

Much of this exam was quite challenging since it required you to apply what you have learned in the first semester to problems that you will not encounter until the second semester. This required original thinking rather than just repeating what you had been told in class or in the book, and original thinking requires time. Given this constraint, I was quite pleased with your performance and predict that you will do well next semester. In preparing for next semester it would be helpful to review these answers and read two new pages (Resonance Structures and ProtonatedMeOHLUMO) on the first semester web site.

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. [average score 14.9/18]

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

Shape of double bonds: Electron difference density maps (formed by subtracting theoretical atomic electron densities from total molecular electron densities observed by x-ray diffraction) show an accumulation of electron density between double-bonded atoms that is greater than that in single bonds and is not completely symmetrical about the internuclear line. Rather it has an ellipsoidal cross section, elongated in the direction perpendicular to the plane of the bonded atoms and their substituent atoms, as one would expect for bent bonds emerging from the nuclei at tetrahedral angles, or for the superposition of sigma and pi bonding electron density.

[See for example the "cumulene" difference density map of Leiserowitz and Berkovich-Yellin on the course web page]

Atomization energy of an element: Chupka and Inghram measured the heat of atomization of graphite by measuring the equilibrium pressure of carbon atoms inside a graphite-lined oven heated in the range 2100-2400 K. The Boltzmann factor relates this pressure (and its temperature dependence) to the difference in heat content between a carbon atom in graphite and one in the gas phase. By using a mass spectrometer they were able to distinguish between species in the gas phase, and thus to measure the carbon pressure independently of the pressure due to other species.

Strain in organic molecules: The original evidence for strain in organic molecules involved reactivity. Baeyer observed that alkenes (2-membered rings) with 0° bond angles reacted readily with many reagents such as HBr, Br₂, Cl₂ and even I₂, while cyclopropanes with 60° bond angles reacted only with HBr, and cyclobutane/cyclopentane with larger bond angles were unreactive with these reagents.

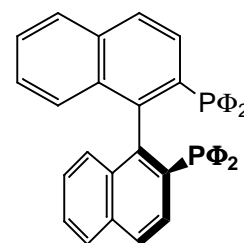
[Another line of evidence involves the heat of combustion per CH₂ group for cycloalkanes of different ring sizes.]

Constitutional isomerism: One of the first examples of constitutional isomerism was Wöhler's observation that Urea had the same composition as ammonium cyanate, but properties inconsistent with such a salt (e.g. did not yield ammonia on treatment with base or lead or silver cyanate on treatment with lead or silver salts). Similarly, Wöhler's cyanates and Liebig's corresponding fulminates had the same analysis, but different properties.

[Of course final proof that such differences were due to differences in the "nature and sequence of bonds" had to wait for bond theory which was not developed until 1858, and agreement on molecular weights, which developed after 1860. After these dates any two alkanes with the same molecular weight and different boiling points would prove constitutional isomerism.]

Chirality in a molecule without a chiral center: van't Hoff proposed in 1874 that compound with two consecutive double bonds and two different substituents on each of the terminal carbons could be resolved. Such molecules finally were resolved 60 years later. [One such molecule had phenyl and naphthyl groups on one end and phenyl and a complex acid group on the other.]

Another example is "diphos" a molecule that is twisted like a propeller about a bond between two naphthalene rings, each containing a diphenylphosphine substituent. When resolved and attached to a metal, it makes the metal a chiral catalyst, capable of catalyzing formation of a single enantiomer of a chiral compound – such as a precursor of the drug ketoprofen – from an achiral precursor



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? [average score 7/8]

All atomic orbitals include the decaying exponential, $\exp(-\rho/2)$. This is reasonable because when the electron is far from the nucleus its kinetic energy is a negative constant, for which the decaying exponential is the appropriate solution to the Schrödinger equation (second derivative divided by amplitude is constant).

3. (3 min) Explain why some reaction might change kinetic order as it progresses. [average score 4.9/6]

A good example is a catalyzed reaction, where the rate “saturates” at high concentration of the “substrate” upon which the catalyst acts. That is, the rate is limited by the amount of catalyst, all of which is working as fast as it can on substrate. When the concentration of substrate falls sufficiently, some of the catalyst is idle, waiting to find substrate molecules. Under such low-concentration conditions, the rate begins to depend on the concentration of substrate. Here the reaction order with respect to substrate changes from zero to first.

Another example would be where a molecular dimer is reactive. At high concentration essentially all of the material is in the form of dimer and doubling the amount of material doubles the rate. However at sufficiently low concentration of material, most of the material is in the form of monomer, and doubling the amount of material increases the concentration of dimer (and hence the rate) by a factor of four. Here the kinetic order changes from first to second.

4. (3 min) What are the two principal assumptions of the transition state theory? [average score 1.5/6]

- That the “transition state” is in equilibrium with the starting material
- That the rate at which transition state proceeds to product is fixed ($10^{13}/\text{sec}$)

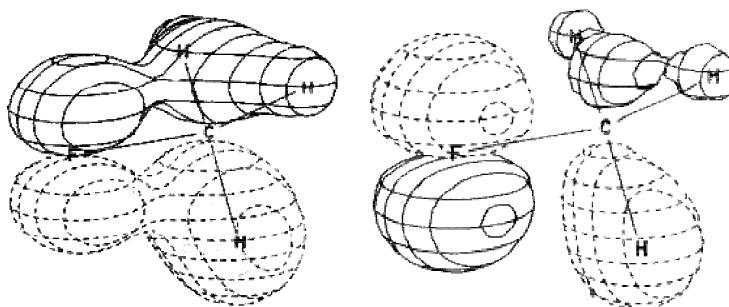
5. (2 min) The diameter of an atomic nucleus is about 100,000 times smaller than that of an atom. How does the ratio of these diameters compare to the diameter ratio between a typical organic molecule and a human hair? [average score 2.6/4]

A typical organic molecule is about 0.5 nm in diameter a typical hair about 50 μm . Again the ratio is about 100,000. [This is the correct answer to the correct question and related to the size scales we discussed in conjunction with scanning probe microscopy. Unfortunately the question in the original exam was misworded, substituting “atom” for “human hair” making it rather stupid. Fortunately this question involved small credit.

Sorry.

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 score 5.8/10]



Each of the molecular orbitals is a combination of a 2p-orbital on fluorine and several C-H bonding orbitals. In the first MO, the component orbitals are combined in a favorable way that builds up electron density between the atoms and lowers the energy. In the second MO they are combined in an unfavorable way that decreases this bonding density. The first, favorable combination should include a larger share of the lower-energy constituent orbital, while the second, unfavorable combination should include a larger share of the higher-energy constituent orbital. Since the 2p-orbital of fluorine is relatively larger in the second orbital than in the first, it must be higher in energy than the C-H bonding orbitals. But the difference in relative sizes is minor, despite the small overlap, so the constituent orbitals are nearly equal in energy.

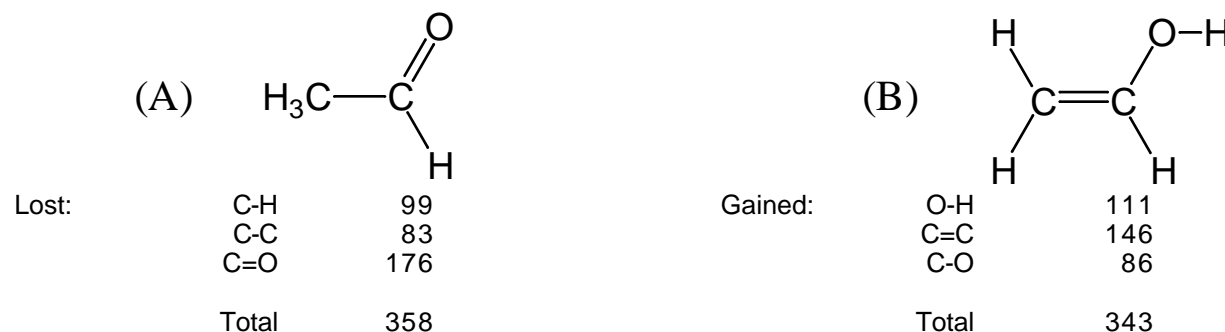
Average Bond Energies, kcal mole⁻¹

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 CF₄.

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.

[average score 10.5/12]



Overall loss in stabilization on converting A to B = 358-343 = 15 kcal/mole

$$[A]/[B] = 10^{-(3/4 * -15)} = 10^{(11.25)} \quad \text{N.B. It would have been more conventional to write } K = [B]/[A] = 10^{(-11.25)}$$

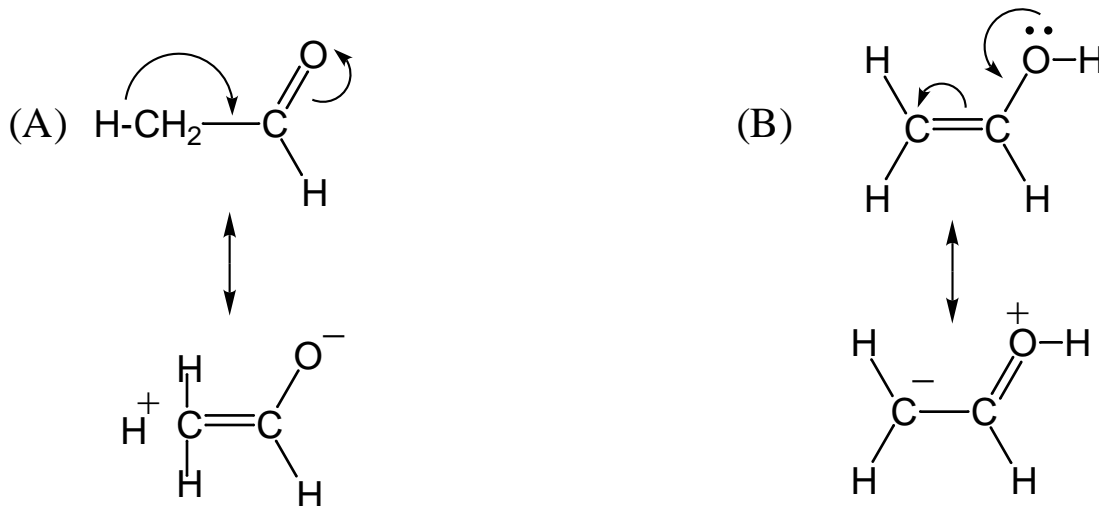
- b) (3 min) Explain how consideration of hybridization might influence your answer in Part a. [average score 2.9/6]

In the comparison above it was assumed that the bonds that persisted between starting material and product would cancel out. However two of these 3 C-H bonds are different between the two molecules. In A two of the C-H bonds involve sp³ carbon hybrids, while on the right they involve sp² carbon hybrids. Since the later hybrids form stronger bonds, this factor should lower the energy of B relative to A and make the equilibrium constant somewhat less drastic (closer to 1). On the other hand the C-C bond in A should be stronger than an average C-C bond energy, because of sp² hybridization of one of the carbons. This effect would be in the opposite direction and would presumably be stronger than the effect of one (of the two) C-H hybridization changes.

[Caution: before getting too picky about such corrections, it would be good to check just where the "average bond energies" came from, since some of the hybridization changes might already have been accounted for indirectly in assigning relative values of C-C and C=C energies.]

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. [average score 5.3/12]



(A) The HOMO is σ_{C-H} ; the LUMO is $\pi^*_{C=O}$

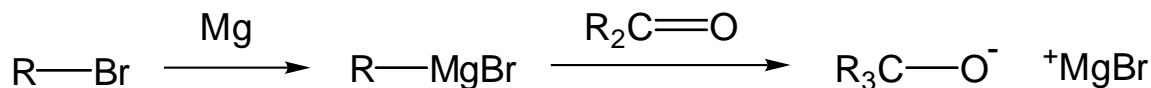
(B) The HOMO is n_O ; the LUMO is $\pi^*_{C=C}$

[This question certainly exercised the imagination. Among 57 papers there were 39 **different** answers for part A (3 of them correct) and 29 **different** answers for part B (3 of them correct)! Some credit was given for simple polar resonance structures that involve making a polar covalent bond ionic, though this did not lend itself to interpretation in terms of OMO/UMO mixing. Because of the prevalence of erroneous structures, and the importance that these concepts will assume in the second semester, you should review the web page on this subject if you had any difficulty.]

- d) (4 min) Which molecule, A or B, should be more stabilized by resonance? Explain your thinking. [ave. 1.6/8]

B should be more stabilized. It has both an unusually high HOMO and an unusually low LUMO. B has an even lower LUMO, BUT σ_{C-H} is a pretty poor excuse for a HOMO.

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.



- a) (6 min) This process begins when Mg donates an electron to R-Br, which then loses Br^- to form the R^\bullet 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. [average score 10.6/12]

The LUMO of R-Br is σ^*_{C-Br} . This is the orbital that should accept the next electron.

This orbital is unusually low in energy (compared with σ^*_{C-H}), because of the high nuclear charge on Br.

The σ^*_{C-Br} LUMO is an antibonding orbital. This means that electrons in this orbital become lower in energy when the bond breaks. Obviously occupancy of this formerly empty orbital weakens the C-Br bond.

Quest. 8 cont.

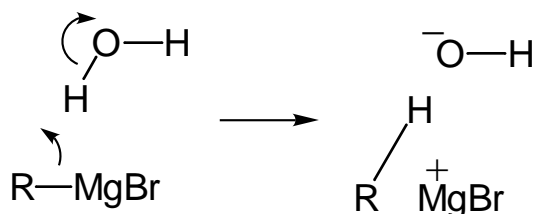
- b) (4 min) Explain in terms of molecular orbitals why the **R-Mg bond** of the Grignard reagent R-MgBr constitutes a **functional group**. [average score 6.1/8]

$\sigma_{\text{C-Mg}}$ is an unusually high-energy HOMO because of the low nuclear charge of Mg (given that it is a third-row element using $n=3$ atomic orbitals). This rather diffuse orbital has relatively poor overlap with C as well.

- 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.

[average score 4.0/8]

The low LUMO of H_2O is $\sigma_{\text{C-H}}^*$.



- d) (5 min) Draw the molecular orbital of the ketone, $\text{R}_2\text{C}=\text{O}$, 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**.

[Average score 7.3/10]

The LUMO which interacts with the Grignard HOMO is $\pi_{\text{C=O}}^*$. Since it is an anti-bonding MO the signs of adjacent p-orbital components are opposite one another. The orbital is larger on C than on O, because most of the more favorable O orbital was used in forming the low-energy $\pi_{\text{C=O}}$ orbital. This orbital is of unusually low energy (compared with $\sigma_{\text{C-C}}^*$) because the side-to-side π overlap of the p-orbitals is much less than the σ overlap of sp^3 hybrids forming the C-C MOs.

- 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. [average score 9.4/12]

Bürgi and Dunitz analyzed the relative position of N atoms near C=O bonds in many different crystal structures. They found that these nitrogens tended to lie near a line that makes an N-C=O angle of about 110° . In structures with the N closer to C, the O was more remote from C, as if these represented frames of a motion picture showing the reaction. That the angle is greater than 90° is consistent with the idea that the incoming HOMO of nitrogen will optimize overlap with the LUMO of C=O by avoiding the AO of oxygen, which is opposite in sign to the AO of C in $\pi_{\text{C=O}}^*$.

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?

[average score 8.9/10]

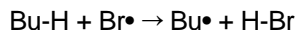
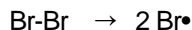
Double decomposition reactions involve the exchange of partners between two substances, as in $\text{A-B} + \text{C-D} \rightarrow \text{A-D} + \text{C-B}$. Here the reaction would be $\text{Bu-OH} + \text{H-Cl} \rightarrow \text{Bu-Cl} + \text{H-OH}$.

The dualistic radical chemists considered that the attraction between components was electrostatic, that is that Bu and H would be electrically positive while OH and Cl would be electrically negative.

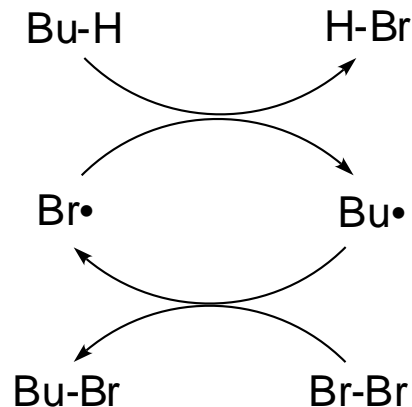
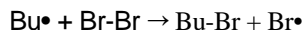
10. One could also imagine preparing 1-bromobutane by reacting n-butane with elemental bromine.

- 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.

[average score 8.6/10]



These central reactions may be written as a "propagation" cycle:



- 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. [average score 4.2/10]

[If one is to use average bond energies to estimate limiting rates, one must be ignoring the (typically much smaller) contributions to rate constants from entropies of activation, which will accelerate the first process (where one molecule is becoming two) and slow the other three (where two molecules must come together to react).]

The lowest possible activation energy would be if there were no "bump" in the reaction coordinate diagram, just a smooth rise or fall in the energy between starting material and product, so that the activation energy would be the same as the overall change in energy for an endothermic reaction and zero for an exothermic reaction.

The limiting activation energies (E_{act} , in kcal/mole) for the four reactions above would then be :

46 (Br-Br)

12 = 99 - 87 (C-H - H-Br)

0 because the reaction is exothermic -22 = 46 - 68 (Br-Br - C-Br)

0 because the radical-radical reactions are exothermic

The corresponding rate constants (ignoring entropy contributions) should be $10^{13}/\text{sec} \times 10^{-3/4 E_{\text{act}}}$ or :

$10^{-21}/\text{sec}$

$10^4/\text{sec}$ [fast enough to get a reasonable rate of reaction even with low concentration of radicals]

$10^{13}/\text{sec}$

$10^{13}/\text{sec}$ [These last two should be very fast, limited only by how fast the reagents can find one another in the solution - "diffusion controlled"]

- c) (2 min) Explain how use of light might avoid the problem posed by the slowest of the reaction steps. [ave. 3.1/4]

$10^{-21}/\text{second}$ means you would need nearly 10^{21} molecules of Br_2 (roughly 1/10 gram) to start even 1 reaction chain per second, which is orders of magnitude too slow, even with chain amplification. Better to pump energy directly into Br_2 molecules using light, rather than to wait for such extraordinary amounts of energy to occur at random. Once light is absorbed and a bonding electron becomes anti-bonding the molecule will break into atoms within one vibration (about 10^{-13} sec).

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.] [average score 7.1/10]

The second reaction above (in which $\text{Br}\cdot$ abstracts H from butane) determines which H atom will be replaced. If it abstracts H from one of the 6 methyl hydrogen atoms (primary), 1-bromobutane would be the product, but if it abstracts one of the 4 methylene hydrogen atoms (secondary), 2-bromobutane would be formed. So the byproduct would be 2-bromobutane.

The yield of 2-bromobutane relative to 1-bromobutane would be the statistical factor (4/6) times the relative rates for abstracting secondary vs. primary hydrogen atoms. This factor is about 80 (gas phase 150°C , the text on p. 113 give an example of 35 at 330°C), so the relative yield of the "byproduct" is about 4/6 of a number between 30 and 100 or so (depending on temperature); that is there would be 20 to 70 times as much "byproduct" as desired product.

- 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. [average score 10.9/16]

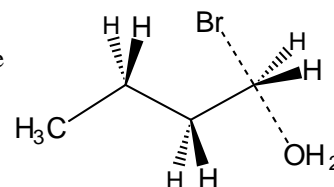
H-abstraction by $\text{Cl}\cdot$ is about thermoneutral, while that by $\text{Br}\cdot$ is endothermic. Thus abstraction by $\text{Cl}\cdot$ is much faster, and (according to the Hammond Postulate) it has an earlier, less selective transition state, where the difference between abstracting primary and secondary H-atoms has not begun to be as strongly felt as it is in the later transition state for $\text{Br}\cdot$ abstraction.

Thus the product ratio should not be as strongly in favor of the secondary product (2-chlorobutane). For chlorination the secondary/primary rate ratio (per hydrogen atom) is 4, so that the relative yield of 2- vs. 1-chlorobutane should be $4 \times 4/6 = 2.7$. The yield of the desired 1-chlorobutane would be about $1/3.7 = 27\%$. Still not so great, but better. [It's hard to get a good yield of primary alkyl halides by radical halogenation, except in very special cases, such as when there are no secondary or tertiary hydrogens.]

- f)** (2 min) Explain why these chlorinations and brominations would have damaged the theory of the chemists mentioned in Question 9. [average score 3.0/4]

In the Dualistic theory radicals were supposed to hold together by the attraction of opposite charges. In these substitutions positive H is replaced by negative Cl (they must have opposite charges to explain the existence of H-Cl), so something is seriously wrong. [Such reactions were why the French chemists abandoned the radical theory and became agnostic about the forces that held molecules together.]

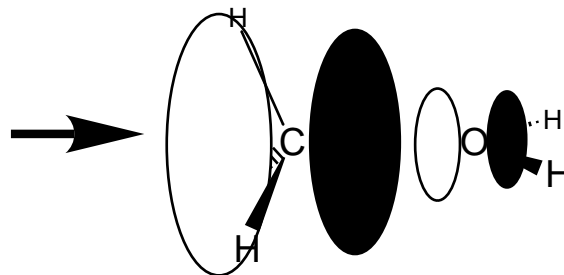
- 11.** Reaction of 1-butanol with HBr involved protonating the OH group to give the molecule a lower LUMO, and then attacking it with the HOMO of Br^- to give a transition state like the one on the right, where the colinear dotted lines show the forming Br-C bond and the breaking C-OH₂ bond.



- 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. [average score 4.9/8]

Protonation generates a positive charge (on the Oxygen atom), which lowers the electron energy for all MOs in the vicinity including that of the LUMO.

The LUMO is $\sigma_{\text{C-O}}^*$ (see right). Best overlap is available from the face of the carbon atom exactly opposite the O, as shown by the arrow. [Incidentally, the true LUMO involves the two $\sigma_{\text{C-H}}^*$ orbitals as well, see web page]



- b) (4 min) Probably the true transition state has a somewhat different **conformation** from that shown above. What should change and why? [average score 4.2/8]

In the transition state structure shown above, the forming Br-C bond is eclipsed with the central C2-C3 bond, and there should be non-bonded repulsion (van der Waals strain) between the Br and the two H atoms on C3. Both of these sources of strain energy should be assuaged by 90° rotation about C1-C2. This is a change in conformation. Residual strain between this CH₂ group and entering Br (and between this CH₂ group and departing H₂O) could be reduced by bending the forming and breaking bonds so that they are not collinear

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 H₂O 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. [average score 7.6/10]

Bonds to trivalent cationic carbon (which involve sp² C hybrids) are stronger than those to tetravalent carbon (which involve sp³ C hybrids). The strengthening effect from increased overlap is more effective for C-C bonds than for C-H bonds. The carbon of a secondary cation forms bonds to two carbons and one hydrogen. The carbon of a primary cation forms bonds to one carbon and two hydrogens. Thus the gain in sigma bond stability is greater for the secondary than for the primary carbon cation.

[There are other factors that also help stabilize secondary carbon cations as compared to primary ones. These include reduction in repulsion between substituent groups as one substituent is removed from the precursor, and “hyperconjugation” – that is mixing of σ_{CH} of the adjacent carbon with the new vacant p-orbital on the cationic C atom, which obviously can't work if there is no adjacent σ_{CH}. You'll talk about this soon.]

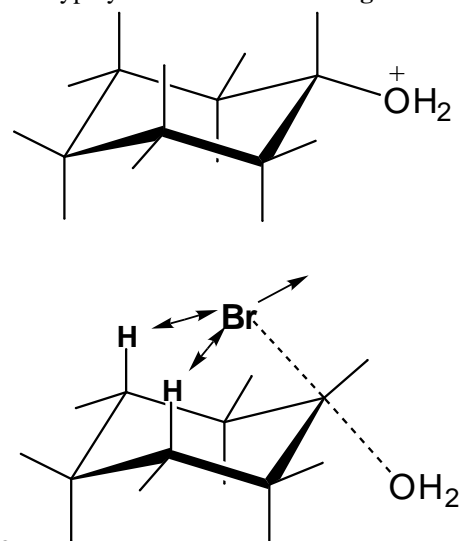
- b) (9 min) Molecular Mechanics would show that the transition state for attack of a HOMO (like Br⁻) on protonated cyclohexanol would be more strained than the analogous transition state from Question 11b. **Carefully draw** two pictures. First draw **protonated cyclohexanol** in its most favorable **chair conformation**, **Then** draw a similar structure modified to show the **transition state** for Br⁻ attacking the carbon bearing OH₂⁺. Name **three kinds of strain** that this transition state might have (think Chem 3D), and explain which type you think would be **largest**. [average score 11.9/18]

Note correct orientation of axial and equatorial C-H bonds and equatorial orientation of the OH₂⁺ “leaving group”.

In the transition state there should be some strain due to partial **eclipsing of the forming C-Br bond and the two next-adjacent C-C bonds** (the ones parallel to the plane of the paper). [Unlike the case in question 11b above, this strain cannot easily be relieved by rotation about the first C-C bond.]

There should also be **non-1,4-van der Waals repulsion** between Br and the axial hydrogen atoms shown by double-headed arrows in the diagram. This strain should be relieved by bending the Br-C-OH₂⁺ angle away from the preferred 180° to move Br in the direction shown by the single-headed arrow. Thus there should also be **angle bending strain**.

When several types of strain compete with one another, **the weakest form typically stores the most strain**, so it would not be surprising if the weak van der Waals repulsion stores more strain than the bond bending. [Note however that it should be much easier to bend a bond that is in the process of forming than to bend a bond that is already fully formed.]



- c) (3 min) Explain whether you think that the entropy of activation (ΔS^\ddagger) is favorable or unfavorable for forming a transition state like that in Question 11b. Should ΔS^\ddagger for your transition state in 12b be more or less favorable than that for 11b? [average score 2.8/6]

The separate reagents Br^- and ROH_2^+ must come together in a definite orientation (with Br^- "behind" the changing carbon) in order to form the transition state (not to mention that the free proton must also have become attached to the alcohol's OH group). This restriction on the freedom of movement of the 2 (or three) objects makes the entropy of activation unfavorable for forming the transition state of Question 11b.

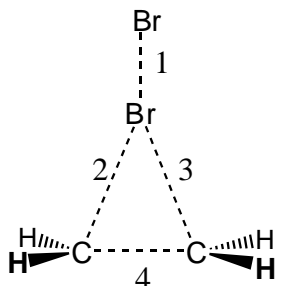
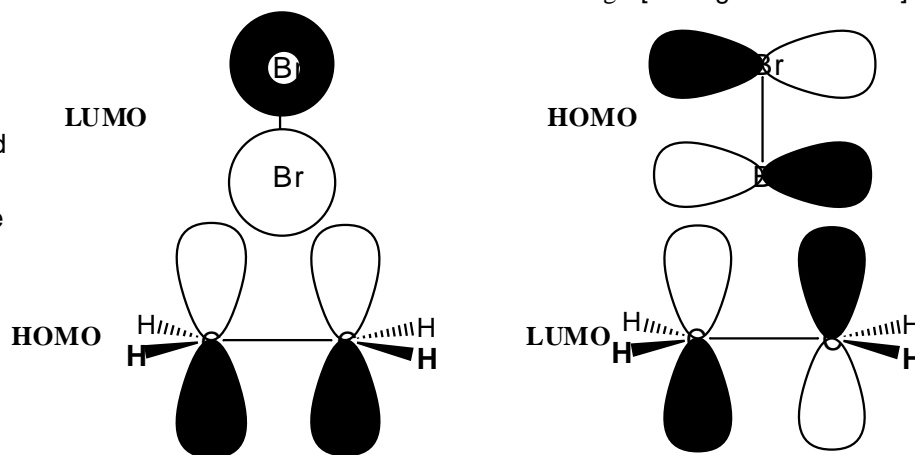
The transition state of question 12b, must be even more restricted, since the ring makes it unable to rotate about the first C-C bond. One would expect that entropy is even more effective in retarding reaction 12b than in retarding 11b.

[So we expected, and gave full credit for, the naïve answer above, but the problem is somewhat more complex, since we are actually interested in the CHANGE of entropy between starting material and transition state. In the acyclic protonated alcohol of question 11b, rotation is possible both in the starting material and in the transition state. In the cyclic analogue of question 12b, rotation is possible in neither. So to a first approximation the CHANGE in rotational freedom is the same in the two cases. Probably rotation would be somewhat easier in the transition state of 11b than in its starting material, so the naïve answer is probably correct, but I don't know the facts. (If you're interested, the reason for my guess is that usually rotors that go through six energy maxima in rotating full circle have smaller barriers than those that go through three energy maxima, but you definitely shouldn't worry about this in Chem 125.)]

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. [average score 4.8/10]

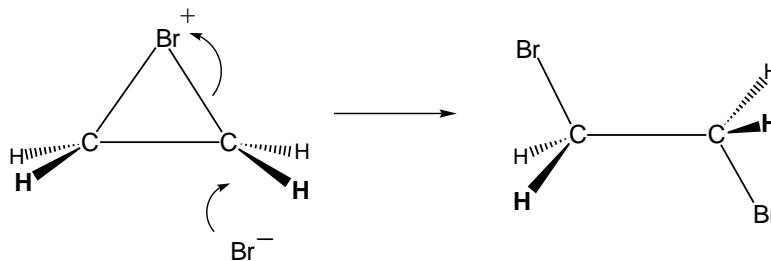
[Remember the unshared pairs from the p_x and p_y orbitals of Br. They occupy both a bonding π and an antibonding π^* combination. The latter is the HOMO for Br_2 . The LUMO is σ^* , where the hybridization is unspecified and not very relevant.]



W	1	S
S	2	S
S	3	S
W	4	W

- 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. [average score 2.1/4]

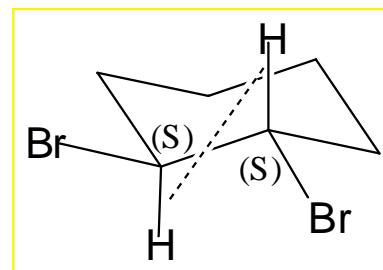
- c) (8 min) The initial product of the $C=C/Br_2$ reaction are a bromide ion and the 3-membered ring "bromonium" ion. These two then react with one another as shown at the right to complete addition of two Br atoms to **OPPOSITE** faces of the initial $C=C$ double bond, so in the case of cyclohexene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



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

The two Bromines are constitutionally, configurationally, and conformationally homotopic (both are on S carbons and both are equatorial).

[Rotation about the dashed axis of symmetry exactly exchanges the two Br atoms.]



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

Two. Being trans implies that the two configurations must be the same, but they can be either (R,R) or (S,S).

[Forming a meso product (R,S) would require attack from the **SAME** face of the double bond, which cannot occur by the mechanism shown above.]

What is the **relationship** between them? They are enantiomers.

[average score 8.6/16]

This brings us to **Question 14**, which was conceived (late at night) as an entertaining way to test your understanding of the principles behind the Boltzmann distribution of energy. The answer I expected to elicit is very counterintuitive, and wrong. I have spent an embarrassingly long time over the holidays trying to really understand the implications of this problem, and although I have learned a lot, I am still not completely comfortable that I know all the ins and outs of why the distribution of energy among molecules is a very different thing from random distribution of material objects among containers.

What is sure is that Boltzmann did the right thing when he assumed that putting two bits of energy randomly into two molecular containers would generate three equally probable distributions: both in one container, both in the other, and one in each. This is what we talked about in class.

Boltzmann developed his theory a quarter of a century before Planck discovered quantization, so he never thought that energy *really* came in bits. For him this was just a convenient mathematical model. For him it would have been meaningless to consider the question of which bit of energy went into which molecule.

If he had cared he might have worried that there should be a double weight for the case with one bit in each molecule, because either bit of energy could be in the first molecule. When one is dealing with raindrops, or dollar bills, or steel balls, one does need to apply this double weighting in the case of two bits of energy in two bins, and analogous "binomial" weighting factors for other distributions. This changes the exponential Boltzmann distribution to bell-shaped "normal" or "Poisson" distributions, which are found for more familiar objects. The key, non trivial, question is what makes objects distinguishable.

The answers given below show what I was looking for. **Even though they are wrong**, they earned full credit if they showed a proper understanding of the basis of the Boltzmann distribution. Substantial credit was also given for truly correct answers, if they were supported by some kind of logical reasoning, and partial credit was given for just honestly expressing the gut feeling that the Poisson distribution is the right answer.

I am sorry for the confusion, but as a practical matter it didn't make the difference in anyone's final grade, and it provides an interesting learning experience for us all. Teachers don't know everything (by a long shot).

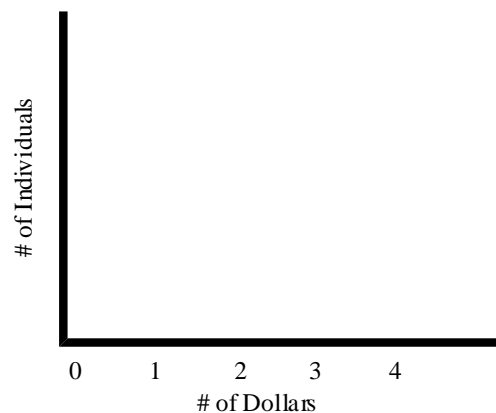
- 14.** Suppose a balloon flew over the Cross Campus during the 300th Anniversary celebration and dumped a bushel of dollar bills, so that they fell **at random** on the crowd, and only on the crowd. Each person collects the bills that fall on his/her space. (Neglect the effect of trees, walls, breezes, uneven spacing – anything that would create a bias in favor of certain members of the crowd.)

- 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. [average 3.7/4]

The expected curve is an exponential decrease, starting from some finite number (NOT asymptotic approach to infinity at \$0) and decreasing so that having \$4 is much less likely than having \$1. (see note below)

- b) (3 min) Give in words a simple rationale for the distribution you plotted. [average score 4.5/6]

The more dollars any one individual gets, the fewer there are to distribute among the others. The fewer there are for the others, the fewer number of ways there are in which the money can be permuted among them. If all possible distributions are equally likely, having fewer that involve a particular number of dollars for a particular individual means that the individual's having that number is less likely. Thus the most likely number to have, if the total number is fixed, is zero, and the probability falls for increasing numbers to any one individual. (see note below)



- 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? [average score 4.8/6]

Each atom of argon has three "degrees of freedom" in which to store energy – motion along each of the three Cartesian axes. So, as Maxwell showed, the most likely total kinetic energy is a finite value, not zero, and the distribution of total energies is more like a bell curve. Although zero is most likely for kinetic energy involving motion along any one component of velocity, the chance that all three components would simultaneously be zero is small.

The temperature of the flask measured the average energy per molecule, or, what is equivalent for a fixed number of molecules, the total energy. It is thus analogous to the total number of dollars that were dropped. (see note below)

- 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. [average score 3.8/6]

The curve stays exponential, with a maximum at zero, but the fall-off becomes much less steep. Thus the chance of having \$1, or \$2, or \$3, or \$4 is only very slightly less than of having \$0, where for a smaller total it was much less.

Bear in mind that the answers given above are NOT correct for \$\$\$ or raindrops, they are just to show what was given full credit because it showed understanding of the Boltzmann distribution of energy.