

Chemistry 125 Fifth Examination
February 8, 2007

Name _____

Average score 66.9/100 1/3 > 75 2/3 > 58

1. (5 minutes) Use as specific an **example** as you can to argue that induced dipole moments can be more important than permanent dipole moments in causing non-bonded attraction between organic halides.

The best example involves the boiling points given in frame 7 of the lecture of 2/2/07. Molecules can attract one another both by interaction of their permanent dipole moments and by interactions involving their induced-dipoles. For the same R groups, R-I is more than 50°C higher boiling than R-F, *i.e.* the R-I molecules hold together much more strongly as a liquid. (Melting shows a similar trend, but is less reliable, because it is less well understood – see the odd-even dibromide phenomenon.)

This is at first surprising, because the fluorides have higher dipole moments than the corresponding iodides (1.8 vs. 1.6 D for CH₃-X), because of the high electronegativity of F. However the iodides have higher polarizabilities (8 vs. 3×10^{-24} cm³ for CH₃-X), because they have more electrons in higher orbitals. Obviously the polarizability wins.

[A number of answers gave some relevant information, but failed to give an example relevant to the **relative** strength of the two phenomena.]

2. (6 min) How did Boltzmann explain that it should be more likely for a “degree of freedom” of a particular individual molecule to have the lowest possible energy than to have the average energy, even when the temperature is very high?

Boltzmann assumed that all ways (complexions) of distributing a certain amount of energy are equally likely, the the more complexions there are that involve a certain amount of energy in a certain degree of freedom (DOF), the more likely it is to have that amount of energy in the DOF. The less energy there is in that DOF, the more there is to slosh around in the other DOFs, and the more complexions. Thus zero is the most likely single value, no matter how much energy is available.

[As temperature increases average energy increases, because the chances increase for having higher amounts of energy in the DOF, but zero remains the single most likely value.]

3. (5 min) What are the **assumptions** of Eyring’s transition state theory, **and** why is it often a more practical theory for understanding rates than a theory involving trajectories on the potential energy surface?

The assumptions of transition state theory are: 1) the transition state is in equilibrium with the starting material (this gives the amount of material heading for product); and 2) that the rate at which the transition state becomes product is a constant ($kT/h \approx 10^{13}/\text{sec}$). [See frame 18 of 1/19/07]

To use trajectories to predict a rate, one must calculate a very large number of them (and sift through much more detail than is necessary to determine a rate). With transition state theory one need only guess the enthalpy and entropy of the transition state (assuming that the values are known for the starting material). Transition state theory treats the molecules collectively.

[I’m sorry that some people were confused by the fact that Henry Eyring did a lot of important work on reaction rates. He developed the PES for H₃, which led some to think that his transition state theory must involve trajectories on this surface. Perhaps I should have left his name out of the question, but it is mentioned in the title of the slide referenced above.]

4. (9 min) Draw four lines to connect each radical in the second column with the corresponding dissociation energy (kcal/mole) in the first column for its bond to the CH₃ group.

It is important to remember from frames 9, 11, and 12 of 1/22/07 that vinyl bonds are unusually strong and allyl bonds are unusually weak. [As we said, this is not a question of brute force memorization but of understanding the reasons given below.]

Then explain the size of the other three values relative to that for the CH₃-CH₃ bond.

The CH₃-C(CH₃)₃ bond is "intrinsically" about the same strength as the CH₃-CH₃ bond, but it is slightly weakened by steric hindrance.

The CH₃-CH=CH₂ bond is unusually strong because it involves an sp² hybrid orbital on the vinyl group, which overlaps better than would an sp³ hybrid. The starting material is unusually stable.

The CH₃-CH₂-CH=CH₂ bond is unusually weak because the allyl radical formed by its cleavage is resonance stabilized. That is, the new SOMO is able to overlap the π and π* orbitals of the C=C double bond, which results in lowering the energy of its π electrons. The starting material is normal, but the product is unusually stable.

BDE CH ₃ -R	R
76.5	CH ₃
87.5	C(CH ₃) ₃
90.1	CH=CH ₂
101.4	CH ₂ -CH=CH ₂

5. (5 min) Propose an example and a plausible mechanistic interpretation of ONE ONLY of these three reaction orders:

0 or 1/6 or pseudo 1st order

(4 points for the example, 6 for the interpretation)

0 Order: catalyst saturated by substrate [first order in catalyst, but its presence might not be recognized]

1/6 Order: Dominant species in solution a hexamer in equilibrium with a small amount of reactive monomer, e.g. (RLi)₆ in equilibrium with RLi in a hydrocarbon solvent.

Pseudo 1st Order: One reactant is in such large excess that its concentration is not significantly reduced by reaction. For example solvolysis of EtBr in EtOH, where the rate as a function of [EtO⁻] has a non-zero intercept. [Frame 8, 2/7/07]

6. The secondary C-H bonds of propane are 2.5 kcal/mole weaker (i.e. lower in BDE) than its primary C-H bonds.

A) (4 min) Use this value to estimate the ratio of secondary to primary propyl radicals in equilibrium at room temperature. Explain your thinking.

$$[5 \text{ points}] k_2/k_1 = 10^{-3/4 \times (2.5)} \approx 10^2$$

[3 points] Correction for statistics. Accepted either 2:6 (hydrogens) or 1:2 (CH_n groups)

$$i.e. \text{ either } k_2/k_1 \times 1/3 \approx 30 \text{ or } k_2/k_1 \times 1/2 \approx 50$$

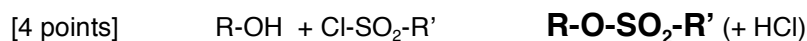
- B) (8 min) Explain why it is curious that free radical bromination of propane at about **twice room temperature** gives a secondary-to-primary product ratio of about 10:1. **Also** say what lesson is to be learned from this fact.

[8 points] At twice room temperature $k_2/k_1 = 10^{-3/8 * (2.5)} \approx 10$ and the statistically corrected product ratio should be about 3 or 5, not the observed 10.

[Increasing temperature decreases selectivity, *i.e.* k_2/k_1 approaches 1]

[8 points] Lesson: the transition state is NOT intermediate (in stabilization by substitution) between reactants and products; $\Delta\Delta G^\ddagger > \Delta\Delta G$ for the overall reaction. This means that free-radical bromination of propane is unusually selective despite high temperature [perhaps because of ionic resonance stabilization in the transition state but not in either starting material or products].

7. (4 min) The first step in the Kenyon & Philips experiment that proved the stereochemistry of S_N2 substitution involved preparing a starting material by reacting a chiral alcohol, ROH with $Cl-SO_2-R'$. **Draw the product** of this first reaction and **explain why** it was prepared.

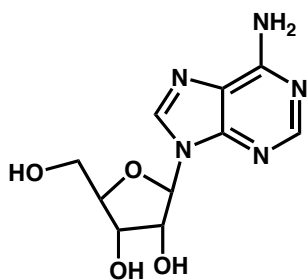


[2 points] Transforms OH (bad leaving group) into "tosylate" (a good leaving group)

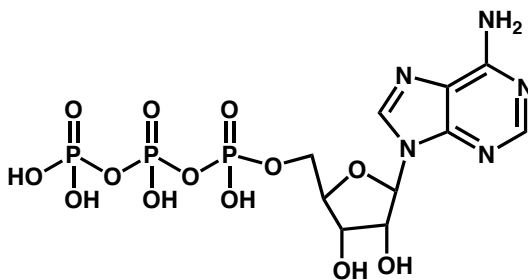
[2 points] Tosylate is a weak base (low HOMO) analogous to $^-OSO_2OH$ of sulfuric acid.

8. A) (2 min) In light of Question 7, suggest why, in making S-Adenosylmethionine, Nature chooses to use ATP rather than Adenosine itself.

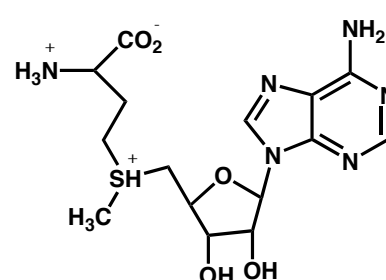
HO- is a bad leaving group [2 points], here it is replaced by a better leaving group, the "triphosphate" anion, analogous to the anion of phosphoric acid [2 points].



Adenosine



ATP



S-Adenosylmethionine

- B) (2 min) Explain why S-Adenosylmethionine is chemically suited for the purpose to which Nature puts it.

Nature uses it as a methylating agent in nucleophilic substitution. It is good because the low C-S σ^* LUMO makes SR_2 a good leaving group (analogous to OH_2 from a protonated alcohol $R-OH_2^+$).