Chemistry 125 First Semester Name ____________________

December 17, 2001 Final Examination

This exam is budgeted for 150 minutes, but you may have 180 minutes to finish it. Good Luck.

1 . (9 min) In a sentence or two, or maybe three, describe **experimental evidence** that demonstrated or measured each of three **(3 ONLY**) of the following five. Be as **specific** as you can.

Shape of double bonds
Atomization energy of an element
Strain in organic molecules
Constitutional isomerism
Chirality in a molecule without a chiral center

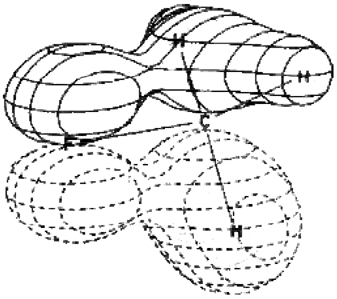
2 . (4 min) What mathematical factor is common to all hydrogen-like atomic orbitals, and why is it reasonable in terms of quantum mechanical kinetic energy?

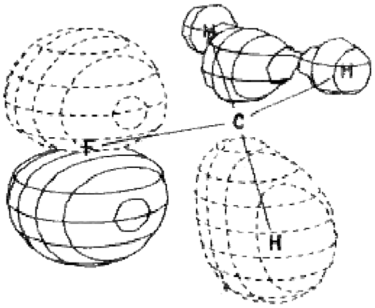
3 . (3 min) Explain why some reaction might change kinetic order as it progresses.

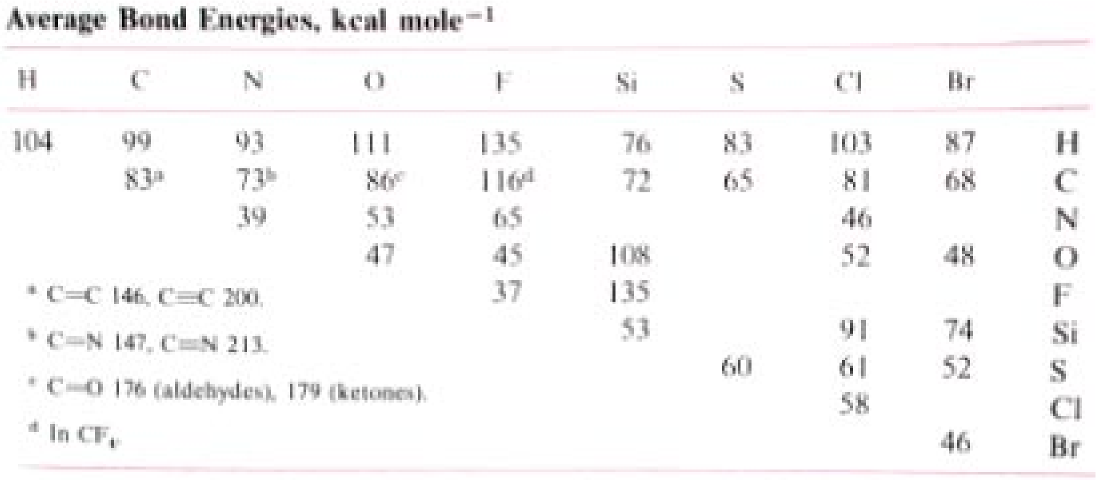
4 . (3 min) What are the two principal assumptions of the transition state theory?

5 . (2 min) The diameter of an atomic nucleus is about 100,000 times smaller than that of an atom. How does the ratio of these diameters compare to the diameter ratio between a typical organic molecule and a human hair?

6 . (5 min) Explain what the **shapes** of the following two molecular orbitals tells about the **energy** of electrons in an unshared-pair of the fluorine atom compared to the energy of electrons in a σ_{CH} orbital.







Average Bond Energies, kcal mole^{-1}

H	C	N	O	F	Si	S	Cl	Br	
104	99	93	111	135	76	83	103	87	**H**
	83^a	73^b	86^c	116^d	72	65	81	68	**C**
		39	53	65			46		**N**
			47	45	108		52	48	**O**
				37	135				**F**
					53		91	74	**Si**
						60	61	52	**S**
							58		**Cl**
								46	**Br**

[a] C=C 146, C≡C 200.

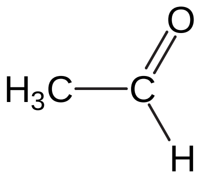
[b] C=N 147, C≡N 213.

[c] C=O 176 (aldehydes), 179 (ketones).

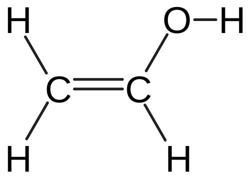
[d] In CF_4.

7 . a) (6 min) Use the table of average bond energies to predict the **energy difference**. between compound A and its isomeric “enol”, B. Predict the **equilibrium constant** K = [A]/[B] at room temperature. Show your work.

(A)



(B)



b) (3 min) Explain how consideration of hybridization might influence your answer in Part **a**.

Continued next page

Quest. 7 cont.

c) (6 min) Draw the best alternative resonance structure you can imagine for A, and the best for B. In each case specify which OMO and which UMO are being mixed to generate the resonance structure.

d) (4 min) Which molecule, A or B, should be more stabilized by resonance? Explain your thinking.

8. Experiment 10 in Chem 126L involved the following transformations, where R = phenyl (C_6H_5). The same “Grignard” reaction works just fine with R = CH_3 and many other groups.

$$\mathrm{R{-}Br} \xrightarrow{\mathrm{Mg}} \mathrm{R{-}MgBr} \xrightarrow{\mathrm{R_2C{=}O}} \mathrm{R_3C{-}O^{-}} \quad \mathrm{{}^{+}MgBr}$$

a) (6 min) This process begins when Mg donates an electron to R-Br, which then loses Br^- to form the R• radical.
Explain **what orbital** in R-Br accepts the electron from Mg,
why this orbital is **unusual** in energy, and
why the R-Br **bond breaks** after the electron transfer.

Quest. 8 cont.

b) (4 min) Explain in terms of molecular orbitals why the **R-Mg bond** of the Grignard reagent R-MgBr constitutes a **functional group**.

c) (4 min) It was important to use dry solvent when working with the Grignard reagent. **What orbital** of water makes it react with the Grignard reagent? Draw a diagram with **curved arrows** that shows the reaction and its products.

d) (5 min) Draw the molecular orbital of the ketone, $R_2C=O$, that makes it react with the Grignard reagent. Explain the **sizes** and **signs** of the atomic orbitals you drew, and explain why the orbital is of unusual **energy**.

e) (6 min) Explain how the **x-ray** work of Bürgi and Dunitz might be relevant to the direction from which the Grignard reagent approaches the ketone.

9. (5 min) In Experiment 8 of Chem 126L you converted 1-butanol to 1-bromobutane by reacting it with HBr. If early 19th Century chemists had conducted this reaction, they might have considered it a “double decomposition.” What would they mean by this, and how would the theory of Liebig, Wöhler, and Berzelius explain the reaction and the forces involved in it?

10. One could also imagine preparing 1-bromobutane by reacting n-butane with elemental bromine.

a) (5 min) Draw a reaction scheme including at least 4 steps to illustrate such a process. Two of the steps should constitute a cycle.

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b) (5 min) Use the table of Average Bond Energies to estimate an upper limit for the rate constant for each of these 4 steps at room temperature.

c) (2 min) Explain how use of light might avoid the problem posed by the slowest of the reaction steps.

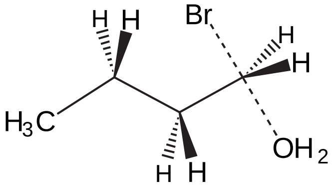
Quest. 10 cont.

d) (5 min) What by-product might make this preparation of 1-bromobutane impractical? Explain how you would estimate the yield of this byproduct. [If you remember relevant numbers, use them, if not say what numbers you would need and give a crude estimate.]

e) (8 min) Should an analogous scheme to prepare 1-chlorobutane give a better or a worse yield than that of the 1-bromobutane? Explain in terms of a relationship between rate and equilibrium for a particular reaction step. One or several pictures might help.

f) (2 min) Explain why these chlorinations and brominations would have damaged the theory of the chemists mentioned in Question 9.

11. Reaction of 1-butanol with HBr involved protonating the OH group to give the molecule a lower LUMO, and then attacking it with the HOMO of Br^- to give a transition state like the one on the right, where the colinear dotted lines show the forming Br-C bond and the breaking $C\text{-}OH_2$ bond.



a) (4 min) Explain why protonation lowers the **energy** of the LUMO, and **draw a picture** of the LUMO to explain the **direction** from which it is attacked by Br^-, and why the dotted lines should be roughly colinear.

b) (4 min) Probably the true transition state has a somewhat different **conformation** from that shown above. What should change and why?

12. In Experiment 9A of Chem 126L you converted cyclohexanol to cyclohexene. When this alcohol was protonated, it lost water spontaneously instead of reacting with a HOMO through a transition state like the one shown in Question 11. There are several reasons for this difference. Two reasons are: easier spontaneous loss of water, and harder formation of the transition state for reaction with HOMO.

a) (5 min) Spontaneous loss of H_2O from protonated 1-butanol would generate a "primary" cation, while loss from protonated cyclohexanol would generate a "secondary" cation (the names are analogous to those of carbon radicals). Explain in terms of bonding why a secondary carbon cation should form more quickly than a primary one.

Quest. 12 cont.

b) (9 min) Molecular Mechanics would show that the transition state for attack of a HOMO (like Br^-) on protonated cyclohexanol would be more strained than the analogous transition state from Question 11b. **Carefully draw** two pictures. First draw **protonated cyclohexanol** in its most favorable **chair conformation**, **Then** draw a similar structure modified to show the **transition state** for Br^- attacking the carbon bearing OH_2. Name **three kinds of strain** that this transition state might have (think Chem 3D), and explain which type you think would be **largest**.

c) (3 min) Explain whether you think that the entropy of activation ($\Delta S^\dagger$) is favorable or unfavorable for forming a transition state like that in Question 11b. Should $\Delta S^\dagger$ for your transition state in 12b be more or less favorable than that for 11b?

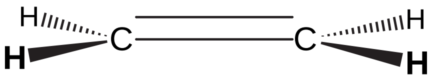
13. In Experiment 9B of Chem 126L you tested for the double bond in cyclohexene by seeing if it decolorized Br_2. This is not a free-radical reaction. Instead it involves the HOMO of the alkene mixing with the LUMO of Br_2 at the same time as the LUMO of the alkene mixes with the HOMO of Br_2.

a) (5 min) Draw the indicated orbitals on the frameworks below to illustrate these two mixings.

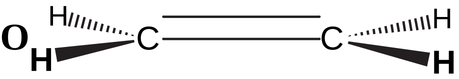
LUMO

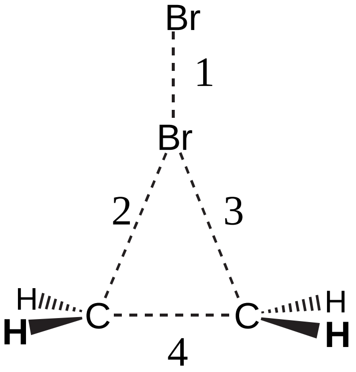
HOMO

HOMO



LUMO

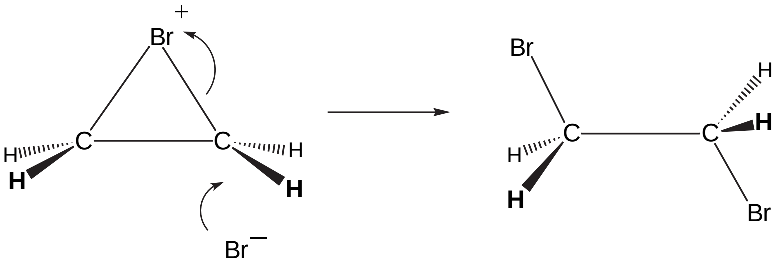




	1	
	2	
	3	
	4	

b) (2 min) Complete the table above by inserting **S** (strengthen), **W** (weaken), or **N** (neither) to indicate the change caused by each of the two orbital mixings above on the strength of the bonding between the indicated pair of atoms.

c) (8 min) The initial product of the C=C/Br_2 reaction are a bromide ion and the 3-membered ring "bromonium" ion. These two then react with one another as shown at the right to complete addition of two Br atoms to **OPPOSITE** faces of the initial C=C double bond, so in the case of cyclohexene the product would be trans-1,2-dibromocyclohexane.



Draw a chair structure for **trans-1,2-dibromo-cyclohexan**e and indicate the **constitutional, configurational, and conformational** topicity relationships between the two bromines of your structure. Label each brominated carbon as (R) or (S).

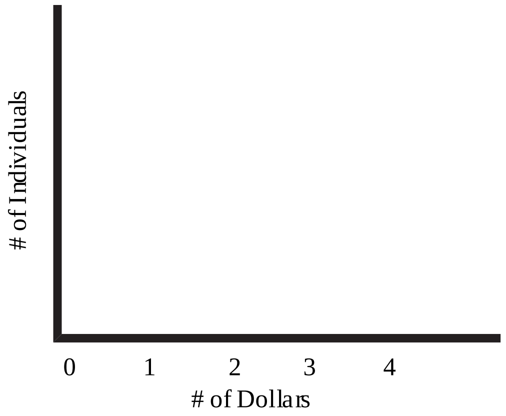
How many configurational isomers should be formed in the reaction of Br_2 with cyclohexene?

What is the **relationship** between them?

14. Suppose a balloon flew over the Cross Campus during the 300th Anniversary celebration and dumped a bushel of dollar bills, so that they fell **at random** on the crowd, and only on the crowd. Each person collects the bills that fall on his/her space. (Neglect the effect of trees, walls, breezes, uneven spacing – anything that would create a bias in favor of certain members of the crowd.) (Caution – this question was ill-conceived. After thinking a bit, see answer key for more information)

a) (2 min) Different numbers of individuals collect different numbers of dollars. Suppose the total number of dollars was about twice as large as the size of the crowd. Sketch on the right a reasonable **qualitative** plot showing the probable number of individuals who collected different numbers of dollars.

b) (3 min) Give in words a simple rationale for the distribution you plotted.



c) (3 min) Compare the Boltzmann distribution of energies among the atoms in a flask full of Argon atoms to the distribution of money among the crowd. To what is the temperature of the flask analogous?

d) (3 min – extra credit) Explain what the distribution should look like if the number of bills dropped were much greater – say 100 per crowd member.