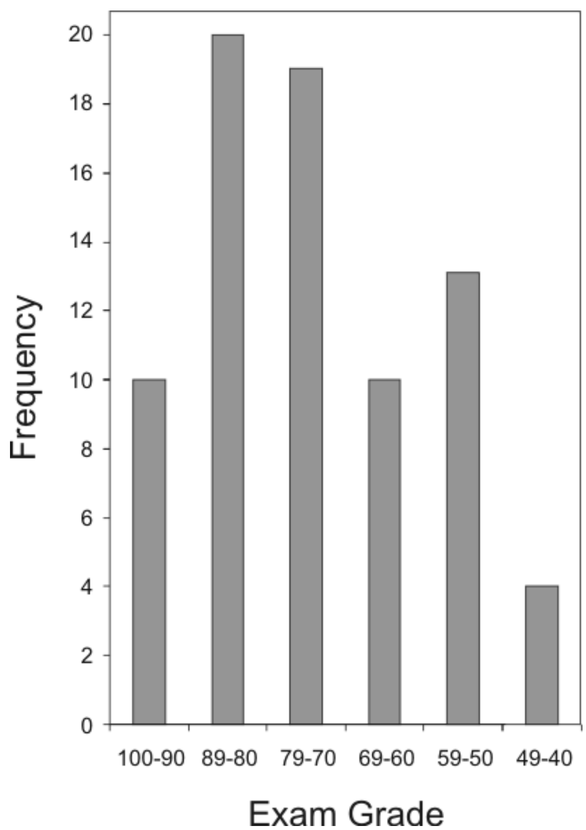
Chemistry 5011/8011 Friday, December 10, 2004

Exam 3
Answer Key

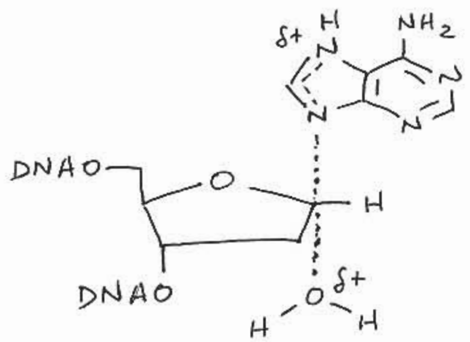
Exam 1 Mean: 75
Exam 1 Median: 74
Exam 1 St. Dev.: 13



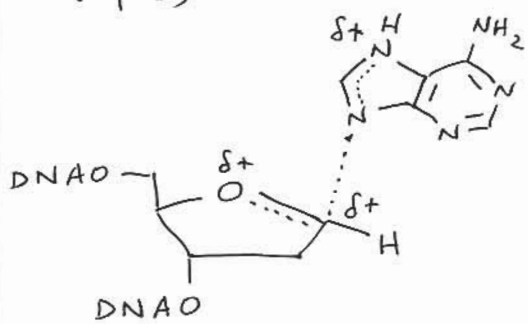
MIDTERM EXAM 3
ANSWER KEY

1. a)

SN2 (5 pts)



SN1 (5 pts)



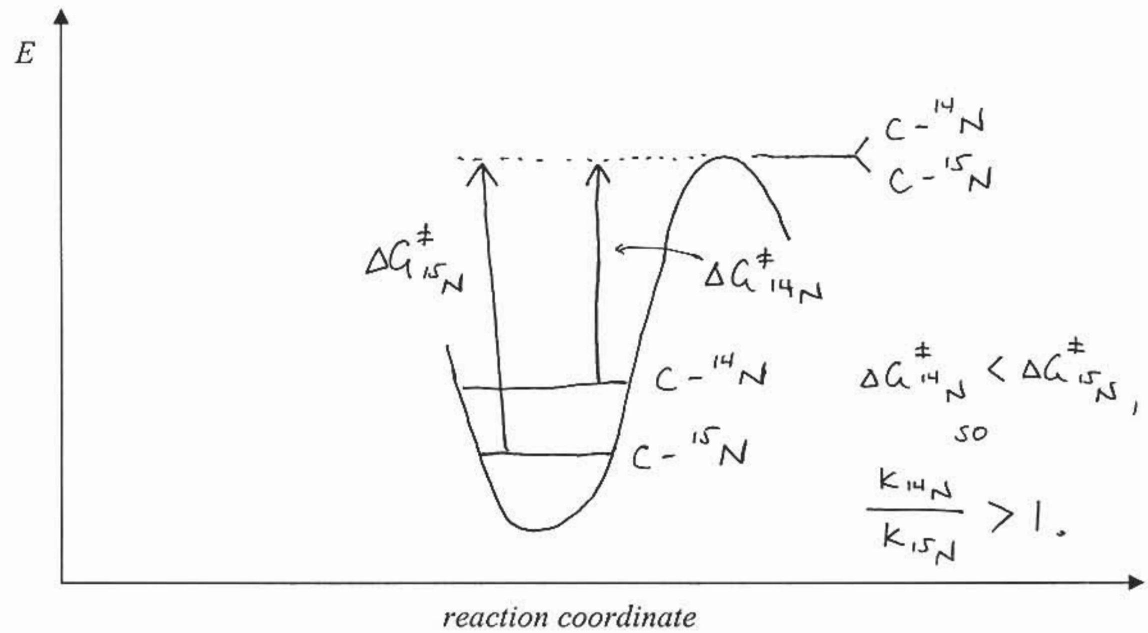
CRITICAL FEATURES:

- CONNECTIVITY (2 PTS)
- NUCLEOPHILE, LEAVING GROUP ANTIPERIPLANAR (2 PTS)
- PARTIAL CHARGE (1 PT)

CRITICAL FEATURES:

- CONNECTIVITY (3 PTS) (PARTIAL BOND TO OXYGEN NOT GRADED)
- DEFORMATION AT C_1 (1 PT)
- PARTIAL CHARGE (1 PT) (AGAIN, OXYGEN NOT GRADED)

b) THE C-$^{14/15}$N BOND IS BROKEN IN THE TRANSITION STATE, SO THIS PROBLEM INVOLVES A <u>PRIMARY</u> ISOTOPE EFFECT. IN THE GROUND (BOUND) STATE, THE HEAVIER REDUCED MASS HAS A LOWER ~~[illegible]~~ ZERO-POINT ENERGY, BUT IN THE EXCITED STATE, EYRING THEORY SAYS $\nu = 0$, C-^{14}N & C-^{15}N ENERGIES ARE EQUAL.



3 PTS FOR VIBRATION IN RXN COORDINATE (PRIMARY KIE);
2 PTS FOR ZPE $(C-{}^{14}N) >$ ZPE $(C-{}^{15}N)$
2 PTS FOR ILLUSTRATING $\Delta G^{\ddagger}_{{}^{15}N} > \Delta G^{\ddagger}_{{}^{14}N}$
3 PTS FOR ZPE $(C-{}^{14}N)^{\ddagger} =$ ZPE $(C-{}^{15}N)^{\ddagger}$ (EYRING)

10 PTS TOTAL.

c)

$$\frac{k_{{}^{14}N}}{k_{{}^{15}N}} = \frac{e^{-\Delta G^{\ddagger}_{{}^{14}N}/RT}}{e^{-\Delta G^{\ddagger}_{{}^{15}N}/RT}} = e^{\frac{\Delta G^{\ddagger}_{{}^{15}N} - \Delta G^{\ddagger}_{{}^{14}N}}{RT}}$$

$$= e^{\frac{\Delta ZPE\,(C-{}^{14/15}N)}{RT}}$$

$$ZPE\,(C-{}^{14}N) = \frac{1}{2}h(c)\nu \quad ; \quad \nu(C-{}^{14}N) = 1080\ cm^{-1}$$

$$'' \quad = 6.46\ kJ/mol$$

$$\nu(C\text{-}^{15}N) = \left[\nu(C\text{-}^{14}N)\right]\frac{\nu(C\text{-}^{15}N)}{\nu(C\text{-}^{14}N)} = \left[\nu(C\text{-}^{14}N)\right]\sqrt{\frac{\mu_{C\text{-}^{14}N}}{\mu_{C\text{-}^{15}N}}}$$

$$\sqrt{\frac{\mu_{C\text{-}^{14}N}}{\mu_{C\text{-}^{15}N}}} = \sqrt{\frac{\frac{(12)(14)}{12+14}}{\frac{(12)(15)}{12+15}}} = \sqrt{0.969} = 0.984$$

$$\nu(C\text{-}^{15}N) = (0.984)\,\nu(C\text{-}^{14}N)$$

$$= ~~[illegible]~~ \; 1062\ cm^{-1}$$

$$ZPE(C\text{-}^{15}N) = ~~[illegible]~~ \; 6.36\ kJ/mol$$

$$\Delta ZPE = 0.10\ kJ/mol$$

$$\left(\frac{k_{^{14}N}}{k_{^{15}N}}\right)_{max} = e^{\frac{0.10\ \frac{kJ}{mol}}{RT}} = \boxed{1.041}.$$

{10 PTS FOR "1.04", ~~or~~ "1.040", "1.041" OR "1.042". **OR**

- 5 PTS FOR CORRECT ANSWER BETWEEN 1.030 AND 1.050.
- 2 PTS FOR CALCULATING ν_{ZPE} FROM $\sqrt{\text{REDUCED MASS}}$
- 1 PT FOR CALCULATING REDUCED MASSES CORRECTLY
- 1 PT FOR CALCULATING ZPE'S FROM ν_{ZPE}
- 1 PT FOR CALCULATING $\frac{k_{^{14}N}}{k_{^{15}N}}$ FROM $e^{\Delta ZPE/RT}$.}

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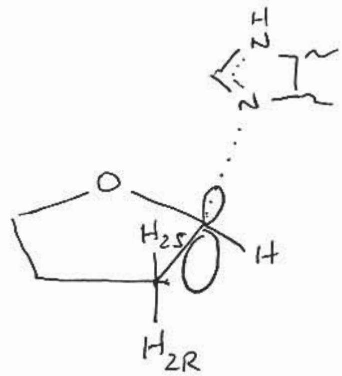
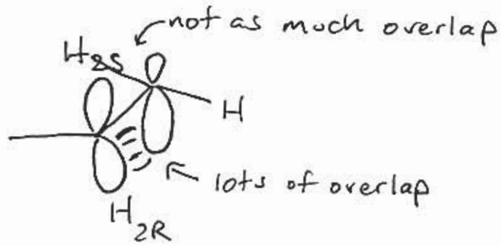
d) i. S_N1. THE REST OF THE PROBLEM EXPLAINS WHY.

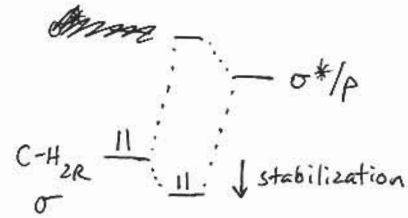
5 POINTS.

d) ii. IF YOU CHOSE S_N1 (THE CORRECT ANSWER) in (i),



AT TRANSITION STATE, EMPTY CATIONIC p-ORBITAL HASN'T FULLY FORMED FROM σ^* ANTIBONDING ORBITAL, AND THERE'S STILL MORE EMPTY ORBITAL DENSITY BELOW THE C_1 THAN ABOVE IT. SO, THERE IS GREATER HYPERCONJUGATION BETWEEN H_{2R} AND σ^*/p THAN H_{2S} AND σ^*/p.





AS A RESULT, $C-H_{2R}$ IS WEAKER IN TRANSITION STATE THAN $C-H_{2S}$, AND SHOULD HAVE LOWER VIBRATIONAL FREQUENCY.

5 POINTS FOR HYPERCONJUGATION / OVERLAP OF $C-H_{2R}$ WITH σ^*/p OF LEAVING GROUP

5 POINTS FOR STRESSING BETTER SPATIAL OVERLAP FOR $C-H_{2R}$ THAN $C-H_{2S}$

5 POINTS FOR CONNECTING THIS TO DRAWING OF TS.

15 POINTS TOTAL.

IF YOU CHOSE S_N2 IN (i), YOU HAVE A MUCH HARDER ARGUMENT TO MAKE; YOU NEED TO EXPLAIN WHY, GEOMETRICALLY, $C-H_{2R}$ INTERACTS W/ TRANSITION STATE MORE THAN $C-H_{2S}$. SINCE S_N2 TRANSITION STATE IS SYMMETRIC (ANTIPERIPLANAR), DON'T KNOW HOW YOU MIGHT DO THIS, BUT FOR ANY ANSWER,

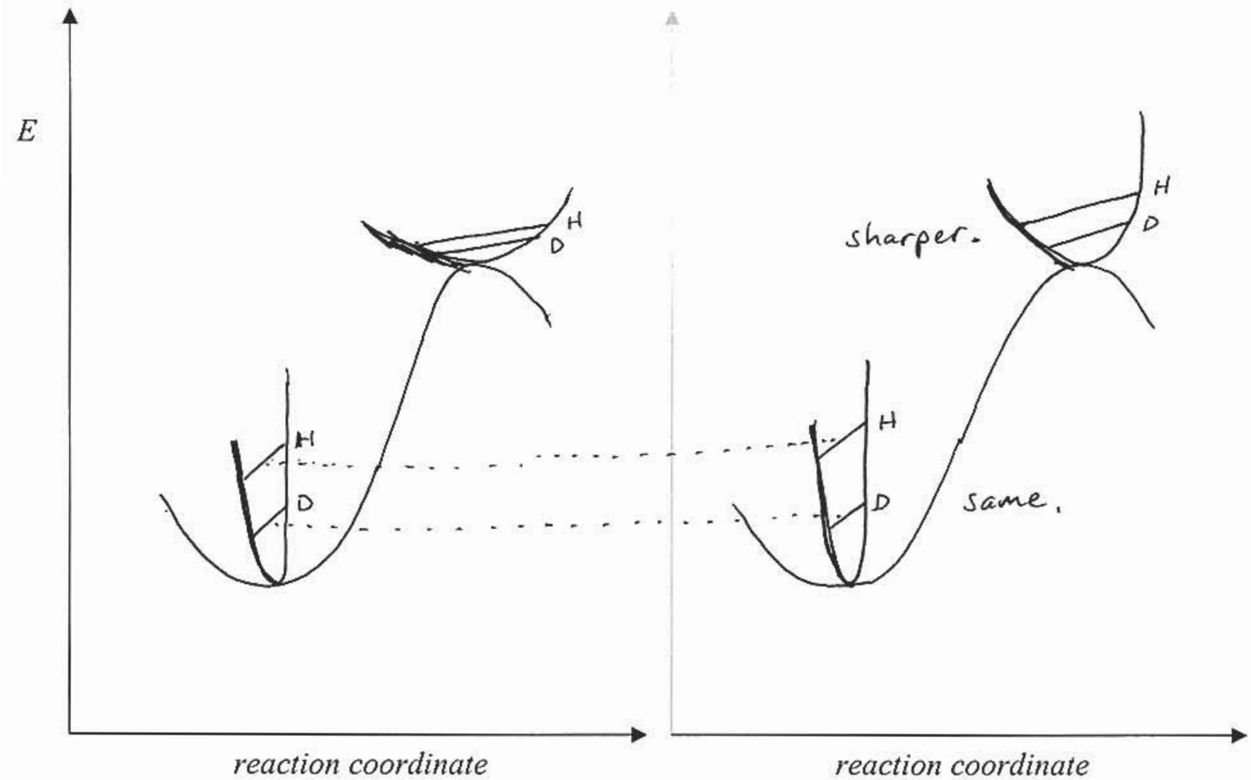
5 POINTS FOR STRESSING SPATIAL DIFFERENCE BETWEEN $C-H_{2R}$ & $C-H_{2S}$ RELATED TO C_1 — BUT C_1 MUST BE ANTIPERIPLANAR

5 POINTS FOR RELATING ABOVE TO ORBITAL INTERACTION / FREQUENCY-RELATED DIFFERENCE

5 POINTS FOR POINTING DIFFERENCE OUT ON DRAWING — BUT DRAWING MUST BE CORRECT.

d) iii. HYPERCONJUGATIVE EFFECT WEAKENS $C-H_{2R}$ MORE THAN $C-H_{2S}$ IN TRANSITION STATE, BUT NO INTERACTION IN GROUND STATE. SO GROUND STATE C-H VIBRATIONAL WELLS SHOULD BE THE SAME FOR H_{2R} & H_{2S}, BUT TRANSITION-STATE $C-H_{2R}$ WELL WILL BE BROADER.

kH_{2R}/kD_{2R} $\qquad$ kH_{2S}/kD_{2S}



3 POINTS FOR GRAPHS HAVING SAME BACKBONE TRACE.

3 POINTS FOR SECONDARY KIE (WELLS DRAWN OUT OF PLANE)

3 POINTS FOR GRAPHS HAVING SAME GROUND-STATE ENERGY DIAGRAM, OR FOR FOLLOWING EXPLICIT EXPLANATION FROM PART (ii) ABOUT WHY DIFFERENT.

3 POINTS FOR TRANSITION-STATE WELLS BROADER THAN GROUND-STATE WELLS.

4 POINTS FOR 2R TRANSITION STATE WELL BROADER THAN 2S TRANSITION STATE.

2 POINTS FOR ENERGY LEVELS (BOTH) LOWER IN 2R WELL THAN 2S;

2 POINTS FOR $\Delta ZPE_{2R} < \Delta ZPE_{2S}$ (2R LEVELS CLOSER THAN 2S LEVELS) IN TRANSITION STATE.

2. a) Tunneling effects are possible for any reaction step in which a very small motion of a hydrogen atom occurs and nothing else. Under these circumstances, H can tunnel through the barrier to motion along the reaction coordinate instead of passing over it. In this reaction,

Step A doesn't involve hydrogen. No tunneling effect possible.

Step B involves H motion, but the H_2 comes from a long way away. Tunneling is unlikely.

Step C splits the H-H bond. In the product, the H's don't look much farther away from each other than they were in the starting material. Tunneling in this step is likely.

Step D moves an H atom to carbon, with no other bonds changing. There are some other very small motions in the molecule, but I would say tunneling is possible here.

Step E involves solvent, not H motion. No tunneling possible.

Step F involves H motion, but there is a lot of other motion here too. Tunneling seems possible, but not likely, here.

Step G involves solvent motion. No tunneling possible.

Rubric for 2(a):

5 points for **C**.
5 points for **D**.
3 points for **F**.

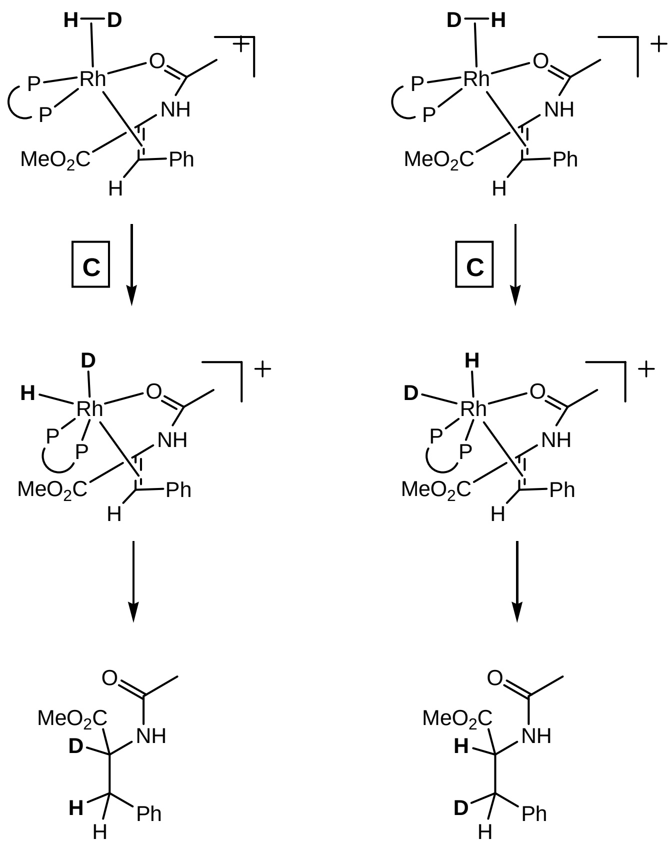
b) Deuterium tunnels more slowly than hydrogen. As a result, $\boldsymbol{k_{H2}/k_{D2}}$ should *always* be greater than one.

Rubric for 2(b):

4 points for each box.

c) Using HD instead of D_2 as a reactant introduces an interesting new variable for each step of the reaction: If there is a choice between H or D moving to make product, which one moves, and what products are formed?

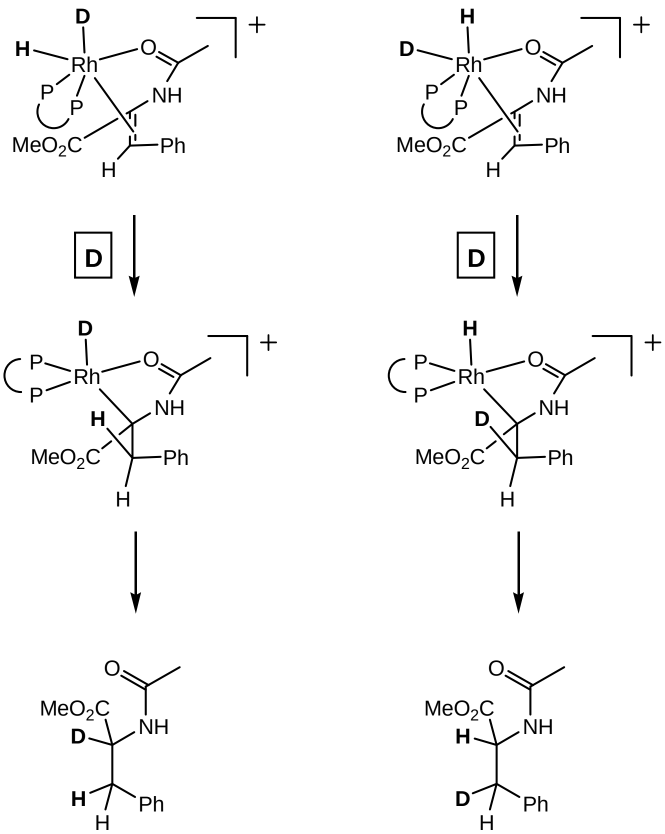
Step C:



2a **2b**

In the case of step **C**, both atoms move, and it is likely that the pathways are not distiniguished by the isotope orientation at the beginning. So, **2a/2b = 1**.

Step D:



2a **2b**

In the case of step **D**, only one H/D moves. If the H moves, **2a** is produced; if the D moves, **2b** is produced. H tunnels faster than D, so **2a/2b > 1**.

Rubric for 2(c):

6 points for each box.