Chem 314

Spring, 2004
Midterm Exam
Chem 314

Name _____

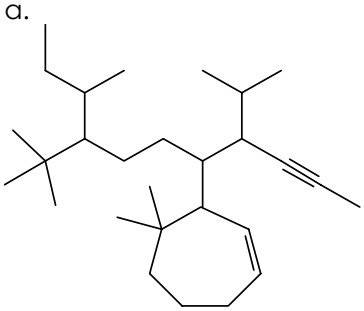
Problem	Points	Credit
1. Nomenclature: a. hydrocarbon, b. functional groups	28	
2. 2D Lewis structures	20	
3. 3D Structures, Formal Charge & Resonance	25	
4. Special Terms and specific bond energies	23	
5. M.O. Diagrams	15	
6. Thermodynamics, Bond Energies & Reactions	24	
7. Physical Properties	20	
8. Acid / Base, curved arrows, formal charge	20	
Total	175	

This is a long exam. It has been designed so that no one question will make or break you. You are not expected to completely finish the exam. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement. Also, consider the point values in your choice of questions. Do your best to show me what you know in the available time.

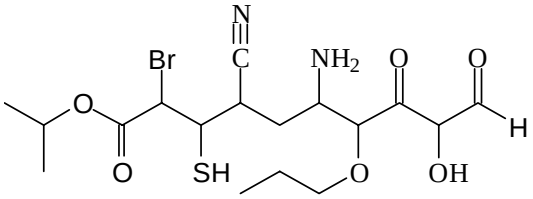
A person who wants to do something will find a way, a person who doesn't will find an excuse.
Stephen Dolley

1. Provide an acceptable name for the following structures. (28 pts)

a.



b.

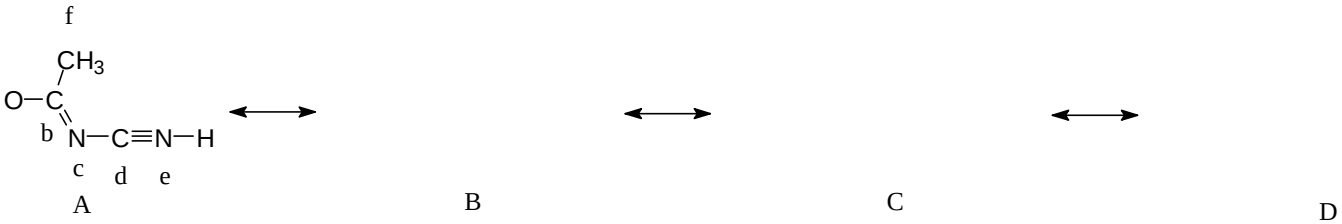


2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present, all lone pair electrons and completely draw out all atoms (e.g. do not write CH_3). (20 pts)

$H_2NOCCH(NO_2)CCC(CH_3)CHCOCH(NH_2)C_6H_4CH(CN)CO_2CH_2CH(OH)CHO$

(has formal charge) (6 carbon ring)

3. First, draw three other reasonable resonance structures as two-dimensional representations. Include proper arrow conventions. Rank your structures from best (= 1) to poorest. If any structures appear similar in energy, state so. Provide reasons for your order. Draw a three-dimensional Lewis structure for the given representation and a better resonance structure or the next best resonance structure. Show σ bonds as lines, wedges and dashes and the p orbitals in π bonds as well as any orbitals holding lone pairs. Indicate any formal charge present and give the hybridization, bond angles and shape of each nonhydrogen atom. **Assume that all nonhydrogens atoms have full octets, unless a carbocation is written**. (25 pts)

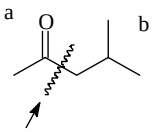


3D (A) 3D (better than A)

Use structure A to fill in the following table.

	Hybridization	Angles	Shape	#σ bonds	#π bonds	lone pairs
a						
b						
c						
d						
e						
f						

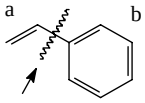
4. Indicate the bond energy between the two atoms indicated. Use the specific bond energy table provided on the last page. Write the common nomenclature term of each carbon group about the bond energy requested. Draw an arrow to any part of any structure to indicate where a methyl, methylene, methine, primary, secondary, tertiary and quaternary carbon is located. (23 pts)



indicated bond energy = _____

fragment a = _____

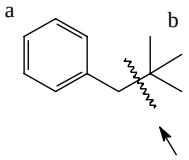
fragment b = _____



indicated bond energy = _____

fragment a = _____

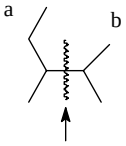
fragment b = _____



indicated bond energy = _____

fragment a = _____

fragment b = _____

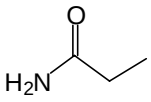


indicated bond energy = _____

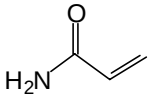
fragment a = _____

fragment b = _____

5. Draw a molecular energy level diagram for molecule A. Include σ type molecular orbitals, π type molecular orbitals and nonbonding atomic orbitals, n. Identify your orbitals with an appropriate label. Fill in the correct number of electrons. Identify the two key orbitals by the terms associated with these two key orbitals? How would the energy difference between these two key orbitals change, if at all, for molecule B? Show this with a qualitative picture of just those two key orbitals. Which molecule would absorb longer wave length light and why? (15 pts)

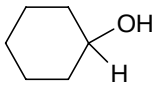
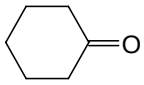


A

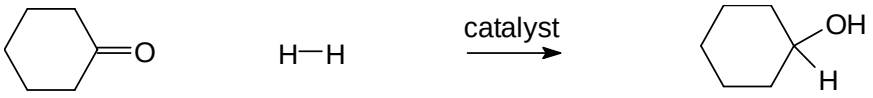


B

6. a. The heat of combustion of cyclohexanone, $C_6H_{10}O$, is –798.0 kcal/mole. Limited heats of formation are provided below. Write a balanced equation for this reaction. Use this information to calculate a heat of formation for cyclohexanone. Draw an energy diagram that includes the zero energy reference point and the various other energy values. (14 pts)

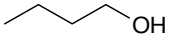
	ΔH_f^o (kcal/mole)
CO_2	-94.0
H_2O	-57.8
H_2	0.0
	-73.0
	?

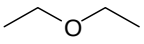
b. Calculate the heat of reaction for the equation below using heats of formation. Clearly show your set up and the appropriate energy values. (4 pts)

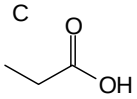


c. Calculate the same heat of reaction in part b using the average bond energies provided on the last page of the exam. Show your work for any calculations of bond energies. How does this value compare to that of part b? (6 pts)

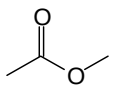
7. Each compound below has a molecular weight between 72 and 76 g. Match the structures with the given properties in the table. (5 pts). Provide a very brief explanation for your choices. (15 pts). (total = 15 pts)

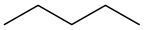
A 

B 

C 

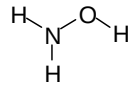
D 

E 

F 

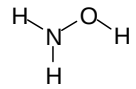
	boiling point	solubility per 100 g water
1.	35	6
2.	36	0.04
3.	57	24
4.	118	6
5.	141	infinite
6.	214	infinite

8. a. Use an arrow pushing mechanism to show all possible ways that hydroxylamine can act as a base with HCl as the acid. Add in lone pairs (**assume full octets in all reactant atoms**), any formal charge and all curved arrows to show the flow of electrons in each equation. State which reaction is the preferred one, with a brief reason for your choice. (10 pts)



hydroxylamine

b. Use an arrow pushing mechanism to show all possible ways that hydroxylamine can act as an acid with sodium hydride, NaH (ionic salt), as the base. Add in lone pairs (**assume noble gas configurations for all reactant atoms**), any formal charge and all curved arrows to show the flow of electrons in each equation. State which reaction is the preferred one, with a brief reason for your choice. (10 pts)



hydroxylamine

Typical Bond Energies for Common Substitution Patterns Found in Organic Chemistry (X-Y)

Y =	H-	Me-	(1°) Et-	(2°) i-Pr-	(3°) t-Bu-	(phenyl) Ph-	F-	Cl-	Br-	I-	HO-	H_2N-	N≡C-
X =													
CH_3- methyl (Me-)	105	90	86	86	84	102	110	85	71	57	93	85	122
CH_3CH_2- primary (Et-)	98	86	82	81	79	98	108	80	68	53	92	82	118
$CH_3CH_2CH_2$- primary (Pr-)	98	86	82	80	79	98	107	81	68	53	92	82	117
$(CH_3)_2CH$- secondary (i-Pr-)	95	86	81	79	76	96	106	80	68	54	93	82	116
$(CH_3)_3C$- tertiary (t-Bu-)	93	84	79	76	71	93	110	80	67	52	93	82	-
C_6H_5- phenyl (Ph-)	111	102	97	96	93	115	126	96	80	65	111	102	131
$C_6H_5CH_2$- benzyl (Bn-)	88	76	72	71	70	90	-	72	58	48	81	71	-
CH_2=$CHCH_2$- allyl (al-)	86	74	70	70	67	-	-	68	54	41	78	-	-
CH_3CO- acyl (Ac-)	86	81	76	74	72	94	119	81	66	49	107	-	-
CH_3CH_2O- alkoxy	104	83	82	-	-	101	-	-	-	-	44	-	-
CH_2=CH- vinyl	110	100	96	95	90	103	-	90	78	-	-	-	130
H- hydrogen-	104	105	98	95	93	111	136	103	88	71	119	107	125

(homolytic cleavage)

Average Bond Energies (kcal/mole)

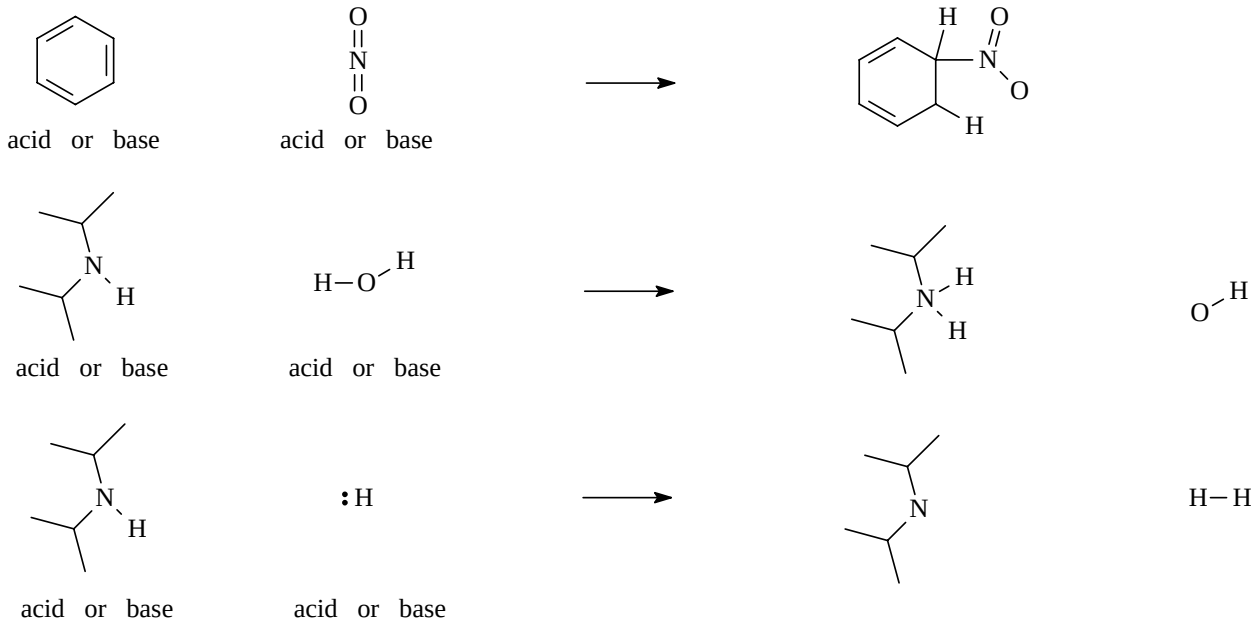
	H	C	Si	N	O	S	F	Cl	Br	I
H	104	98	76	92	109	83	135	103	87	71
C		81	72	66	79	65	116	79	66	52
Si			-	-	108	-	135	91	74	56
N				39	39	-	65	46	-	-
O					34	-	45	52	48	56
S						60	-	61	52	-
F							37	-	-	-
Cl								58	-	-
Br									46	-
I										36

Bond Energy for multiple bonds

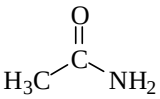
C=C	145/146
C=N	147
C=O	173/176
C≡C	198/200
C≡N	204/213

Not used on this exam, but considered as questions.

Specify each base and acid in the equations below. Add in lone pairs (assume full octets in all reactant atoms), any formal charge and all curved arrows to show the flow of electrons in each equation. (21 pts)

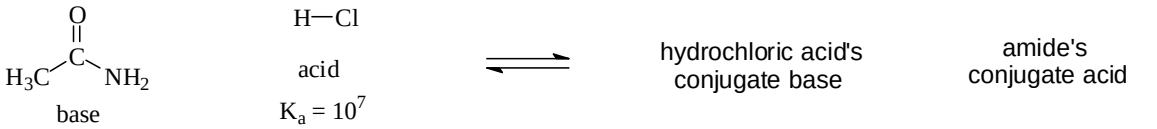


c. Show all possible ways that ethanamide can act as a base with HCl as the acid. Add in lone pairs (**assume full octets in all reactant atoms**), any formal charge and all curved arrows to show the flow of electrons in each equation. State which reaction is the preferred one, using any additional structures to explain your choice. (10 pts)

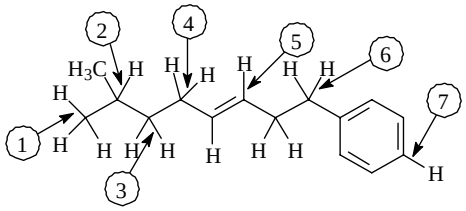


ethanamide

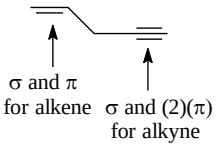
d. What is an approximate equilibrium constant, ΔG and which side is favored in the reaction?



K_{eq} = _____ ΔG = _____ Side favored = _____



1 = 98 (primary)
2 = 93 (tertiary)
3 = 95 (secondary)
4 = 86 (allyl)
5 = 110 (vinyl)
6 = 88 (benzyl)
7 = 111 (phenyl)



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$CH_2=CHCH_2$- allyl (al-)	86	74	70	70	67	-	-	68	54	41	78	-	-
CH_3CO- acyl (Ac-)	86	81	76	74	72	94	119	81	66	49	107	-	-
CH_3CH_2O- alkoxy	104	83	82	-	-	101	-	-	-	-	44	-	-
$CH_2=CH$- vinyl	110	100	96	95	90	103	-	90	78	-	-	-	130
H- hydrogen-	104	105	98	95	93	111	136	103	88	71	119	107	125

X:Y ⟶ X· ·Y (homolytic cleavage)

Average Bond Energies (kcal/mole)

	H	C	Si	N	O	S	F	Cl	Br	I
H	104	98	76	92	109	83	135	103	87	71
C		81	72	66	79	65	116	79	66	52
Si			-	-	108	-	135	91	74	56
N				39	39	-	65	46	-	-
O					34	-	45	52	48	56
S						60	-	61	52	-
F							37	-	-	-
Cl								58	-	-
Br									46	-
I										36

Bond Energy for multiple bonds

C=C	145/146
C=N	147
C=O	173/176
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C≡N	204/213

When the student is ready, the teacher will appear.