Exam 2
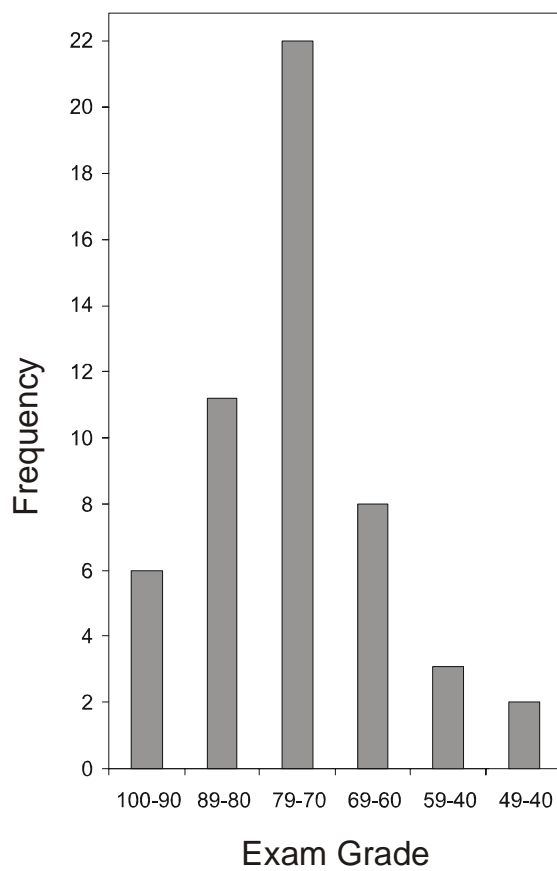**Answer Key**

Exam 2 Mean: 75
Exam 2 Median: 77
Exam 2 St. Dev.: 12

Exam 2 Solutions

1. a. We can define the rate of H_2 production in terms of step 3:

$$\frac{\partial[H_2]}{\partial t} = k_3[\textbf{INT}^+]$$

As is usually the case for multistep mechanisms, this elementary rate law has something in it that we can't measure. So we'll need to substitute for it. If Step 2 is fast and reversible, we can make a pre-equilibrium assumption about this step and write an equilibrium expression

$$[\textbf{INT}^+] = \frac{k_2[H_2BNH_3^+][H_3BNH_3]}{k_{-2}},$$

$$\frac{\partial[H_2]}{\partial t} = \frac{k_2 k_3[H_2BNH_3^+][H_3BNH_3]}{k_{-2}}.$$

This expression also has something we can't measure, $[H_2BNH_3^+]$. If Step 1 is also fast, we can also make a pre-equilibrium assumption here:

$$[H_2BNH_3^+] = \frac{k_1[(C_6F_5)_3B][H_3BNH_3]}{k_{-1}[(C_6F_5)_3BH^-]},$$

$$\frac{\partial[H_2]}{\partial t} = \frac{k_1 k_2 k_3[(C_6F_5)_3B][H_3BNH_3]^2}{k_{-1}k_{-2}[(C_6F_5)_3BH^-]}.$$

Rubric:
   3 points for original setup of $\partial[H_2]/\partial t$;
   4 points for setting up first pre-equilibrium correctly;
   4 points for setting up second pre-equilibrium correctly;
   4 points for the correct answer.
      1 point off for each trivial algebra error, but not for errors in defining things.

b. As in part (a), we can write

$$\frac{\partial[\text{H}_2]}{\partial t} = k_3[\textbf{INT}^+].$$

Previously, we needed to substitute for [INT$^+$]. We still need to do this. The problem instructs us to make a steady-state approximation

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

One way to do this would be to write individual steady-state expressions for $\partial[\text{H}_2\text{BNH}_3{}^+]/\partial t$ and $\partial[\text{INT}^+]/\partial t$ and to add them. (That would work fine.) Instead, I'm going to just state that Step 2 doesn't change the amount of cationic intermediate (because it just exchanges one for the other), and argue that

$$\frac{\partial\big([\text{H}_2\text{BNH}_3{}^+]+[\text{INT}^+]\big)}{\partial t} = (\text{Step 1 forward}) - (\text{Step 1 reverse}) - (\text{Step 3 forward})$$

$$= k_1[(\text{C}_6\text{F}_5)_3\text{B}][\text{H}_3\text{BNH}_3] - k_{-1}[(\text{C}_6\text{F}_5)_3\text{BH}^-][\text{H}_2\text{BNH}_3{}^+] - k_3[\textbf{INT}^+] = 0.$$

This has both [INT$^+$] and [H$_2$BNH$_3{}^+$] in it, and we need to get rid of the [H$_2$BNH$_3{}^+$] to solve for [INT$^+$] alone. We can use the Step 2 equilibrium to substitute for it:

$$[\text{H}_2\text{BNH}_3{}^+] = \frac{k_{-2}[\textbf{INT}^+]}{k_2[\text{H}_3\text{BNH}_3]}$$

$$k_1[(\text{C}_6\text{F}_5)_3\text{B}][\text{H}_3\text{BNH}_3] - k_{-1}[(\text{C}_6\text{F}_5)_3\text{BH}^-]\left(\frac{k_{-2}[\textbf{INT}^+]}{k_2[\text{H}_3\text{BNH}_3]}\right) - k_3[\textbf{INT}^+] = 0;$$

solving for [**INT$^+$**],

$$[\text{INT}^+] = \frac{k_1[(\text{C}_6\text{F}_5)_3\text{B}][\text{H}_3\text{BNH}_3]}{\left(k_3 + \dfrac{k_{-1}k_{-2}[(\text{C}_6\text{F}_5)_3\text{BH}^-]}{k_2[\text{H}_3\text{BNH}_3]}\right)} = \frac{k_1k_2[(\text{C}_6\text{F}_5)_3\text{B}][\text{H}_3\text{BNH}_3]^2}{k_2k_3[\text{H}_3\text{BNH}_3] + k_{-1}k_{-2}[(\text{C}_6\text{F}_5)_3\text{BH}^-]}.$$

So,

$$\frac{\partial[\text{H}_2]}{\partial t} = \frac{k_1k_2k_3[(\text{C}_6\text{F}_5)_3\text{B}][\text{H}_3\text{BNH}_3]^2}{k_2k_3[\text{H}_3\text{BNH}_3] + k_{-1}k_{-2}[(\text{C}_6\text{F}_5)_3\text{BH}^-]}.$$

Overall, there are a couple of different ways you could have ordered the substitutions you needed to make—the Step 2 equilibrium and the overall steady-state approximation—but you had to use them both to get this answer.

There was another route you could have taken to solve this problem, by setting both $[H_2BNH_3^+]$ and $[INT^+]$ as steady-state intermediates, such that

$$\frac{\partial[H_2BNH_3^+]}{\partial t} = 0 \quad \text{and} \quad \frac{\partial[INT^+]}{\partial t} = 0.$$

I'm not sure this was warranted by the conditions of the problem, and it involved some pretty hairy math. But if you did it perfect, you ended up with the answer

$$\frac{\partial[H_2]}{\partial t} = \frac{k_1 k_2 k_3 [(C_6F_5)_3B][H_3BNH_3]^2}{k_2 k_3 [H_3BNH_3] + k_{-1}k_3[H_3BNH_3] + k_{-1}k_{-2}[(C_6F_5)_3BH^-]}.$$

If you came up with this answer perfectly, we gave you all but one point.

Rubric:
3 points for original setup of $\partial[H_2]/\partial t$;
4 points for setting up steady-state approximation correctly;
   2 points partial for setting up any steady-state approximation.
4 points for using second pre-equilibrium;
4 points for the correct answer.
   1 point off for each trivial algebra error, but not for errors in defining things.

or, 14 points total for using two separate steady-state approximations perfectly.

c. From Eyring's equation,

$$\ln\left(\frac{k_{rxn}}{T}\right) = \left(\ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}\right) - \frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T}\right)$$

$$slope = -\Delta H^{\ddagger}/R$$
$$intercept = \ln(k_B/h) + \Delta S^{\ddagger}/R$$

$\Delta H^{\ddagger}$ = -(*slope*)(R)
   = -(-9.49 × 10^3 K)(1.99 cal mol^{-1} K^{-1})
   = **18.9 kcal/mol = 79 kJ/mol**

$\Delta S^{\ddagger}$ = (R)[(*intercept*) - ln(k_B/h)]
   = (1.99 cal mol^{-1} K^{-1})[(27.5) − ln(2.94 × 10^{-24} cal K^{-1}/1.58 × 10^{-34} cal sec)]
   = **7.7 cal mol^{-1} K^{-1} = 32 J mol^{-1} K^{-1}**
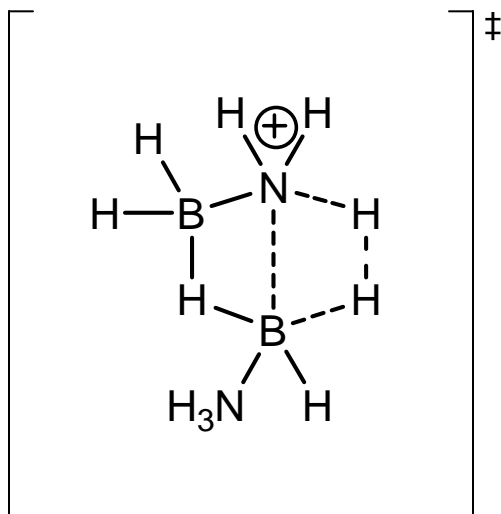
Rubric:
   5 points *each.*
   -1 point *for no units.*
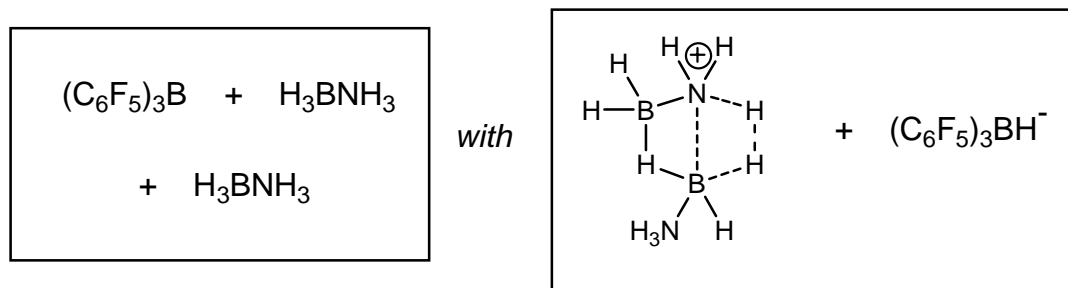   -1 point *for wrong sign.*

d.

Rubric:
   5 points total.
      1 point for each partial bond. (4 points here.)
      1 point for accounting for charge.

e. In this problem, we're comparing starting materials to the rate-determining transition state. A total accounting of molecules says that we're comparing

$(C_6F_5)_3B$ + H_3BNH_3

+ H_3BNH_3

with

[transition state structure] + $(C_6F_5)_3BH^-$

I have to admit, because the transition state has fewer molecules than the starting materials (2½, sort of, vs. 3), I would have expected that $\Delta S^{\ddagger}$ would be negative.

*What about the reaction contributes to a **higher** $\Delta S^{\ddagger}$?* (In other words, what makes entropy increase at the transition state?)

Again, doesn't make a lot of sense based on the reaction; this wasn't a very good question to ask. We gave everyone credit for this half of the problem (we didn't grade it).

- The transition state is creating a new molecule of H_2 (*g*) (assuming that the H_2 immediately becomes a gas, which is only somewhat likely), and that will create a lot of entropy. Some of that created entropy will be reflected in the transition state.

*What about the reaction contributes to a **lower** $\Delta S^{\ddagger}$?* (In other words, what makes entropy decrease at the transition state?)

- As I mentioned above, the effective number of molecules decreases between starting materials and the transition state. That would decrease entropy and lead to lower $\Delta S^{\ddagger}$.
- The transition state is also extremely organized—two bonds are being made, two are being broken, and the positions of all of the atoms involved are very specific. Again, this would decrease entropy and lead to lower $\Delta S^{\ddagger}$.

Rubric:
    5 points automatic for the first box!
    5 points for correct answer in second box.

2. a.

$$\rho_X(\sigma < 0.25) = \qquad \rho_X(\sigma > 0.25) = \qquad \rho_Y =$$
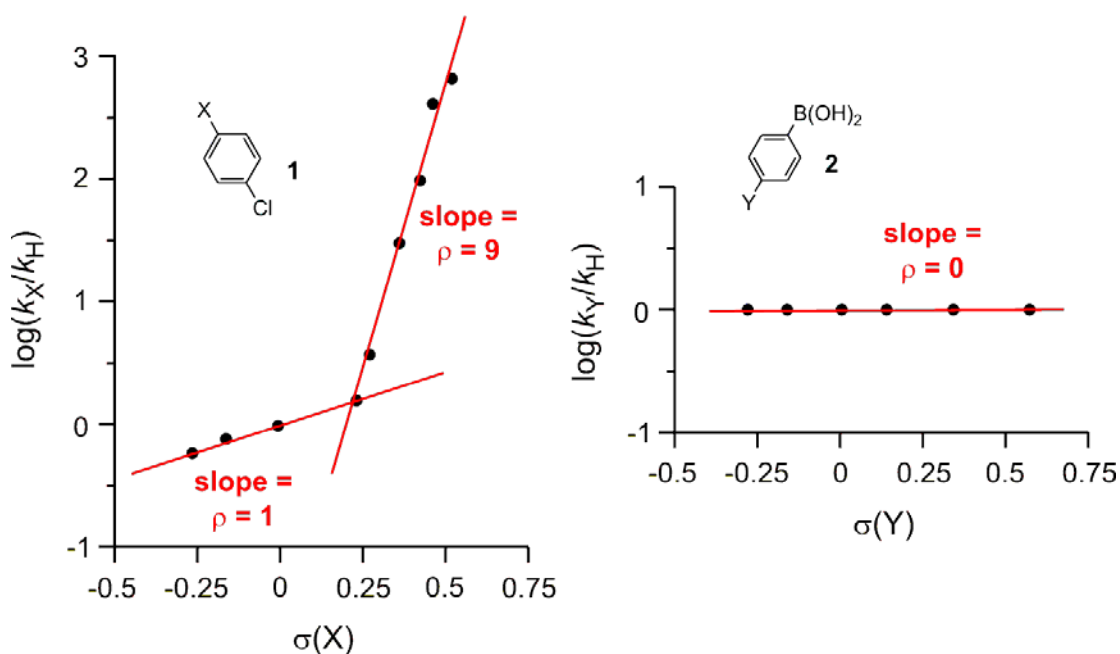
1	9	0

Rubric:
3 points for each box. (+/- 20%). 9 total here.
1 point for getting all three.

b. Before discussing the answer to this question, it's important to note that changes in substituents on a molecule are only going to have an impact on rates if the molecule is somehow involved in the rate-determining transition state. (By definition; otherwise, substitution affects the starting material and transition state the same.) So, substitution that leads to $\rho \neq 0$ automatically means that the substituent is part of the rate-determining transition state structure.

Clearly, substituents X have an effect on rate, and it likely has to do with the transition state for insertion of NiL_n into the C-Cl bond. Ordinarily, given the choice between one- and two-step transition states, we would be asking ourselves which mechanism corresponded to the measured ρ value. Interestingly though, the graph shows two ρ values, one much larger than the other. So we've got two

questions to answer: which mechanism operates, and why does the graph kink? One explanation is that different mechanisms operate for electron-withdrawing ($\rho > 0.25$) and electron-donating ($\rho < 0.25$) substituents. (If you hadn't guessed this explanation, you might also have gotten the idea from the example on p.452 of *MPOC*.) The problem suggests two potential transition states for step A:
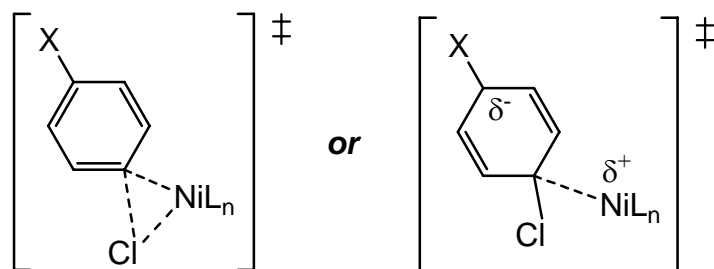
(The one on the left is from the problem; the one on the right assumes that the first step of the two-step mechanism is rate limiting. If the second step were rate-limiting, the charge distribution would be similar.) The TS on the left is more consistent with a lower value for ρ, and the TS on the right with a higher value of ρ. So that's the answer here; the mechanism is single-step for $\rho < 0.25$, and two-step zwitterionic for $\rho > 0.25$. (Or, in the words of the problem, "some combination of these two".)

Rubric:

6 points for any explanation that correlates $\rho > 0$ with electron-withdrawing group acceleration at X.

3 points for two different mechanisms.

3 points for correct match: ionic for $\rho = 9$, concerted for $\rho = 1$.

c. The aryl boronate is added in step B, after the addition discussed in the previous problem. If the answer to the previous question has the substituent impacting the rate-determining step in step A, then step B cannot be the rate-determining step, and substituents B should have no effect on reaction rate. That is in fact what is observed—not only is $\rho_Y = 0$, it's exactly 0, with no variation in the data points at all. That means that this data tells us nothing at all about which mechanism operates in step B, only that the transition-state energy must be below that for step A.
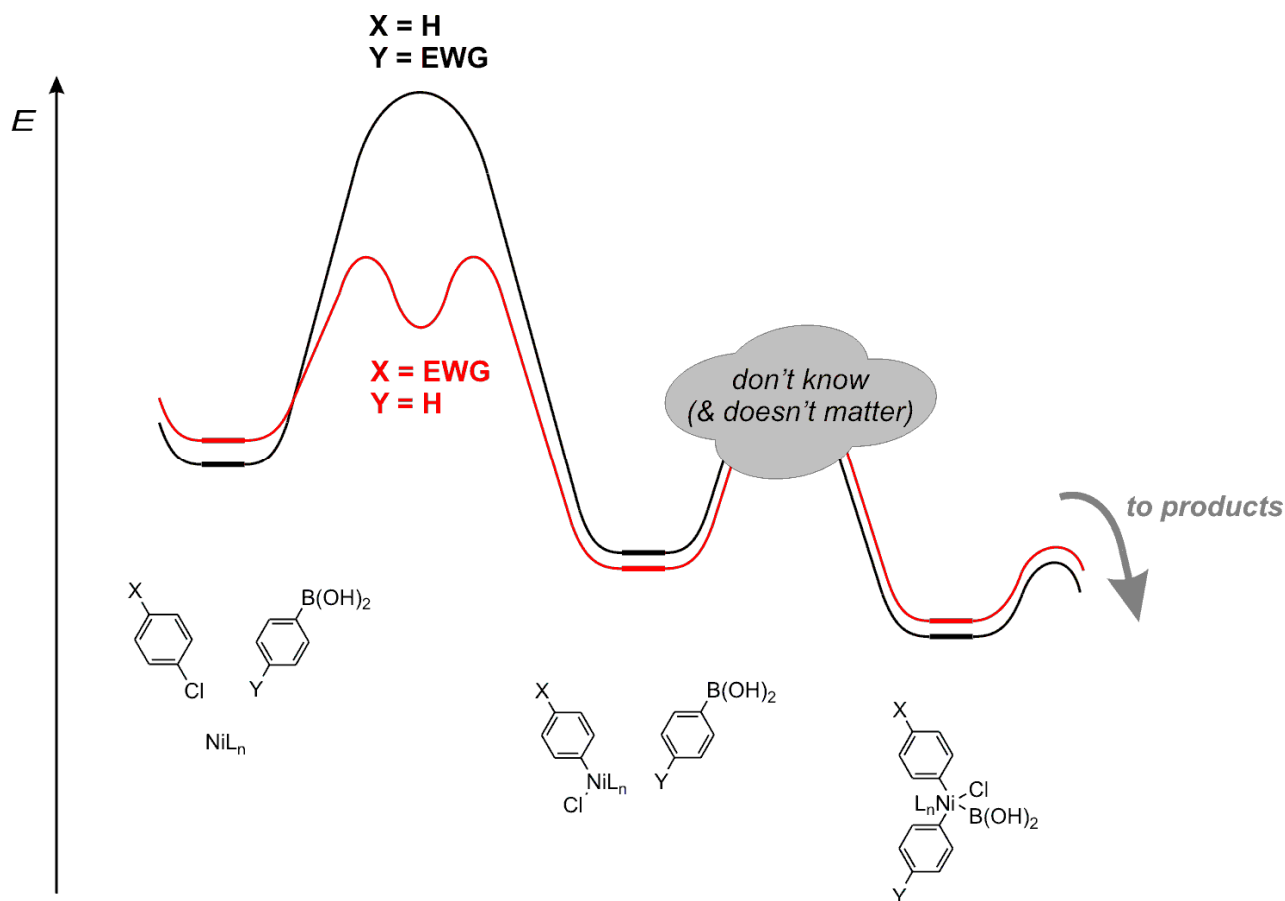
Rubric:

6 points for any explanation that correlates $\rho = 0$ with substituents having no effect on rate. (That includes concerted mechanism for step B, though to argue this would be incorrect.)

6 points for linking $\rho = 0$ to step B not being rate-determining.

d. The ketone (COCH$_3$) group is an electron-withdrawing group ($\sigma > 0$); in the diagram below, I've just labeled it "EWG".

There were really only a few things that you had enough data to illustrate here:

1. The rate-determining transition state for X = H is higher in energy that for X = COCH$_3$, relative to their respective starting materials. You know that because $\rho_X > 0$ under all circumstances.
2. The case X = COCH$_3$ has an intermediate in step A, while X = H does not. This you get from the kink in the graph. It isn't clear, however, which of the two transition states in this step is higher. (I drew them at the same height— maybe they are, maybe they aren't.)
3. There is nothing specific we can say about the transition states for step B (in either case), but we do know that they are lower in energy than those for step A.

In my diagram, I've also drawn different relative ground-state energies for each step, such that the EWG-substituted intermediates are progressively lower in energy than their unsubstituted relatives. I've done this because the Ni^0 species is

serving as a reducing agent at the beginning of the reaction ($\rho > 0$ tells you that), and that should be more exothermic for electron-poor substrates than unsubstituted substrates. So, any time an EWG is incorporated into the Ni complex, its energy should decrease. But it's tough to know how big an effect this will be, and the data doesn't really say anything about it, so we didn't grade on placement of ground-state energies—just on transition states. I've also drawn each step as being exothermic, but we don't really know that either; each time around the whole cycle is exothermic, because the reaction goes, but we don't know where the intermediates sit in energy.

Rubric:

6 points for step A.

3 points partial for drawing the transition state for X = H higher in energy than the TS for X = EWG;

3 points partial for self-consistency with your interpretation of the Hammett plot in (b); 1 point of these 3 if you explained a two-step process in (b) but drew only one TS.

5 points for step B.

2 points for a logical placement of the TS, based on your interpretation of the Hammett plot,

2 points for similar/unknown energies for the TS for both curves, and

1 point for a logical height of the transition state based on your intepretation of the Hammett plot.