#2 continued

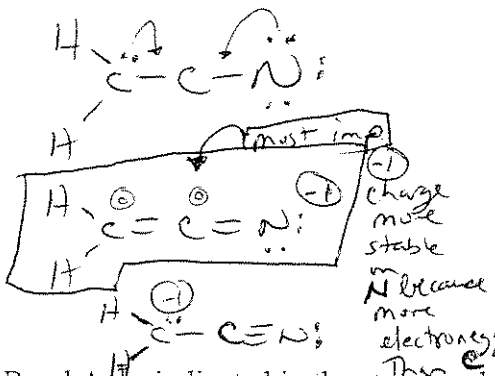
Since bond (A) is formed from a longer sp^3 hybrid orbital overlapping an sp^2 hybrid compared to Bond (B), which is formed from a shorter sp hybrid overlapping a sp^2 hybrid, bond (A) is LONGER.

Chem 2061 – Fall 2008 – **EXAM #1** Name KEY

1. (9 pts) Draw the **most important** Lewis structure for each of the following molecules or ions. Show all valence electrons and all formal charges other than zero. *If a molecule or ion below is best described by two equivalent Lewis structures, please draw both of them.*

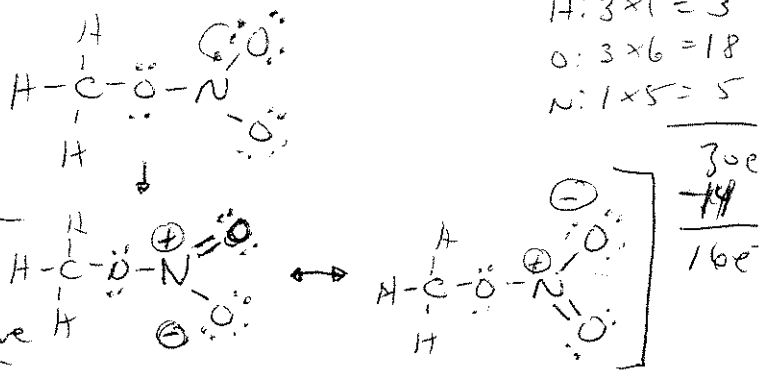
i) $^-CH_2CN$

val e⁻
C: 2×4 = 8
H: 2×1 = 2
N: 1×5 = 5
1 for -1 = +1
16e⁻
−8
8e

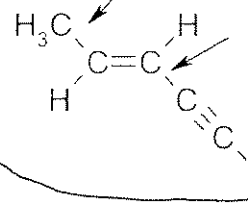


ii) CH_3ONO_2

val e
C: 1×4 = 4
H: 3×1 = 3
O: 3×6 = 18
N: 1×5 = 5
30e
−14
16e



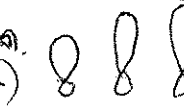
2. (4 pts) Bond A, as indicated in the structure below, is longer than bond B. **Briefly explain why this is the case.**



A ← σ-bond formed from sp^3-sp^2 hybrid orbitals overlapping

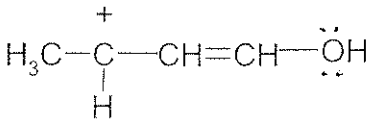
B ← σ-bond formed from sp-sp^2 hybrid orbitals overlapping

• Although sp, sp^2 + sp^3 hybrid orbitals all have the same general shape, they have different lengths due to the varying percentages of s + p atomic orbitals in them. (See here →)

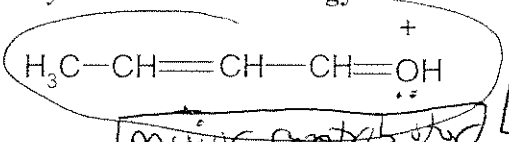


3. (10 pts) Determine whether the following pairs are actually different compounds or resonance structures of the same compound. For those that are resonance structures, indicate which one is the **major contributor** *or* whether they have the **same energy**.

a)



and

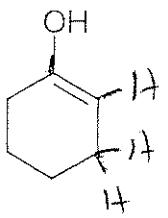


major contrib other

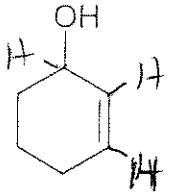
(everything has octets)

Resonance Structures

b)

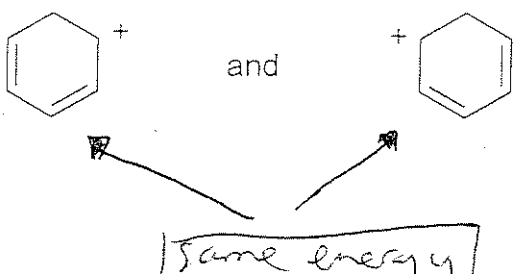


and



Different compounds

c)

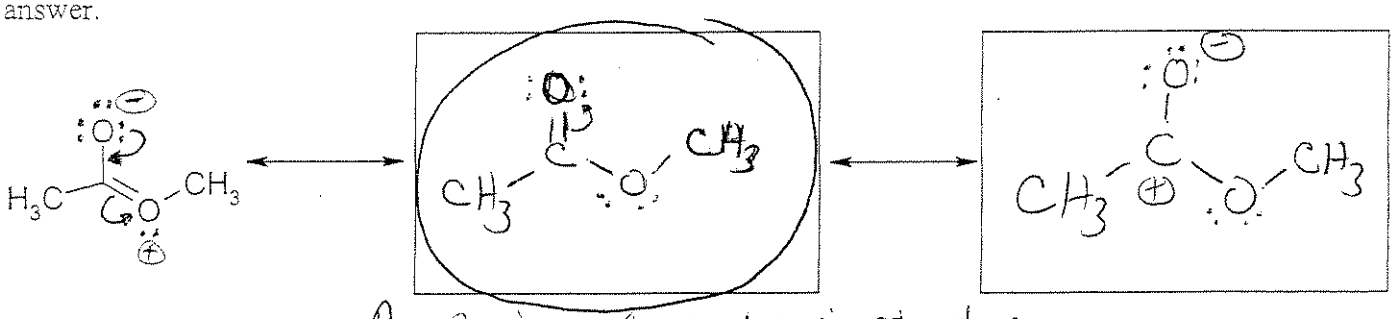


and

Resonance structures

same energy

4. (7 pts) a) For the structure below, **draw two other resonance structures** and USE CURVED ARROWS to indicate the movement of electrons from one resonance structure to the next. b) Circle the most important resonance structure and briefly explain why you chose your answer.

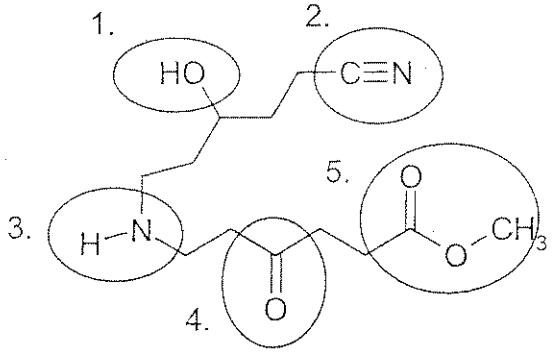


Most important Lewis structure because all atoms have octets and all formal charges are zero.

5. (10 pts) Identify the circled functional groups found in the compound below.

1. alcohol 2. nitrile 3. amine

4. ketone 5. ester

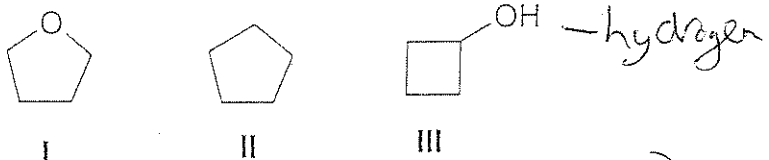


6. (3 pts) Rank the compounds in order of **increasing** boiling point (lowest to highest).

I) $CH_3(CH_2)_4$-I II) $CH_3(CH_2)_8$-I III) $CH_3(CH_2)_6$-I

a) I<II<III b) I<III<II c) II<III<I d) II<I<III e) III<II<I

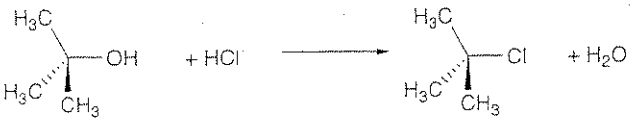
7. (3 pts) Rank the compounds below in order of **decreasing** boiling point (highest to lowest).



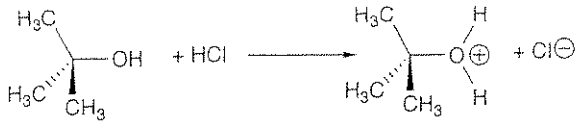
hydrogen

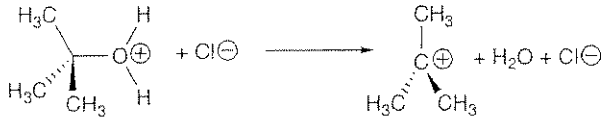
a) I>II>III b) I>III>II c) II>III>I d) III>II>I e) III>I>II

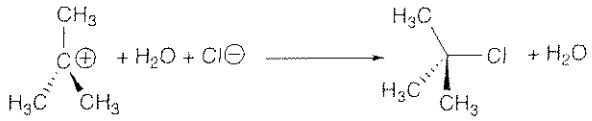
7. (18 pts) Consider the following overall reaction, which you have NOT seen before:



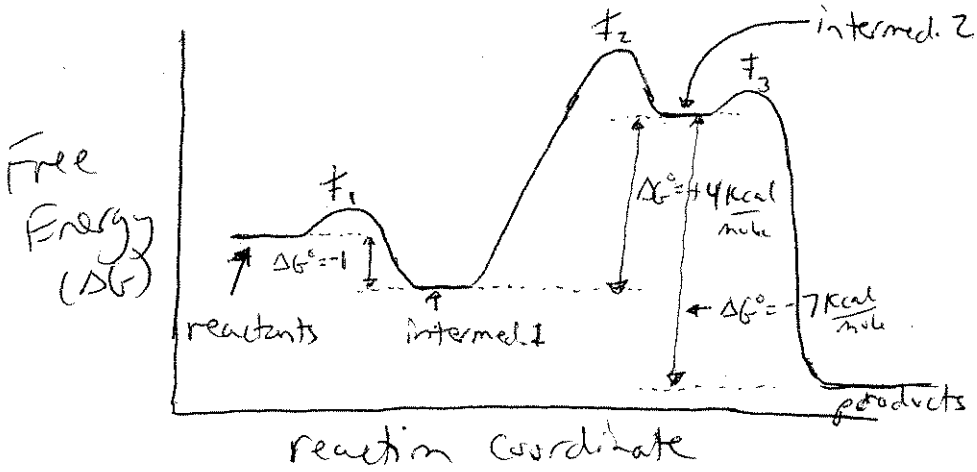
This reaction takes place in 3 steps, as follows:

Step 1  ΔG° = -1 kcal/mol

Step 2  ΔG° = +4 kcal/mol

Step 3  ΔG° = -7 kcal/mol

a) Draw the Free-Energy Diagram for this reaction, assuming steps with positive ΔG° have a considerably higher activation energy than steps with negative ΔG°.



b) Label on your diagram above: "reactants", "intermediates 1", "intermediates 2", and "products".

c) Draw double-daggers at the transition state(s).

d) Of the three steps, which is rate-limiting? 2nd step

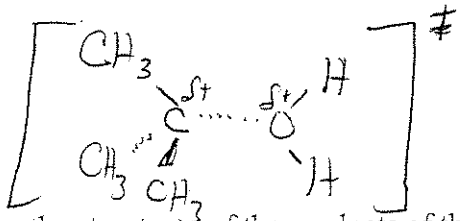
e) If the free energy change (ΔG°_r) of this reaction is –4 kcal/mol, the equilibrium constant

1) is greater than 1. 2) is less than 1. 3) is equal to 1. 4) can't be determined.

f) If the rate equation for this reaction is: Rate = $k_r[\ (CH_3)_3COH\ ]\ [\ HCl\ ]$
What is the order of this reaction?

2nd order

g) Draw the **transition state structure** for step 2 of this reaction.



8. (8 pts) A) Give the structures of the products of the following acid-base reactions. B) From the pK_a values given below, ***write in the appropriate equilibrium arrows*** which indicate whether the products or reactants are favored. (For compounds with more than one type of hydrogen, the acidic hydrogen that correlates with the given pK_a value is in bold).

	pK_a		pK_a
HCl	-2.2	NH_4^+	9.24
$HCO_2\mathbf{H}$	3.76	$CH_3\mathbf{O}H$	15.5
$CH_3CO_2\mathbf{H}$	4.74	H_2O	15.7
HCN	9.22	NH_3	33

Favors the reactants

a) $CH_3CH_2CO_2^-$ + CH_3OH ⟵ $CH_3CH_2CO_2H$ + CH_3O^-

$pK_a = 15.5$ $pK_a = 4.74$

b) $Na^+ {}^-OCH_3$ + HCN ⟶ $HOCH_3$ + $NaCN$

$pK_a = 9.22$ $pK_a = 15.5$

Favors the products

9. (4 pts) ~~Label the~~ **reactants** in the following reactions as nucleophiles or electrophiles.

a) $CH_3CH_2\ddot{I}$ + $:\ddot{O}H$ ⟶ CH_3CH_2OH + I^-

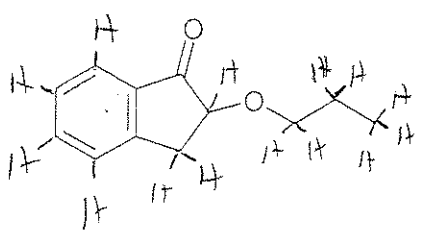
electrophile nucleophile

b) $CH_3CH_2\ddot{O}CH_3$ + H^+ ⟶ $CH_3CH_2\overset{H}{\overset{|}{O}}CH_3$

nucleophile electrophile

10. (2 pt) **True** or **False** According to molecular orbital theory, a bonding molecular orbital is formed when two atomic orbitals with the same phase overlap.

11. (3 pts) What is the **empirical formula** for a compound with the following structure?



$C_{12}H_{14}O_2$ ⟶ C_6H_7O

molecular formula → empirical formula

C.B. = Conjugate base

12. (6 pts) Briefly explain why: $CH_3CH_2\ddot{S}:^{\ominus}$ (A) $CH_3CH_2-\ddot{O}:^{\ominus}$ (B)

a) CH_3CH_2SH is more acidic than CH_3CH_2OH.

The Thiol (A) is more acidic than the alcohol (B) because when the Conj. bases of both are formed (see above) the (-1) charge is spread out more, and consequently more stable, on the larger sulfur atom compared to the smaller oxygen atom. Because the C.B. of (A) is more stable than the C.B. of (B) the parent acid CH_3CH_2SH more easily loses a proton + is a stronger acid compared to CH_3CH_2OH.

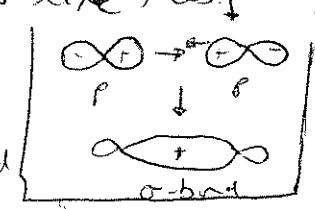
b) CH_3OH is more acidic than CH_3NH_2 → $CH_3-\ddot{N}-H^{\ominus}$ (A) → $CH_3-\ddot{O}:^{\ominus}$ (B)

Conj. base (C.B.) — Conj. base (C.B.)

Methanol (A) is a stronger acid than methylamine (B) because when the conj. bases of both are formed, the (-1) charge is on the more electronegative oxygen atom in the C.B. of (A) and on the less electronegative Nitrogen atom in the C.B. of (B). The (-1) charge is more stable on the more electronegative element - hence w/ a more stable C.B. the parent acid more easily loses a proton + is a stronger acid

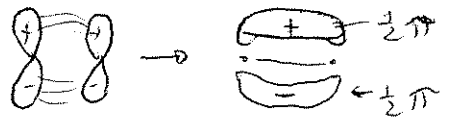
13. (6 pts) Both σ and π bonds can be formed by overlapping p-orbitals. Describe the difference, using orbital drawings to aid in your explanation.

Sigma bonds (σ) are formed by head-to-head overlap of atomic or hybrid orbitals. In the case of a σ-bond formed by overlapping p-orbitals, the overlap looks like this:



Two p-orbitals in the same phase overlap head-to-head

In the case of π-bonds, the p-orbitals overlap in a sidewise fashion like this:



In a π-bond there is e⁻ density above + below the plane of the molecule.

Lobes in the same phase for a bonding M.O.

14. (7 pts) a) Give the Markovnikov product for the electrophilic addition reaction of HBr and 1-butene. b) Write the complete mechanism of this reaction, being sure to draw in arrows to show the direction of electron movement and to write the structure of the intermediate formed. (Note: You do not need to draw the transition state structures in this mechanism).