## CHEM 2430 - Organic Chemistry I - Fall 2015

Instructor: Paul J. Bracher

## Quiz #1

Due: Friday, September 4<sup>th</sup>, 2015 5:00 p.m. (in class or mailbox outside Monsanto Hall 103)

| Student Name (Printed) |  |
|------------------------|--|
| Student Signature      |  |

## **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<br>Earned | Points<br>Available |
|---------|------------------|---------------------|
| I       |                  | 50                  |
| II      |                  | 19                  |
| III     |                  | 17                  |
| IV      |                  | 14                  |
| TOTAL   |                  | 100                 |

**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) \_\_\_\_\_ How many nonbonding valence electrons are borne by the sulfur atom of compound **A**?

Α

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

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

HCI 
$$CH_3CH_2SH$$
  $H_3C$   $CH$   $pK_a = -7$   $pK_a = 10.6$   $pK_a = 19.2$  (a) (b) (c)

$$pK_a = 4.2$$
  $pK_a = 15.7$  (d) (e)

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

| 1  | 3)  |            |                | / l l' \    | \          | electrons does  | ! ' D             | 1     |
|----|-----|------------|----------------|-------------|------------|-----------------|-------------------|-------|
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| ١, | JI  | TIOW IIIai | IV LULAI IUIIC | (HOHDOHUHE  | ı balıs ül | CICCLIOIIS GOES | , cation <b>b</b> | mave: |
|    |     |            |                |             |            |                 |                   |       |

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

| (4) | The $\sigma$ bond marked with the blue arrow in cation ${\bf B}$ 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

| ( | 5 | ) | How many | hyc | lrogen | atoms of | loes cat | ion <b>B</b> | have? |
|---|---|---|----------|-----|--------|----------|----------|--------------|-------|
|   |   |   |          |     |        |          |          |              |       |

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

(6)

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

- (a) -2
- (b) -1
- (c) 0
- (d) +1
- (e) +2

(7)

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)  $sp^3d$

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

| CH₄ | CHCI <sub>3</sub> | CH <sub>2</sub> Cl <sub>2</sub> | CH₃CI | CCI <sub>4</sub> |
|-----|-------------------|---------------------------------|-------|------------------|
| E   | F                 | G                               | н     | J                |

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

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) \_\_\_\_\_ 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) \_\_\_\_\_ 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 with it).

- (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

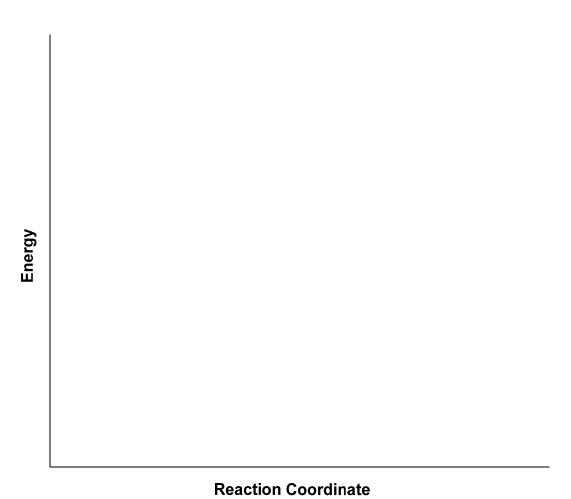
**Problem II.** Lewis Structures (19 points). Draw sensible Lewis structures for molecules that meet the given criteria. Explicitly label all atoms (with their elemental symbol) and show all valence electrons involved in bonding pairs (as lines) and non-bonding pairs (as ":"). Label the formal charge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

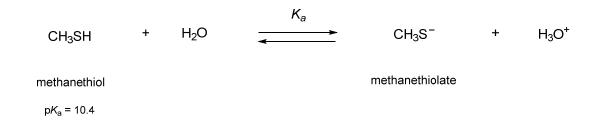
**Problem III.** Reaction Diagram (17 points). Consider a hypothetical reaction where compound **P** isomerizes into a different compound, **P'**. The conversion from **P** to **P'** takes place in a single step, with one transition state. At room temperature, a sample reaction mixture at equilibrium 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 ( $\Delta G^{\circ}$ ) on your plot.



(2) (8 points) What is the value of  $\Delta G^{\circ}$  for the reaction in kJ/mol? Assume room temperature is 25 °C. Show your work for this calculation.

**Problem IV.** Calculations (14 points). Methanethiol, CH<sub>3</sub>SH, 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:



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.

(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".

(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.