CHEM 346 – Organic Chemistry I – Fall 2014

Instructor: Paul J. Bracher

Quiz #1

Due: Friday, September 5th, 2014

6:00 p.m. (in Monsanto Hall 103)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

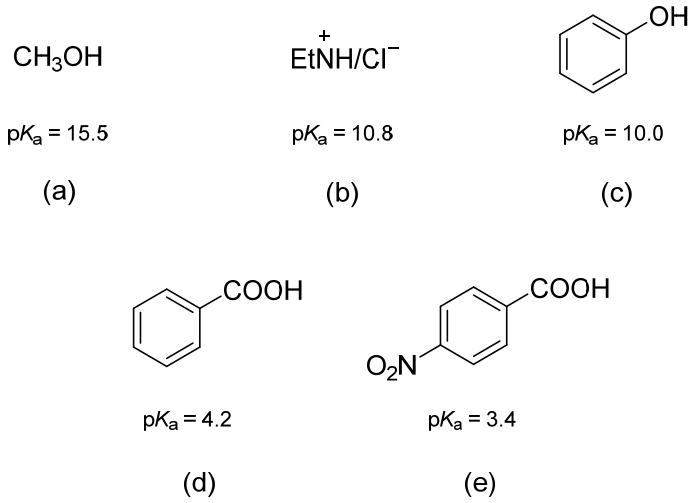
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. Submissions submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should be posted to the Blackboard discussion board so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

Problem	Points Earned	Points Available
I		70
II		9
III		9
IV		12
TOTAL		100

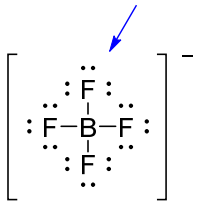
Questions, Required Information, Supplementary Information

Problem I. Multiple choice (70 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) E Which of the following compounds is the strongest Brønsted–Lowry acid?



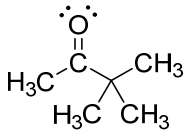
(2) D In the structure drawn below of the tetrafluoroborate anion (**A**), what is the formal charge on the indicated fluorine atom?



A

(a) −1
(b) −¼
(c) −⅕
(d) 0
(e) +1

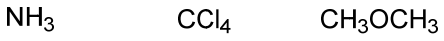
(3) A In compound **B**, drawn below, the π bond between the carbon and oxygen atoms is formed by the interaction of what two types of orbitals?



B

(a) *p* orbitals
(b) *sp* orbitals
(c) sp^2 orbitals
(d) sp^3 orbitals
(e) sp^4 orbitals

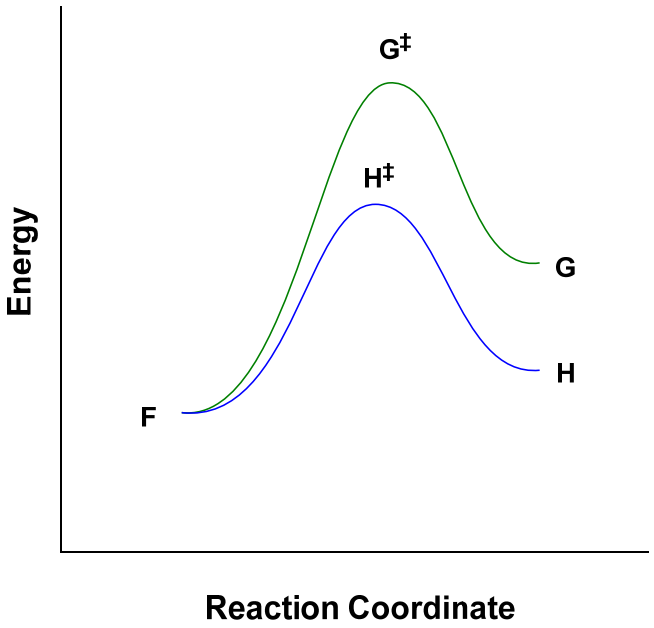
(4) E What statement offers the most accurate and complete description of the following molecules (**C**–**E**)?



C **D** **E**

(a) **C** is polar
(b) **D** is polar
(c) **E** is polar
(d) **C** and **D** are polar
(e) **C** and **E** are polar
(f) **D** and **E** are polar
(g) **C**, **D**, and **E** are all polar

For questions 5 and 6, consider the reaction diagram for the hypothetical competition between two reactions: **F**⟶**G** and **F**⟶**H**.



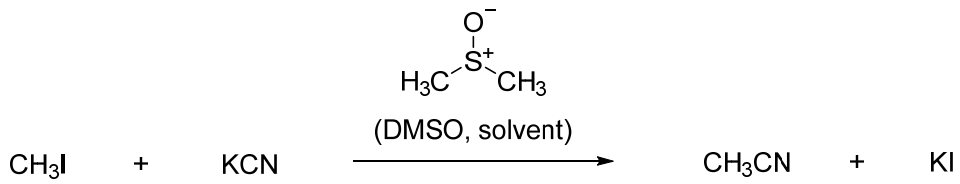
(5) A What statement is true about the kinetics of the system described above?

(a) the formation of **G** from **F** is slower than the formation of **H** from **F**
(b) the formation of **G** from **F** is faster than the formation of **H** from **F**
(c) the formation of **G** from **F** occurs at the same rate as the formation of **H** from **F**

(6) A When this system reaches equilibrium, what compound will be present in the highest concentration?

(a) compound **F**
(b) compound **G**
(c) compound **H**
(d) compounds **F**, **G**, and **H** will be present in equal concentrations

For questions 7–9, consider the following reaction, the kinetics of which are governed by the stated rate law.



$$\text{rate} = k[CH_3I][CN^-]$$

(7) D _____ What effect will doubling the concentration of cyanide ion (CN^-) 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
(f) it is impossible to determine the change in rate without more info

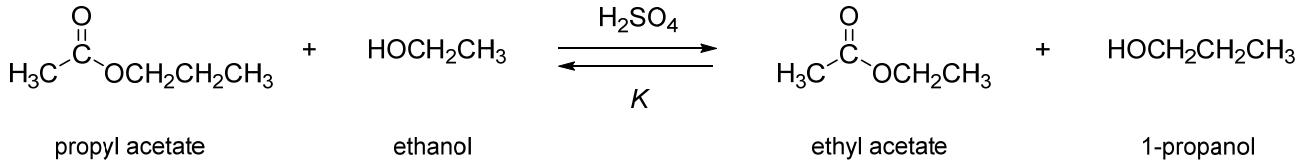
(8) A _____ What effect will doubling the amount of DMSO have on the reaction?

(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
(f) it is impossible to determine the change in rate without more info

(9) F _____ What effect will doubling the temperature from 300 K to 600 K have on the reaction?

(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
(f) it is impossible to determine the change in rate without more info

For questions 10–12, consider the reaction drawn below, the transesterification of propyl acetate to ethyl acetate. Sulfuric acid serves as a catalyst for the reaction, and *K* is the equilibrium constant for the reaction at 25 °C. Assume that the reaction depicted is the only reaction that can occur in the system. Also, assume that when the indicated reagents are added, the addition does not affect the volume of the reaction mixture.



(10) C Addition of extra ethyl acetate to this system at equilibrium would…

(a) increase the value of *K*
(b) decrease the value of *K*
(c) have no significant effect on the value of *K*

(11) C Assuming the system depicted above had reached equilibrium, which of the following observations would be true if the reaction were given sufficient time to reach equilibrium again following the addition of a drop of sulfuric acid? Assume the addition of the drop of sulfuric acid has no effect of the volume of the reaction mixture.

(a) the concentration of ethyl acetate would be higher at the final equilibrium relative to the initial equilibrium
(b) the concentration of ethyl acetate would be lower at the final equilibrium relative to the initial equilibrium
(c) the concentration of ethyl acetate would be the same at both the initial and final equilibria

(12) E Assuming the system depicted above had reached equilibrium, which of the following observations would be true if the reaction were given sufficient time to reach equilibrium again following the addition of a drop of ethanol? Assume the addition of the drop of ethanol has no effect of the volume of the reaction mixture.

(a) the concentration of ethyl acetate would be higher at the final equilibrium relative to the initial equilibrium
(b) the concentration of 1-propanol would be higher at the final equilibrium relative to the initial equilibrium
(c) the concentration of ethanol would be higher at the final equilibrium relative to the initial equilibrium
(d) both (a) and (b) are correct
(e) (a), (b), and (c) are all correct

(13) B Which of the following species does not have an electron configuration that matches the ground state of a noble gas (Group 18 element)?

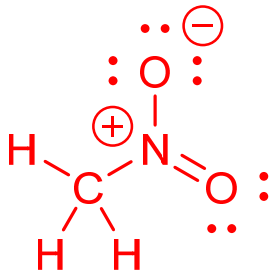
(a) Na^+
(b) Li^-
(c) Ca^{2+}
(d) H^-
(e) Br^-

(14) D Which of the following molecules has the most ionic character to its bond(s)?

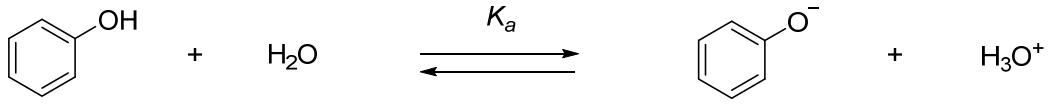
(a) F_2
(b) IBr
(c) BH_3
(d) CaO
(e) CO_2

Problem II. Short Answer (9 points). Draw a sensible Lewis structure for a compound with two fluorine atoms and two carbon atoms. 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.

Problem III. Short Answer (9 points). Draw a sensible Lewis structure for a compound with one carbon atom, one nitrogen atom, two oxygen atoms, and three hydrogen atoms in which the carbon atom is sp^3 hybridized and there are no bonds between carbon and oxygen. 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.



Problem IV. Calculations (12 points). Consider the ability of phenol to serve as a Brønsted–Lowry acid in water:



phenol

pK_a = 10.0

phenoxide ion

For the calculations requested below, assume that a small amount of phenol 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 $[PhO^-]:[PhOH] = 10^{pH-10.0} : 1$

(1) (4 points) Calculate the ratio of $[PhO^-]:[PhOH]$ at pH 10.

$[PhO^-]:[PhOH] = 10^{10-10.0} : 1 = 1:1$ (or 50%)

(2) (4 points) Calculate the ratio of $[PhO^-]:[PhOH]$ at pH 11.

$[PhO^-]:[PhOH] = 10^{11-10.0} : 1 = 10:1$ (or 91%)

(3) (4 points) Calculate the ratio of $[PhO^-]:[PhOH]$ at pH 12.

$[PhO^-]:[PhOH] = 10^{12-10.0} : 1 = 100:1$ (or 99%)

Notice that for each pK_a unit of difference, the fraction of deprotonated phenol changes by an order of magnitude. This is because the pH and pK_a scales are based on logarithms of base 10.