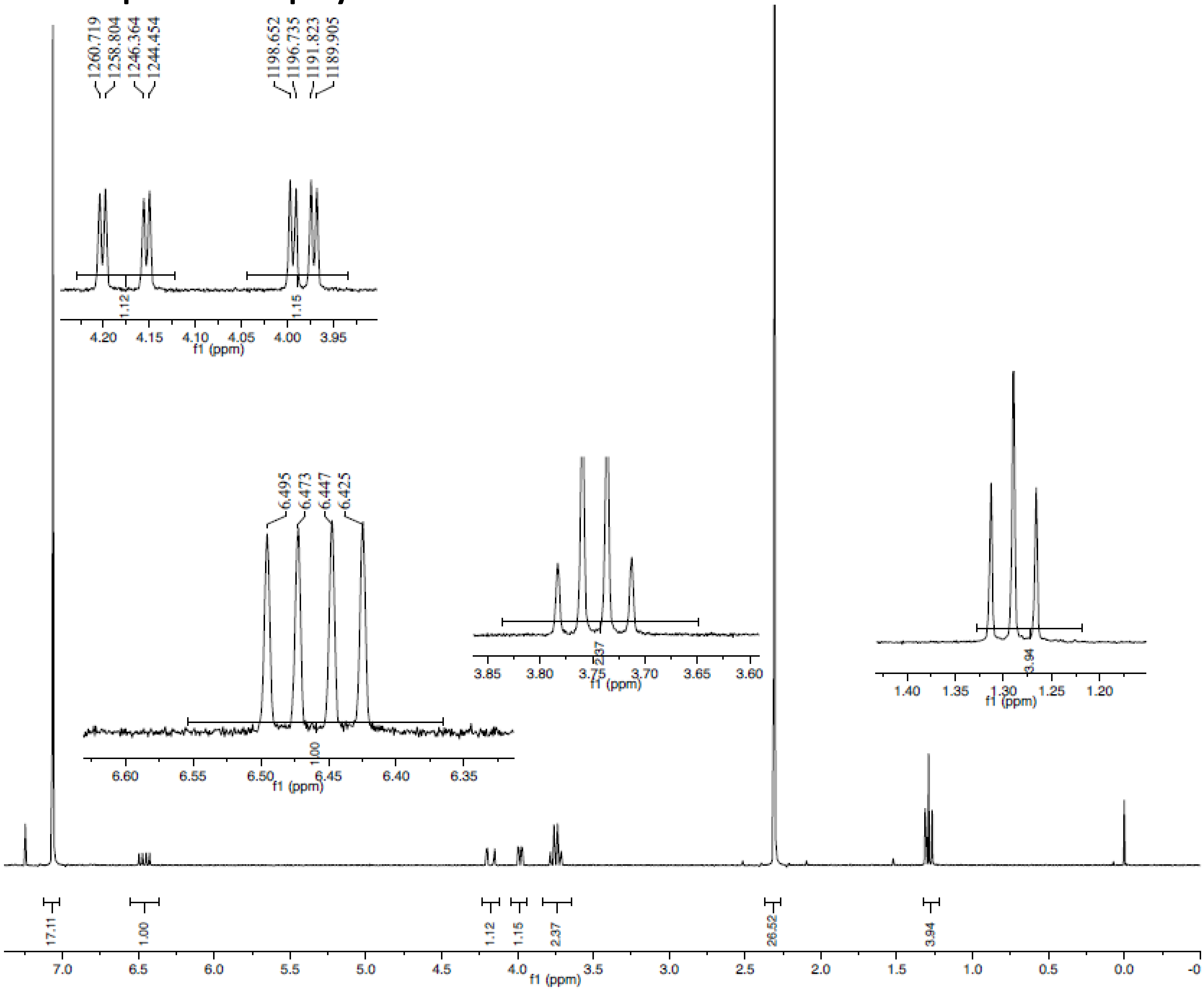
b) Draw a square around the signals due to the contaminant;

c) Draw the structure of the contaminant, assigning the signals using the H_a, H_b etc notation used in problem sets, quizzes, and lab reports;

d) Calculate the ratio 1,4-dimethylbenzene : contaminant in terms of *x*:1.

(14 pts total)

Q4) ¹H-NMR spectrum of p-xylene and contaminant



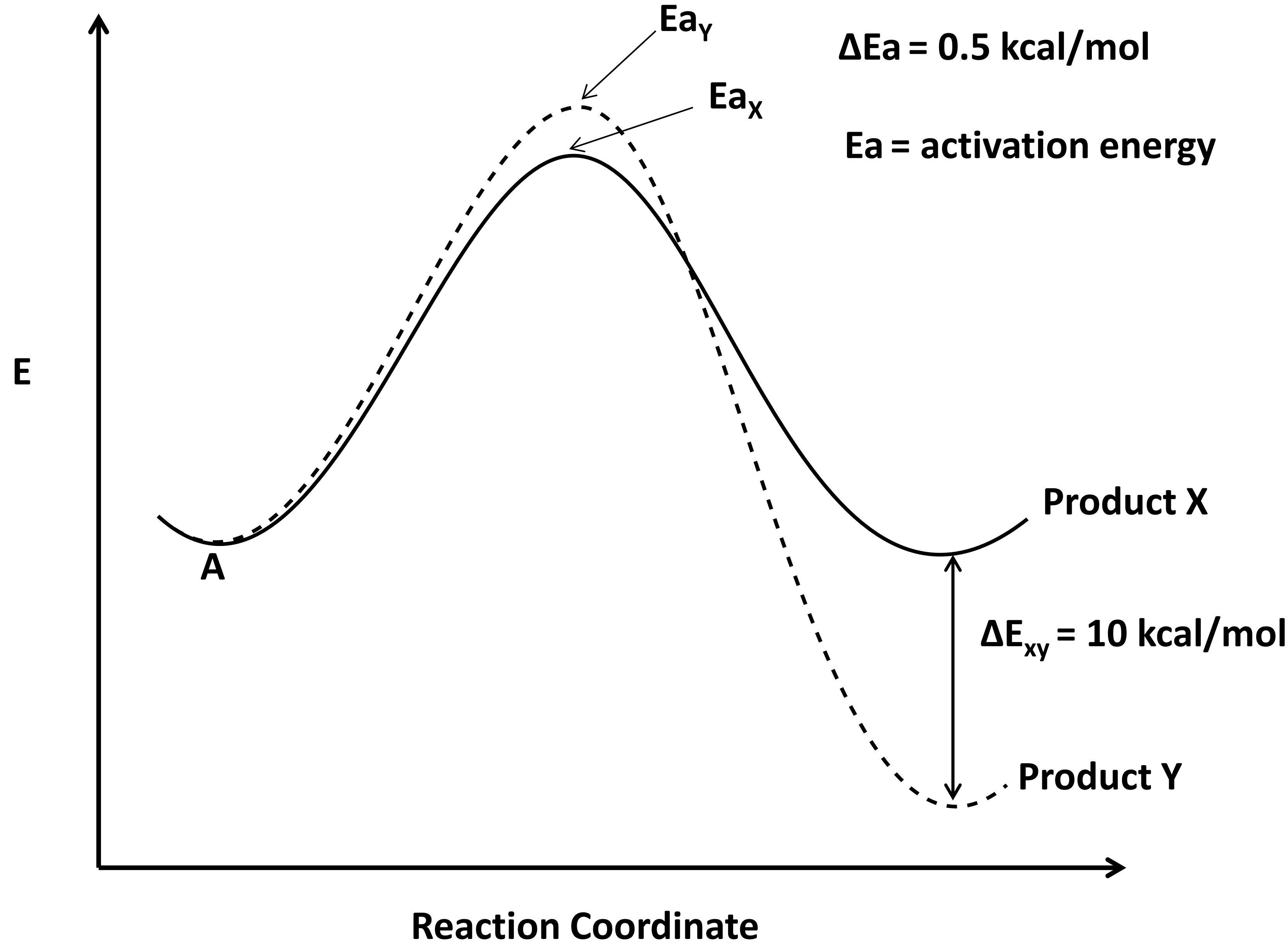
5) A potential energy (PE) surface for the reaction A $\rightarrow$ X+Y is shown over the page.

a) On the PE surface, draw a circle around the kinetic product and draw a square around the thermodynamic product (4 pts)

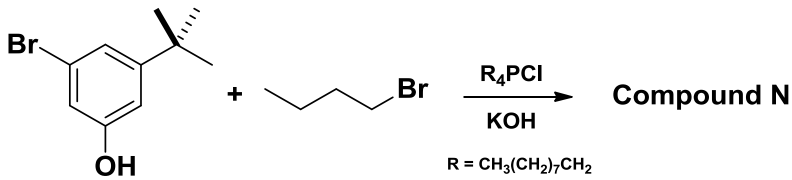
b) The ratio of products X:Y was calculated to be 3:2 by ^{1}H-NMR and GC data. Has the reaction has achieved equilibrium under the experimental conditions? Explain our answer (4 pts).

c) Assume that, **under different experimental conditions**, that the reaction A $\rightarrow$ X+Y is fully reversible. How would such reversibility affect the ratio X:Y? Explain your answer (4 pts).

Q5 Potential energy surface A→ X + Y



6) In the lab you performed a reaction similar to the one shown below.



a) State the mechanism of the above reaction and draw compound N (3 pts).

b) State the role of R_4PCl in this reaction (2 pts).

c) State the role of KOH in this reaction. Include a balanced electron-pushing mechanism in your answer (3 pts).

d) Compound N is soluble in hexane at room temperature. Would hexane be a good solvent for recrystalization of the Compound N? Briefly explain your answer (2 pts)

7) In the lab you performed a reaction similar to the one shown below.

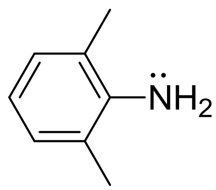
Compound G

a) State the mechanism of the reaction being performed and draw the structure of compound H (3 pts).

b) In error, a student used conc. H_2SO_4 rather than conc. HBr in this reaction. Draw the organic product(s) of the reaction between compound G and conc. H_2SO_4 (3 pts).

c) During the work-up of the reaction performed in *b*) the organic layer was washed with 2 x 5 mL saturated aq. K_2CO_3 solution. Briefly explain why this step was performed. Include a balanced chemical equation in your answer (4 pts).

8) 2,6-Dimethylaniline was submitted for a B3LYP/6-31G(d) Opt+Vib Freq calculation in WebMO. The resultant vibrational mode table is shown below.

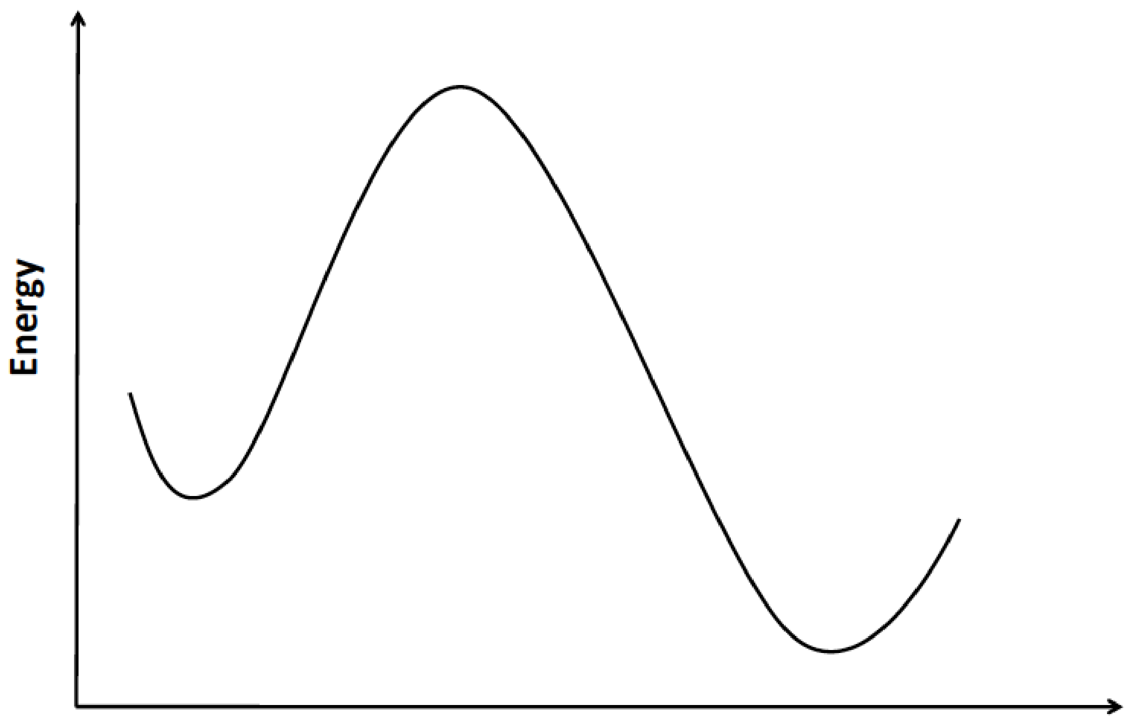


2,6-Dimethylaniline

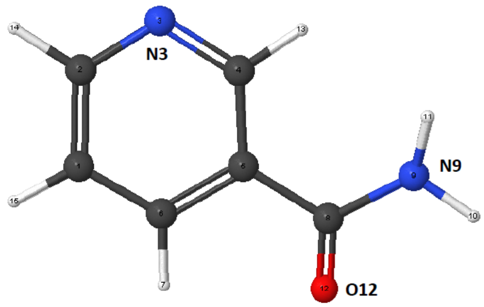
Vibrational Modes

Mode	Symmetry	Frequency (cm^{-1})	IR (Raman)
1	A	-19.1986	4.9413
2	A	113.1442	1.5951
3	A	197.4688	1.5510
4	A	211.5421	0.4963
5	A	281.3731	0.6775

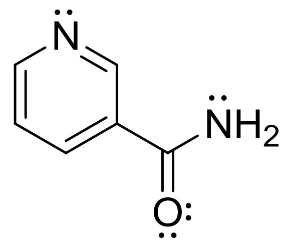
Identify a possible location on the potential energy surface for this optimized molecule and briefly explain your reasoning (4 pts).



9) A table of Natural Hybrid Orbitals for nicotinamide is shown below.



Nicotinamide



(ChemDraw figure)

Natural Hybrid Orbitals

Display Range 48 - 51 / 147

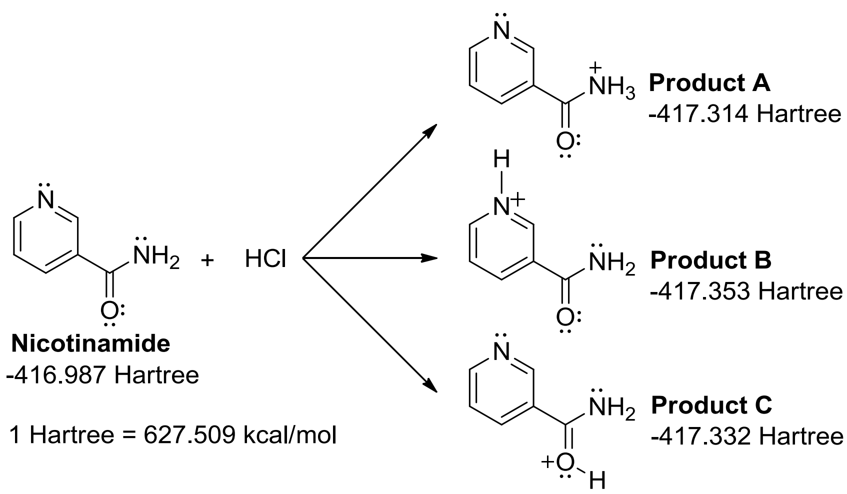
Orbital	Description	Occupancy	Energy
48	LP(1)N3 s(29.16%)p2.42(70.71%)d0.00(0.13%)	1.924568335	-0.344889145 Hartree
49	LP(1)N9 s(5.13%)p18.48(94.83%)d0.01(0.04%)	1.765996541	-0.285684798 Hartree
50	LP(1)O12 s(58.94%)p0.70(41.02%)d0.00(0.05%)	1.977298351	-0.673973638 Hartree
51	LP(2)O12 s(0.01%)p1.00(99.80%)d0.00(0.19%)	1.863419533	-0.242736987 Hartree

a) How many atoms are involved in the π-system of nicotinamide (2 pts)?

b) Are the N-atom lone pairs of nicotinamide degenerate? How do you know? (2 pts)

c) Express the hybridization of each lone pair in nicotinamide in terms of sp^x and label each lone pair on the ChemDraw figure above with the appropriate hybridization (4 pts).

10) Three isomeric products can be formed upon treatment of nicotinamide with HCl.



Showing all work, use the B3LYP/6-31G(d) data shown above to calculate:

a) the absolute energies (kcal/mol) of products A, B, and C;

b) the relative energy difference (kcal/mol) between A, B, and C. Use the lowest absolute energy (obtained from part *a*) as your reference value (9 pts total).

c) Which atom in nicotinamide is the most basic? Explain your answer (5 pts).

11) In the lab you oxidized 4-*t*Bu-cyclohexanol to the corresponding ketone. The oxidizing agent was generated *in situ* by reaction of sodium hypochlorite (NaOCl) with acetic acid. The oxidizing agent was quenched with an aqueous solution of $NaHSO_3$.

a) Draw the balanced reaction of sodium hypochlorite with acetic acid and circle the oxidizing agent so formed (3 pts).

b) State the solvent you would use to prepare an aqueous $NaHSO_3$ solution (2 pts).

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Name:

Q1	**/6**
Q2	**/6**
Q3	**/11**
Q4	**/14**
Q5	**/12**
Q6	**/10**
Q7	**/10**
Q8	**/4**
Q9	**/8**
Q10	**/14**
Q11	**/5**

Total = **/100**