CHEM 2430 – Organic Chemistry I – Fall 2015

Instructor: Paul Bracher

Quiz #1

Due: Friday, September 4th, 2015

5:00 p.m. (in class or mailbox outside Monsanto Hall 103)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

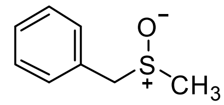
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. Submissions submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should be posted to the Blackboard discussion board so all students have equal access to the information.
- Your quiz answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		50
II		19
III		17
IV		14
TOTAL		100

Questions, Required Information, Supplementary Information

Problem I. Multiple choice (50 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

(1) ___C___ How many nonbonding valence electrons are borne by the sulfur atom of compound **A**?



A

(a) zero
(b) one
(c) two
(d) three
(e) four

The formula for calculating the formal charge on an atom is the number of valence electrons expected of that element minus the number of electrons it “owns” in the structure, i.e., half of the electrons in covalent bonds to the atom and all of the electrons in lone pairs on the atom:

formal charge = # valence electrons for the atom − # electrons the atom “owns”

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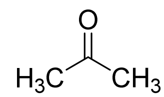
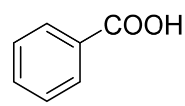
(2) ___C___ Which of the following compounds is the <u>weakest</u> Brønsted–Lowry acid?

(a) HCl, pK_a = –7

(b) CH_3CH_2SH, pK_a = 10.6

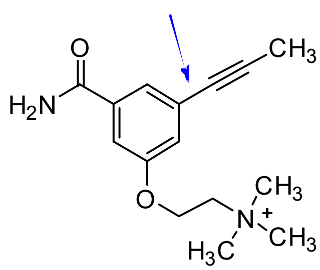
(c) 
pK_a = 19.2

(d) 
pK_a = 4.2

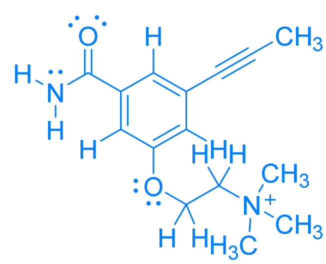
(e) H_2O, pK_a = 15.7

This problem is simple—the weakest Brønsted–Lowry acid will be the compound with the lowest acidity constant (K_a), and hence, highest pK_a (as pK_a = – log K_a). Here, choice (c), acetone, has the highest pK_a and is the weakest acid.

Refer to the structure of cation **B** for questions 3, 4, and 5.



B



B

(3) ___D___ How many total lone (nonbonding) pairs of electrons does cation **B** have?

(a) zero
(b) one
(c) four
(d) five
(e) six

A more complete Lewis structure for **B** is drawn above. You can use the formal charges for each atom to determine if it bears one or more lone pairs of electrons. Here, each oxygen atom has two lone pairs and the nitrogen atom has one lone pair.

(4) ___E___ The σ bond marked with the blue arrow in cation **B** is formed predominantly by the mixing of what two types of orbitals?

(a) two *p* orbitals
(b) two *sp* orbitals
(c) two sp^2 orbitals
(d) two sp^3 orbitals
(e) one *sp* orbital and one sp^2 orbital

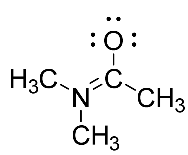
The indicated C–C bond is formed between one sp^2-hybridized carbon and one *sp*-hybridized carbon. These are the orbitals used to make the σ bond.

(5) ___D___ How many hydrogen atoms does cation **B** have?

(a) 0
(b) 14
(c) between 15 and 19, inclusive
(d) between 20 and 23, inclusive
(e) more than 23

The structure has 21 hydrogen atoms (shown in the elaborated structure above).

(6) ___D___ What is the formal charge on the nitrogen atom in the structure (**C**) of *N*,*N*-dimethylacetamide drawn below?

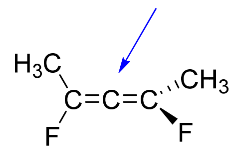


C

(a) −2
(b) −1
(c) 0
(d) +1
(e) +2

We expect nitrogen to have 5 valence electrons. Here, it "owns" one electron for each of the 4 covalent bonds it forms. 5 – 4 = +1.

(7) ____B____ In compound **D**, drawn below, what is the hybridization of the central carbon atom?



D

(a) *p*
(b) *sp*
(c) sp^2
(d) sp^3
(e) sp^3d

This is an allene. The central carbon is bonded to two groups (or "structural pairs"), so it is *sp*-hybridized. The two π bonds—one on each side of the central carbon—are formed by the two remaining unhybridized *p* orbitals on the atom.

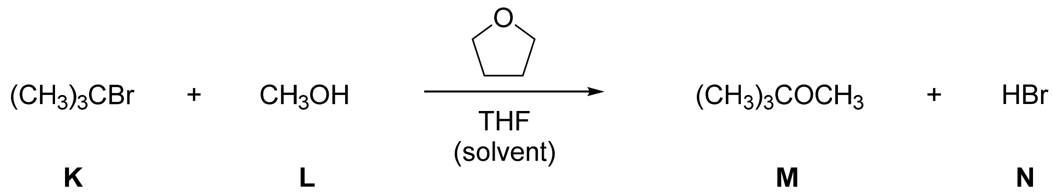
(8) ____C____ How many of the following molecules are polar?

CH_4	$CHCl_3$	CH_2Cl_2	CH_3Cl	CCl_4
E	**F**	**G**	**H**	**J**

(a) one
(b) two
(c) three
(d) four
(e) five

Compounds **F**, **G**, and **H** are polar. Compounds **E** and **J** are not.

For questions 9 and 10, consider the following reaction, the kinetics of which are governed by the stated rate law.



rate = $k[(CH_3)_3CBr]$

(9) C What effect will doubling the concentration of methanol (CH_3OH) have on the rate of this reaction, assuming all other variables are held constant?

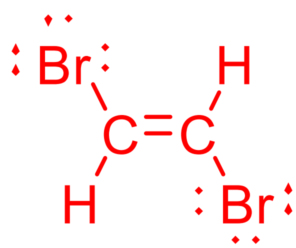
(a) the new rate will be approximately one-quarter of the original rate
(b) the new rate will be approximately one-half of the original rate
(c) the rate will be approximately unchanged
(d) the new rate will be approximately double the original rate
(e) the new rate will be approximately quadruple the original rate

(10) A Adding more **K** to a reaction mixture at equilibrium would have which of the following effects? Assume that **K** is the limiting reagent (i.e., there is plenty of available **L** to react).

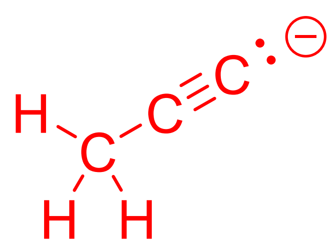
(a) the total yield of **M** (in grams) would increase
(b) the percent yield of **M** would increase
(c) both (a) and (b) would happen
(d) neither (a) nor (b) would happen

Problem II. Lewis Structures (19 points). Draw sensible Lewis structures for molecules that meet the given criteria. Explicitly label all atoms (with their elemental symbol) and show all valence electrons involved in bonding pairs (as lines) and non-bonding pairs (as “:”). Label the formal charge on atoms that have a formal charge other than zero.

(1) (9 points) The neutral compound with two bromine atoms, two hydrogen atoms, and two carbon atoms that has the lowest net dipole moment. None of the atoms bears a formal charge.

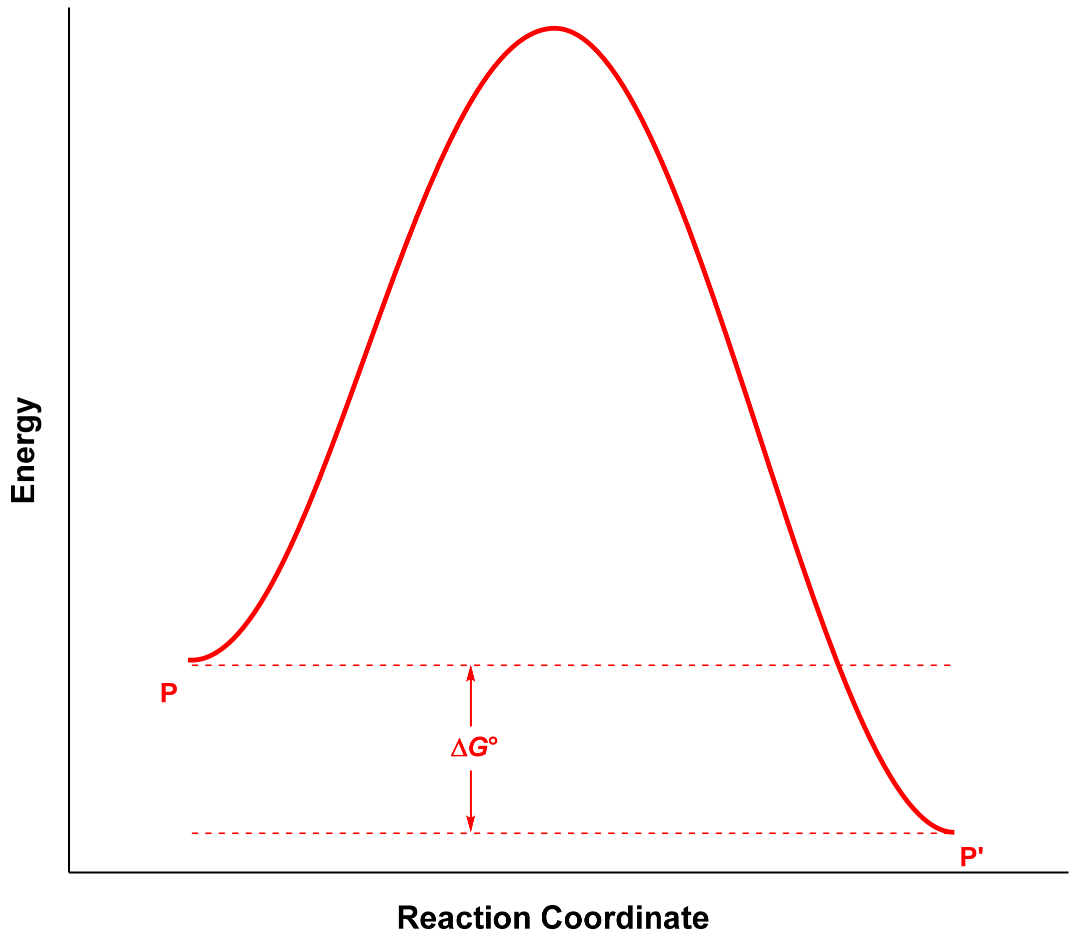


(2) (10 points). An anion with three carbon atoms, three hydrogen atoms, and an overall charge of −1. The anion has at least one atom that is sp^3 hybridized and no bond angles that are strained (far from the values expected of an atom’s hybridization).



Problem III. Reaction Diagram (17 points). Consider a hypothetical reaction where compound **P** isomerizes into a different compound, **P’**. The conversion from **P** to **P’** takes place at room temperature in a single step, with one transition state. At room temperature, a sample reaction mixture at equilibrium contains 20% **P** and 80% **P’**.

(1) (9 points) Draw a reaction diagram for the conversion of **P** to **P’** on the set of axes found on your answer sheet. Label **P**, **P’**, and the Gibbs free energy for the reaction (Δ*G*°) on your plot.



- **P** must be located higher in energy than **P’**
- Δ*G*° is the difference in energy between **P’** and **P**
- Since the transition occurs in one step—with one transition state—the diagram must have one hump

(2) (8 points) Estimate the value of Δ*G*° for the reaction in kJ/mol. Show your work for this calculation.

$$\begin{aligned}
\Delta G^\circ = -RT \ln K = -RT \ln ([\mathbf{P'}]/[\mathbf{P}]) &= -(8.315 \times 10^{-3}\ \text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K}) \ln (0.80\ \#\ \text{of mols}/0.20\ \#\ \text{of mols}) \\
&= -(8.315 \times 10^{-3}\ \text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K}) \ln (0.80/0.20) \\
&= -(2.4779\ \text{kJ}\cdot\text{mol}^{-1}) \ln (4) \\
&= -(2.4779\ \text{kJ}\cdot\text{mol}^{-1}) \ln (4) \\
\Delta G^\circ &= -3.4\ \text{kJ}\cdot\text{mol}^{-1}
\end{aligned}$$

Problem IV. Calculations (14 points). Methanethiol, CH_3SH, is an alkyl mercaptan that contributes to the foul smell of flatus (known colloquially as “farts”, “gas”, “beef”, “wind”, “air biscuits”, and “heinie hiccups”, among other alternatives). Consider the ability of methanethiol to serve as a Brønsted–Lowry acid in water:

$$\underset{\substack{\text{methanethiol} \\ \text{p}K_a = 10.4}}{CH_3SH} + H_2O \xrightleftharpoons{K_a} \underset{\text{methanethiolate}}{CH_3S^-} + H_3O^+$$

For the calculations requested below, assume that a small amount of methanethiol is added to an aqueous solution buffered at the indicated pH by a large amount of buffer salt, i.e., assume that you are not exceeding the buffer capacity of the solution. Write your answers in the boxes on the answer sheet and show your work.

We begin by identifying the reaction at play (1) in which the phenol is serving as a Brønsted–Lowry acid in water. The equilibrium constant for this reaction is defined by equation (2). Equations (3) and (4) are the definitions of pK_a and pH.

(1) $HA + H_2O \longrightarrow H_3O^+ + A^-$

(2) $K_a = ([H_3O^+][A^-])/[HA]$

(3) $pK_a = -\log K_a$

(4) $pH = -\log [H_3O^+]$

Rearrangement of equation (2) gives:

$[A^-] / [HA] = K_a / [H_3O^+]$

Further substitution with (3) and (4) gives:

$[A^-] / [HA] = 10^{-pKa} / 10^{-pH} = 10^{pH-pKa}$

So, at any given pH in water, the ratio of $[CH_3S^-]$:$[CH_3SH]$ $= 10^{pH-10.0} : 1$

(1) (7 points) Calculate the ratio of $[CH_3S^-]:[CH_3SH]$ present at pH 11. Show your work and write your final answer in the box in the form "## : 1".

$[CH_3S^-]:[CH_3SH] = 10^{pH-pKa} : 1 = 10^{11-10.4} : 1 = 3.98 : 1$

(2) (7 points) At what pH would only 0.2% of the added methanethiol be converted to methanethiolate? Show your work and write your final answer in the box.

$[CH_3S^-]/[CH_3SH] = 0.002/0.998 = 10^{pH-pKa}$

Take the log of both sides and rearrange:

$pH = pK_a + \log(0.002/0.998) = 10.4 + (-2.698) = 7.702 = 7.7$