

Midterm Exam 2

Please do not open or sign this packet until you are instructed to do so.

Please write all of your answers for this exam in this exam packet. Although you may use as many blue books for scratch work as you would like, the blue books will not be collected at the end of the exam or graded. Answer each question in the space provided if you can, but feel free to continue your answer on the back of the page if you need more room. (Please write a note by your answer pointing us to the continuation if you do this.) You will be given 2 hours total to finish the exam.

This exam contains two problems, which are split into parts. *Do not get stuck* on one part and then assume that you will be unable to answer the rest of the question—move on. In addition, partial credit will be given for incorrect but plausible or consistent answers, so *guess* on problems you cannot answer perfectly.

At the end of the 2-hour exam period you will be asked to return your exam to the proctor. (You may, of course, also turn the packet in earlier if you choose.) This exam is *open-resource*—you may use any books, notes, calculator, etc. you have brought with you to the exam. However, you are not allowed to communicate with anyone during the exam, or to bring any materials in or out of the room while you are taking the exam. You are also not allowed to use any devices that could be used to communicate with anyone (laptop computers, cellphones, etc.). Please do not take any part of the exam packet with you when you are done; everything will be returned to you after the exams are graded.

This packet should contain 12 pages, including this one. Please check to make sure that your packet contains 12 pages before beginning your exam.

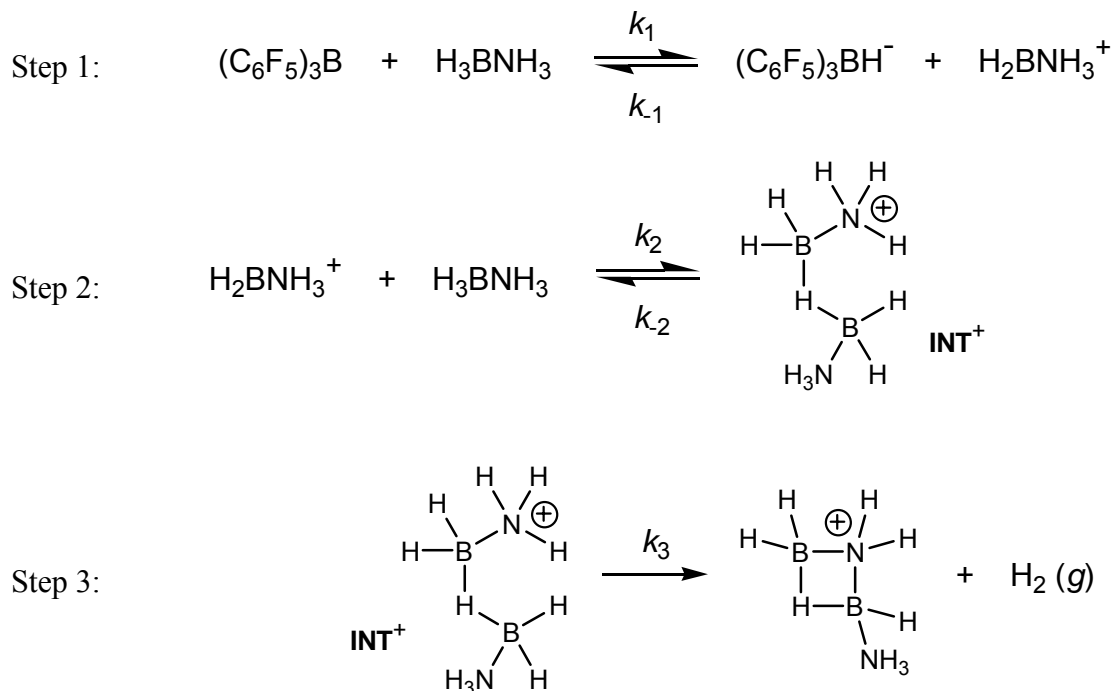
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Helpful constants to know for this exam:

Boltzmann's constant:	$k_B = 2.94 \times 10^{-24} \text{ cal K}^{-1}$	$= 1.38 \times 10^{-23} \text{ J K}^{-1}$
Gas constant:	$R = 1.99 \text{ cal K}^{-1} \text{ mol}^{-1}$	$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Planck's constant:	$h = 1.58 \times 10^{-34} \text{ cal sec}$	$= 6.626 \times 10^{-34} \text{ J sec}$
	$e = 2.718$	

1. (55 pts total) The success of any “hydrogen economy”—in which H₂ replaces petroleum as our primary fuel—will depend on hydrogen storage materials that safely hold a high weight fraction of H₂ and that release the H₂ to engines or fuel cells on demand. One potential H₂ storage material is ammonia borane, H₃NBH₃, which can release all of its hydrogen atoms as H₂ molecules. Tom Autrey (Pacific Northwest National Laboratory), David Dixon (University of Alabama), and coworkers found that release of the first H₂ molecule is catalyzed by hydride acceptors like electron deficient boranes, and proposed the following mechanism for catalyzed H₂ release from a concentrated solution of H₃NBH₃:^{1,2}



Things about this mechanism to keep in mind:

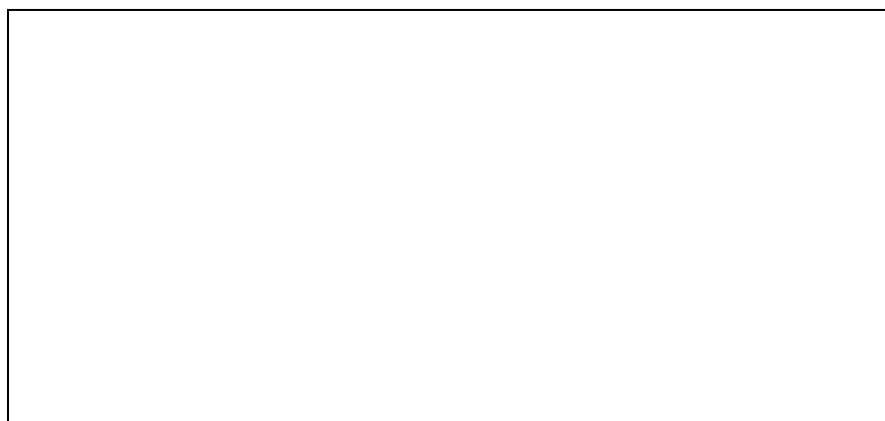
- Step 2 is extremely fast in both forward and reverse directions.
 - A computational study showed the transition state for Step 3 to be the highest-energy (rate-determining) transition state.
- a. (15 pts) The kinetic expression for the rate of production of H₂ gas ($\partial[H_2]/\partial t$) depends on the assumptions you make about the reaction. On the next page, **derive an instantaneous rate expression for $\partial[H_2]/\partial t$** in which you assume that Step 1 is also extremely fast in both directions. Put your expression in terms of the measurable quantities [H₃NBH₃], [(C₆F₅)₃B], and [(C₆F₅)₃BH⁻].

¹ Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem. Int. Ed.* **2006**, in press.

² Gutowska, A.; Li, L.; Shin, Y.; Wang, C. M.; Li, X. S.; Linehan, J. C.; Smith, R. S.; Kay, B. D.; Schmid, B.; Shaw, W.; Gutowski, M.; Autrey, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 3578-3582.

Derivation:

$$\frac{\partial[\text{H}_2]}{\partial t} =$$



- b. (15 pts) Instead, you could also make the steady-state assumption that the two cationic intermediates (together) are consumed as fast as they are generated; in other words, that

$$\frac{\partial([\text{H}_2\text{BNH}_3^+] + [\text{INT}^+])}{\partial t} = \frac{\partial[\text{H}_2\text{BNH}_3^+]}{\partial t} + \frac{\partial[\text{INT}^+]}{\partial t} = 0$$

Derive a different rate expression for $\partial[\text{H}_2]/\partial t$ in which you make this assumption. Again, write your expression in terms of $[\text{H}_3\text{BNH}_3]$, $[(\text{C}_6\text{F}_5)_3\text{B}]$, and $[(\text{C}_6\text{F}_5)_3\text{BH}^-]$ only.

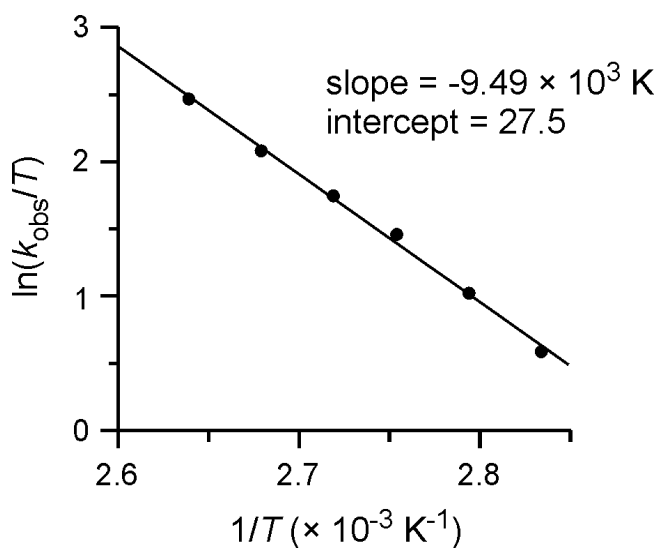
Derivation:

(write your final rate expression on the next page)

$$\frac{\partial[\text{H}_2]}{\partial t} =$$



- c. (10 pts) Autrey and coworkers performed initial rate experiments at different temperatures, under pseudo-order conditions, to evaluate the relationship between k_{obs} and T for the overall reaction. That data is plotted as an Eyring plot below:



Calculate ΔH^\ddagger and ΔS^\ddagger for the overall reaction from this plot. Include units in your answer.

$$\Delta H^\ddagger =$$

$$\Delta S^\ddagger =$$

- d. (5 pts) Draw the rate-determining transition state for the overall reaction.

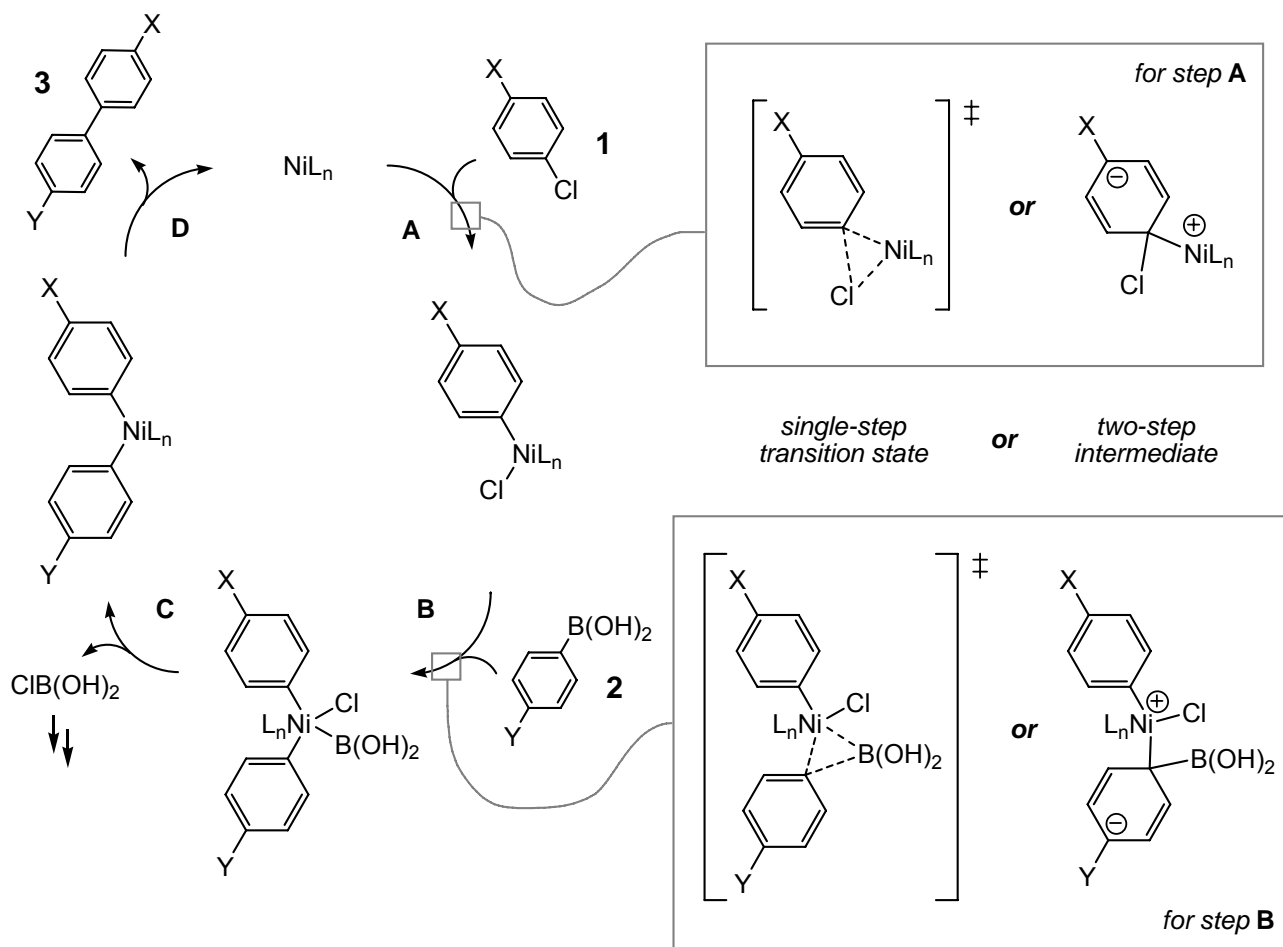


- e. (10 pts) There are a number of competing factors that influence the sign and magnitude of ΔS^\ddagger for this reaction. Using the transition-state structure you drew above, **describe one feature of the reaction which increases** (contributes to a more positive or less negative) ΔS^\ddagger . Then, **describe another, competing feature that decreases** (contributes to a less positive or more negative) ΔS^\ddagger .

*What about the reaction contributes to a **higher** ΔS^\ddagger ?*

*What about the reaction contributes to a **lower** ΔS^\ddagger ?*

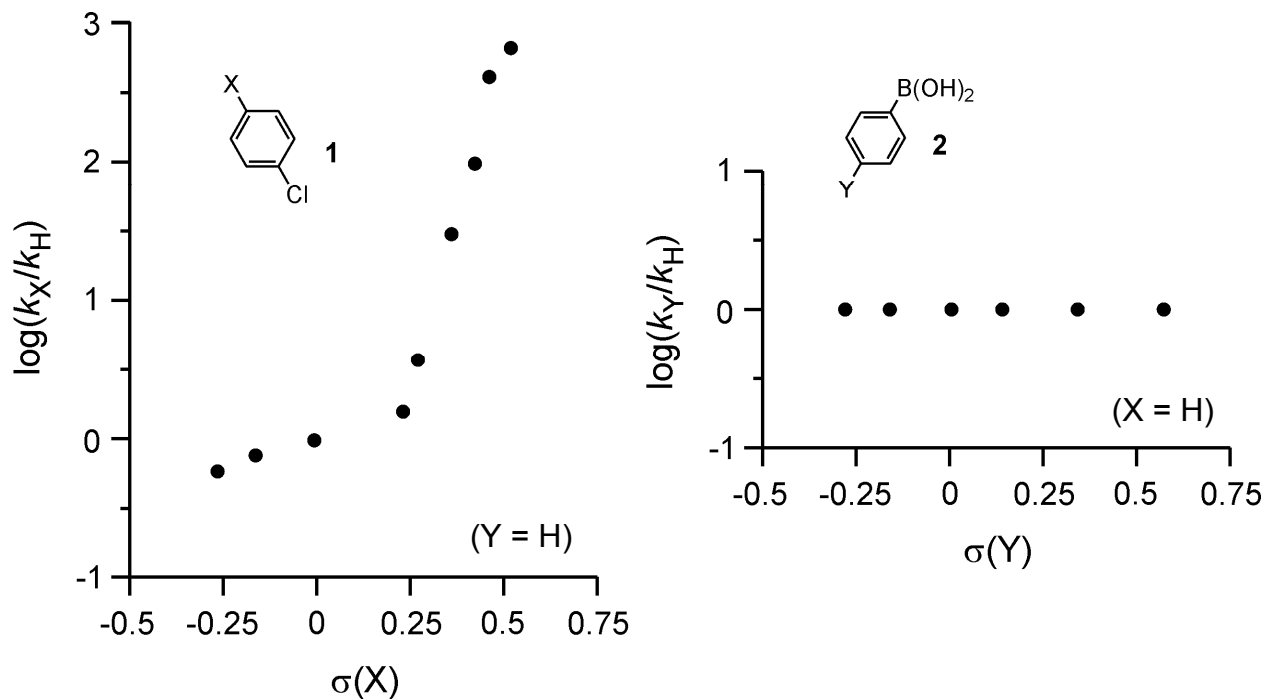
2. (45 pts total) Suzuki coupling of an aryl halide (**1**) and an aryl boronate (**2**) is catalyzed by complexes of zero-valent nickel, which undergo successive insertion reactions with the two reactants before joining them into the biaryl product **3**. The catalytic cycle for the nickel complex is shown below:



(The “ L_n ” on each nickel refers to ligands that are free to associate and dissociate but do not take part in the reaction. Ignore them.) As shown in the boxes on the right, each addition of nickel to either substrate **1** or **2** could be concerted, with a single transition state; or it could be stepwise, going through a zwitterionic intermediate. Cassar³ and Miyaura⁴ measured the rates of this reaction ($\partial[\mathbf{3}]/\partial t$) for different substituents X and Y to try to distinguish the mechanism or mechanisms active in steps **A** and **B**. Their results are plotted on the next page.

³ Foá, M.; Cassar, L. *J. Chem. Soc. Dalton Trans.* **1975**, 2572-2576.

⁴ Saito, S.; Oh-tani, S.; Miyaura, N. *J. Org. Chem.* **1997**, 62, 8024-8030.



The plots for the two substrates were distinctive in two ways:

- The graphs didn't show the same trend, even though the overall process of insertion was the same for steps A and B; and
- The graph for substituents X had a distinct kink at $\sigma(X) = 0.25$.

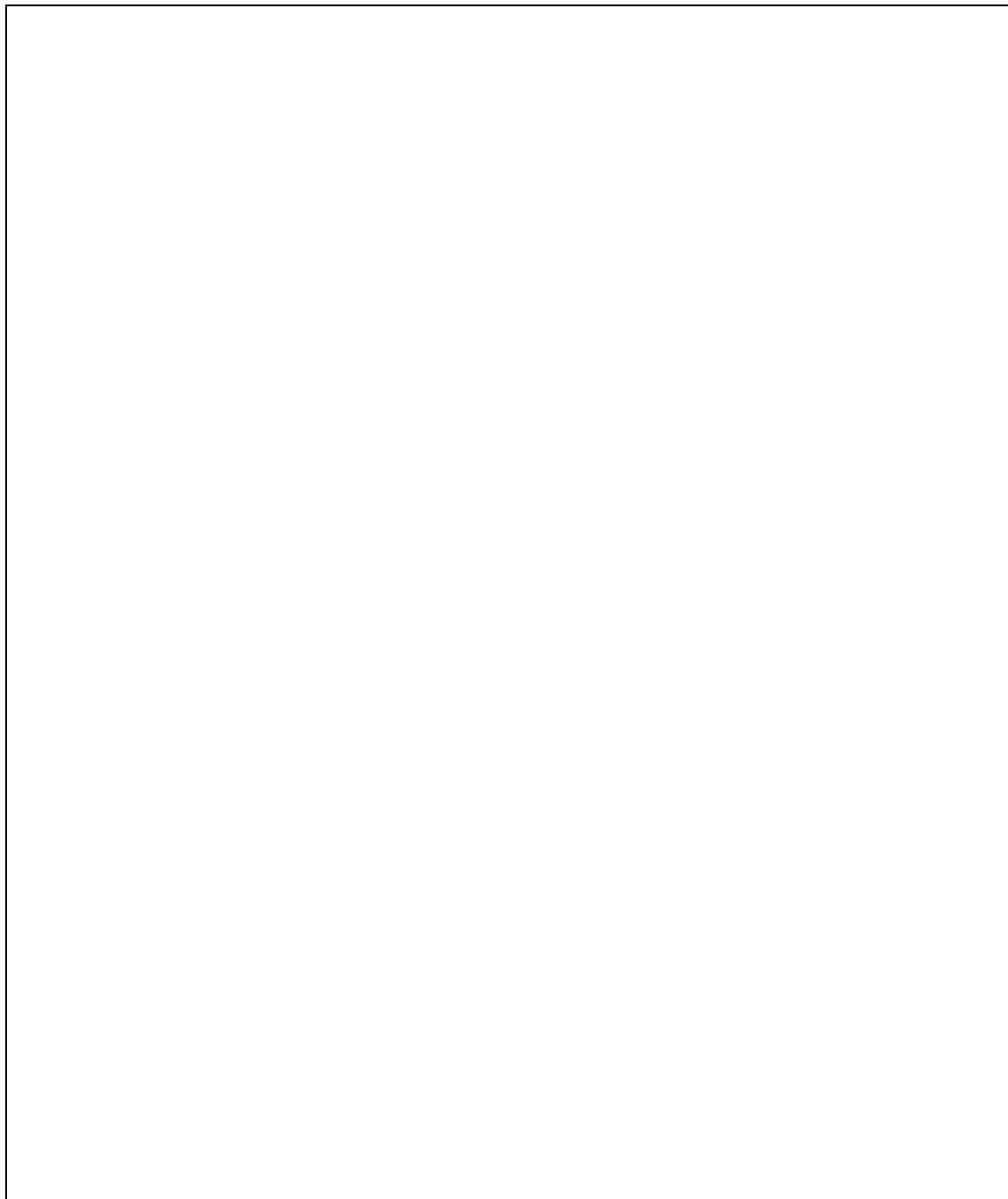
a. (10 pts) Calculate Hammett ρ values for the two regions of the $\sigma(X)$ graph and for the $\sigma(Y)$ graph.

$\rho_X(\sigma < 0.25) =$ $\rho_X(\sigma > 0.25) =$ $\rho_Y =$

b. (12 pts) **What information does the $\sigma(X)$ graph give** about the mechanism of the reaction? Does nickel insertion into the aryl chloride **1** (step **A**) occur

- via a single concerted step?
- via two steps through a zwitterionic intermediate?
- via some combination of these two?
- or does the data not help you answer this question?

Make sure to explain your answer in terms of the ρ_X values you calculated. Also make sure your answer explains the kink in the graph.



- c. (12 pts) **What information does the $\sigma(Y)$ graph give** about the mechanism of the reaction? Does nickel insertion into the aryl boronate **2** (step **B**) occur
- via a single concerted step?
 - via two steps through a zwitterionic intermediate?
 - via some combination of these two?
 - or does the data not help you answer this question?
- Make sure to explain your answer in terms of the ρ_Y value you calculated.

- d. (11 pts) On the axes below, **draw potential energy diagrams** for the first two segments (**A** and **B**) of the catalytic cycle. Draw curves for two cases: X = COCH₃, Y = H; and X = H, Y = COCH₃. { $\sigma(\text{COCH}_3) = +0.5$.} Draw relative energy levels as precisely as you can. If there is anything (e.g., relative energies) that the data does not allow you to determine or predict, indicate that on your drawing.

