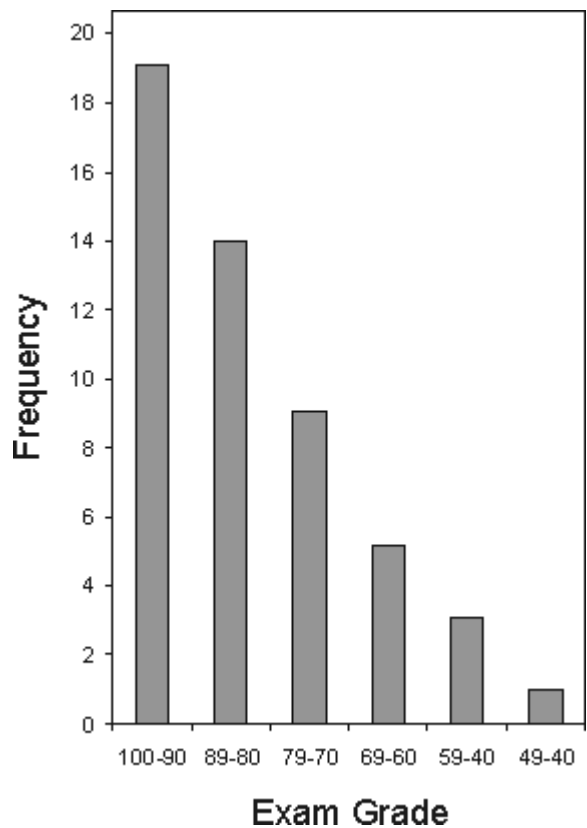


**Exam 1  
Answer Key**

Exam 1 Mean: 82  
Exam 1 Median: 86  
Exam 1 St. Dev.: 13



## Exam 1 Solutions

## 1. a.

$$\begin{aligned}\Delta G_{\text{up/down}} &= -RT \ln K_{\text{up/down}} \\ &= -(1.99 \text{ cal mol}^{-1} \text{ K})(298 \text{ K}) \ln(2.6) \\ &= -0.57 \text{ kcal/mol}\end{aligned}$$

So, the complex with **2<sub>up</sub>** is **more stable** than the complex with **2<sub>down</sub>** by **0.57 kcal/mol**.

*Rubric:*

3 points for “more stable”;

4 points for any  $\Delta G$  between 0.5 and 0.7 kcal/mol.

*2 points partial credit for any attempt to calculate Gibbs free energy.*

- b. 2b** already exhibits a preference for **2b<sub>up</sub>** over **2b<sub>down</sub>**, in the absence of any weak interaction, for some reason—maybe the molecule fits better in the cavity up than down, or maybe there’s some interaction between **2** and the cavity we haven’t imagined. In any case, any preference that we observe for any **2b-3** pair will include this background energetic component, and we’ll need to subtract it out.

So, for **(1)<sub>2</sub>•2b•3b**,

$$\begin{aligned}\Delta G_{\text{up/down}} &= -RT \ln K_{\text{up/down}} \\ &= -(1.99 \text{ cal mol}^{-1} \text{ K})(298 \text{ K}) \ln(8.9) \\ &= -1.3 \text{ kcal/mol}\end{aligned}$$

Meaning

$$\begin{aligned}\text{“BDE”}_{\text{H-bond}} &= (1.3 \text{ kcal/mol})_{3b} - (0.6 \text{ kcal/mol})_{\text{background}} \\ &= \mathbf{0.7 \text{ kcal/mol}}.\end{aligned}$$

*Rubric:*

5 points for calculation.

*2 points partial credit for including  $K = 8.9$  in calculation (even if correction for background is ignored);*

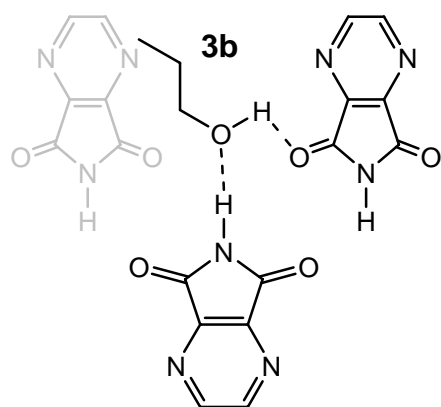
*2 points partial credit for correcting for 3a preference;*

*1 point for correct answer.*

3 points for explanation of correction factor.

- c. For a hydrogen bond between species in a noninteracting solvent like mesitylene (which is like benzene or toluene), inside a capsule that is intended to further isolate the molecules, 0.7 kcal/mol seems awfully low. For comparison, *MPOC* (p. 173) lists H-bond strengths in noninteracting  $\text{CCl}_4$  as being between 3 and 5 kcal/mol. We discussed in class that H-bonds in water are “weaker” (have a smaller  $\Delta G$  for breaking)—between 0.5 and 1.5 kcal/mol—because of competition for the H-bond site by water. So a strength of 0.7 kcal/mol in a non-competing environment is surprisingly **smaller** than what one would expect.

In principle, there could be a number of factors that could affect the formation of an H-bond either between the propanol H and the toluidine N, or between the



propanol O and the toluidine H. (The problem doesn't indicate which is formed, although the model on page 2 makes it look as though the H-bond is between toluidine N and propanol H.) One possibility is that there *is* a competition, maybe by the ring of amides around the middle of the molecule, for the 1-propanol donor or acceptor. (Shown on the left; here, if **2b** were pointed down, there would still be stabilizing H-bonds between **3b** and the cavity.)

Alternately, maybe the shape of the cavity forces the molecules into a conformation that prevents the H-donor and acceptor from adopting the optimum, co-linear orientation (that would normally maximize H-bond strength); maybe the cavity squeezes the OH of the propanol down too far or too close to appropriately bond with **2b**.

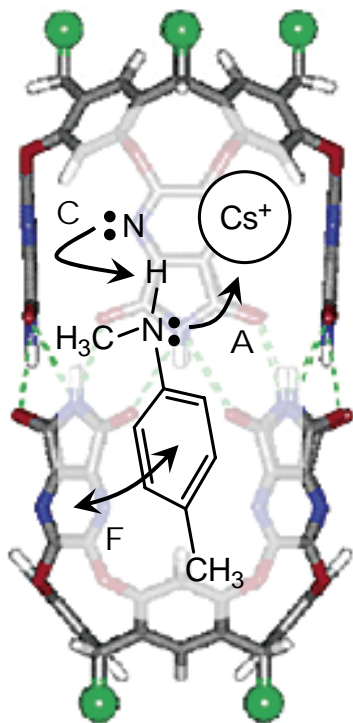
*Rubric:*

3 points for “smaller” than expected.

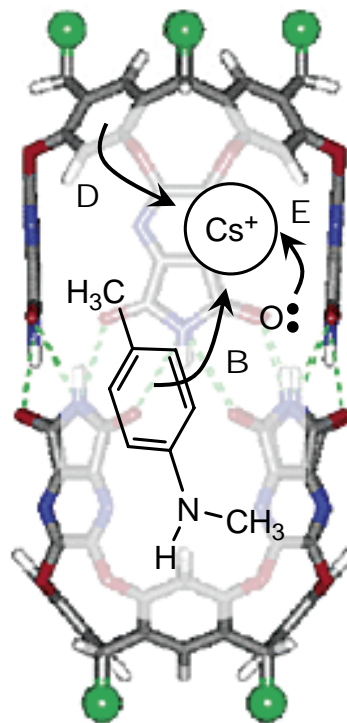
7 points for discussion of at least one factor that could lead to  $K$  being smaller.

(*Partial credit items?*)

- d. Lots of possible answers here. We accepted many potential orientations and interactions, including interactions between **2b** and  $\text{Cs}^+$  as well as interactions between either molecule and the host:



$(1)_2 \bullet 2b_{\text{up}} \bullet \text{Cs}^+$



$(1)_2 \bullet 2b_{\text{down}} \bullet \text{Cs}^+$

**2b**• $\text{Cs}^+$  interactions:

**A:** Lewis acid-base between toluidine N and  $\text{Cs}^+$ . Not going to be very strong, because the toluidine N electrons are already conjugated with the aromatic ring, but it will happen. Makes  $K_{\text{up/down}}$  larger.

**B:** Cation- $\pi$  interactions between the toluidine ring and  $\text{Cs}^+$ . Will occur more for **2b<sub>down</sub>** than **2b<sub>up</sub>** because aromatic ring is closer (in my opinion). So, makes  $K_{\text{up/down}}$  smaller.

Confounding,  $(1)_2 \bullet \text{Cs}^+$  and  $(1)_2 \bullet 2b$  interactions:

**C:** H-bonding between the host and toluidine N-H. I think there are more H-bond acceptors near the center of the cage than near the ends, so I would guess H-bonding would favor **2<sub>up</sub>** over **2<sub>down</sub>** (and make  $K_{\text{up/down}}$  larger), but you could probably argue it the other way as well.

**D:** Cation- $\pi$  interactions between aromatic groups in the host and  $\text{Cs}^+$ . This is a weak interaction, but because it would occur for either orientation of **2b**, it isn't clear how this would bias  $K$  either way. We gave partial credit for this answer.

**E:** Lewis acid-base between host donor atoms and  $\text{Cs}^+$ . As with **D** above, because this would also occur for either orientation of **2b**, it isn't clear how this interaction would bias  $K$  either way. We gave partial credit for this answer.

**F:**  $\pi$ - $\pi$  interactions between the host and the aromatic toluidine ring. Again, this would probably occur for either orientation of **2b**, and shouldn't bias  $K$  either way. We gave partial credit for this answer.

*Rubric:*

5 points for each weak interaction:

*2 points for drawing an arrow to any viable noncovalent interaction, even one that doesn't influence  $K$ .*

*1 point for naming it in the box.*

*2 points for accurately identifying its influence on  $K$ . If you chose an interaction that shouldn't have an influence on  $K$ , you cannot get these points.*

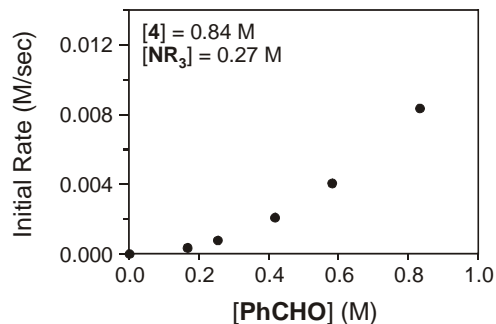
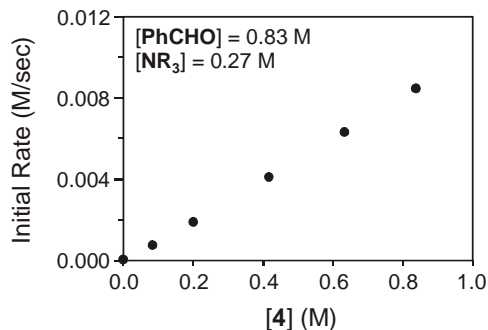
2. a. Each of the graphs essentially reduces the expression

$$\text{rate} = -\frac{\partial[\mathbf{4}]}{\partial t} = k[\mathbf{4}]^x[\text{PhCHO}]^y[\text{NR}_3]^z$$

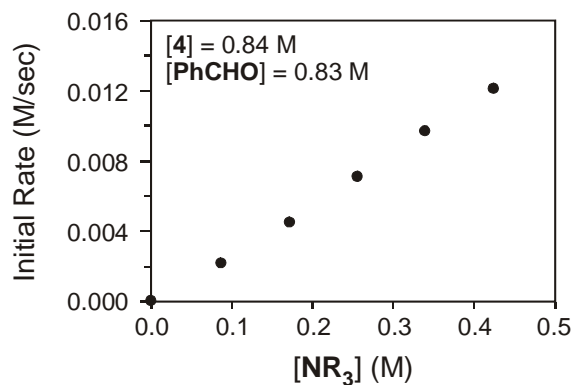
to

$$\text{rate} = k[\mathbf{4}]^x(\text{constant})$$

$$\text{rate} = k[\text{PhCHO}]^y(\text{constant})$$

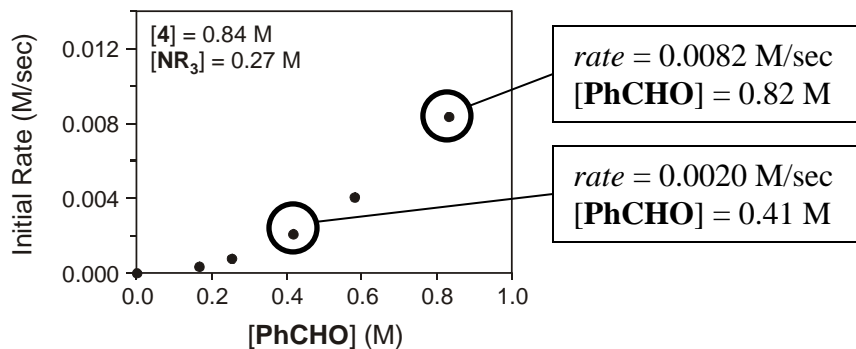


$$\text{rate} = k[\text{NR}_3]^z(\text{constant})$$



One way that we discussed in class to evaluate  $k$ ,  $x$ ,  $y$  and  $z$  is to set up systems of simultaneous equations. But, before we do that, I think it's fairly obvious that the data shown in the  $x$  and  $z$  graphs above look like straight lines—i.e., graphs of the form  $\text{rate} = k_{\text{obs}}[\mathbf{4}]$  and  $\text{rate} = k_{\text{obs}}[\text{NR}_3]$ , where  $x$  and  $z$  both = 1 (one). You can do simultaneous equations for these if you want, but you really don't need to.

The  $y$  graph, on the other hand, is nonlinear and needs some mathematical analysis.



$$\frac{rate_1}{rate_2} = \frac{[PhCHO]_1^y}{[PhCHO]_2^y}$$

$$= \left( \frac{[PhCHO]_1}{[PhCHO]_2} \right)^y$$

$$\frac{0.0082}{0.0020} = \left( \frac{0.82}{0.41} \right)^y$$

$$4 = (2)^y$$

$$y = 2.$$

Substituting concentrations,  $x$ ,  $y$  and  $z$  into the instantaneous rate equation for the upper data point circled above,

$$rate = k[4]^x [PhCHO]^y [NR_3]^z$$

$$k = \frac{rate}{[4]^x [PhCHO]^y [NR_3]^z}$$

$$= \frac{0.0082 \text{ M/sec}}{(0.84 \text{ M})(0.82 \text{ M})^2 (0.27 \text{ M})}$$

$$k = \boxed{0.054 \text{ M}^{-3} \text{ sec}^{-1}}$$

$$x = \boxed{1}$$

$$y = \boxed{2}$$

$$z = \boxed{1}$$

*Rubric:*

2 points each for  $x$ ,  $y$  and  $z$ . (+/- 20%). 6 total here.

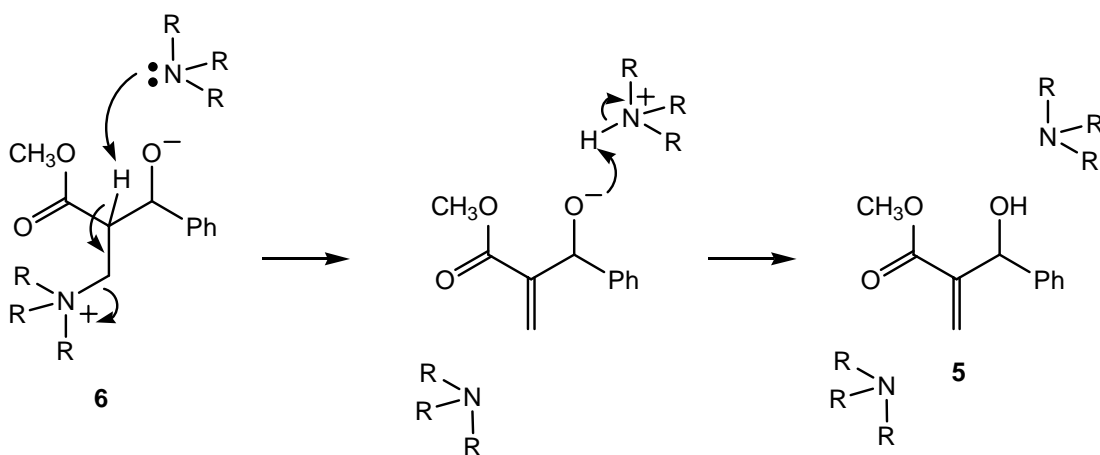
(So  $x$ ,  $z$  can be between 0.8-1.2,  $y$  can be between 1.6-2.4.)

4 points for  $k$ .

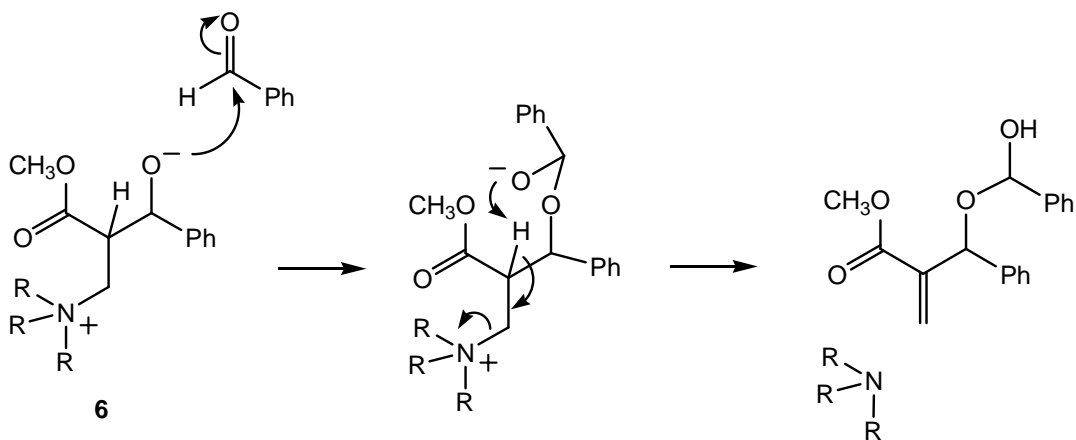
2 points for units—must be  $\text{sec}^{-1} \text{M}^{-(x+y+z-1)}$  or internally consistent.

2 points for correct value or internally consistent calculation.

**b. Mechanism (i):**

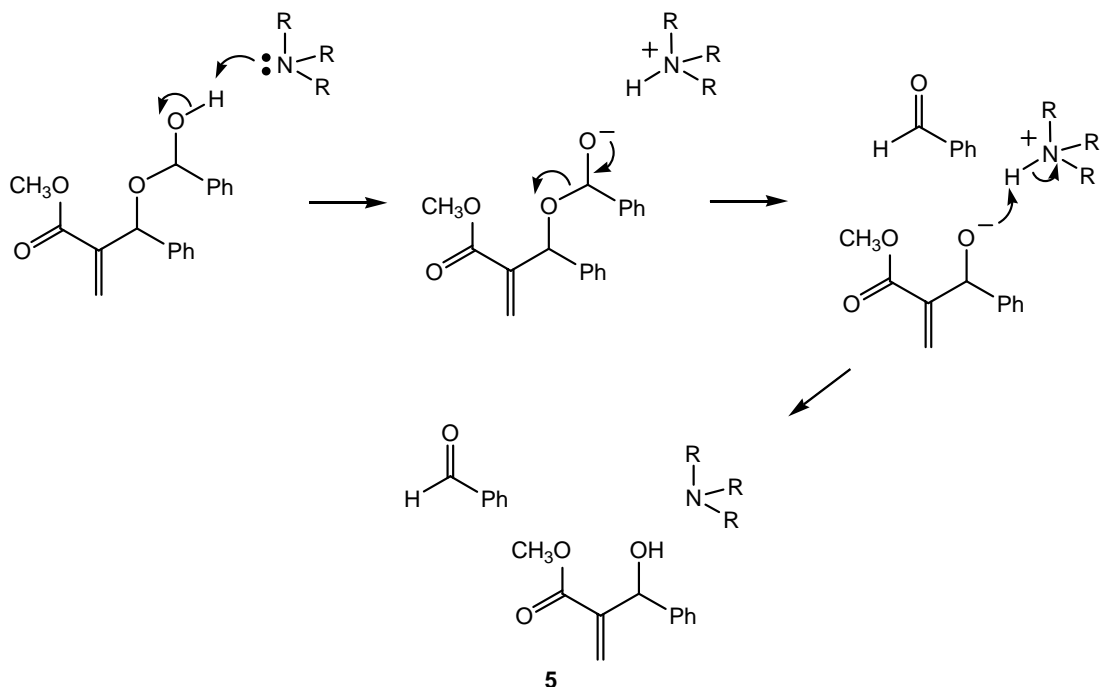


**Mechanism (ii):**

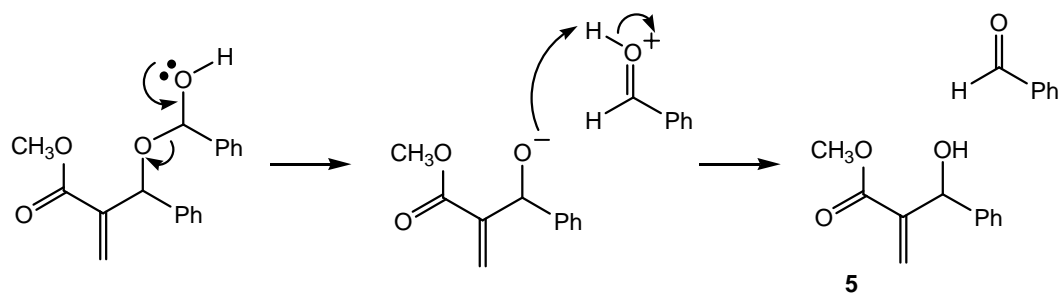


Then,





**OR**



I think the second of these two options is less likely, because it isn't likely that the protonated aldehyde would be observed in concentrated (0.27 M) trialkylamine base.

*Rubric:*

5 points for Mechanism (i).

*2 points partial credit for something intramolecular. Very unlikely, but if you did the accounting correct, we'll give it to you.*

10 points for Mechanism (ii).

*2 points for initial addition of aldehyde.*

*3 points for subsequent intramolecular elimination.*

*5 points for loss of aldehyde and proton transfers.*

*4 of these 5 points if protonated species formed in presence of NR<sub>3</sub> base.*

- c. The slow (elementary) step of mechanism (i) involves reaction of **6** with a molecule of **NR<sub>3</sub>**; the slow step of mechanism (ii) involves reaction of **6** with a molecule of **PhCHO**. A single rate expression that combines these two steps would be

$$\text{rate} = -\frac{\partial[\mathbf{6}]}{\partial t} = k_1[\mathbf{6}][\mathbf{NR}_3] + k_2[\mathbf{6}][\mathbf{PhCHO}]$$

*Rubric:*

5 points for each part of expression.

*2 points partial for “ $k_1[\mathbf{6}](\text{anything})$ ”.*

*2 points partial for “ $k_2[\mathbf{6}](\text{anything})$ ”.*

*Answers that are incorrect, but consistent with mechanisms drawn in (b), receive full credit.*

- d. Exam starts to get a little tricky here. There are *three* variables in the expression above, and we want to get rid of two of them. We might try to express either, or both, of the variables in terms of **[6]** by using a  $\Delta_0$ -like substitution (as we did in class for second-order kinetics), but all three variables are dependent. In other words, we can't define **[NR<sub>3</sub>]** in terms of how much **6** is consumed, because some of that **6** will have been consumed by reacting with **PhCHO**. This is true even if we made a pseudo-first-order assumption for one of the variables—the second variable still couldn't be expressed in terms of **6**. So, as a result, we have to do a pseudo-order approximation on both **[NR<sub>3</sub>]** and **[PhCHO]**.

To do this experiment, we would have to run kinetics experiments under an excess of both **NR<sub>3</sub>** and **PhCHO**, such that both **[NR<sub>3</sub>]** and **[PhCHO]** were constant. Under those circumstances,

$$\text{rate} = -\frac{\partial[\mathbf{6}]}{\partial t} = k_{\text{obs}}[\mathbf{6}]$$

$$k_{\text{obs}} = k_1[\mathbf{NR}_3] + k_2[\mathbf{PhCHO}]$$

Integration of the top equation is easy; it's just the first-order rate law we have dealt with many times.

$$\frac{\partial[\mathbf{6}]}{[\mathbf{6}]} = -k_{\text{obs}}\partial t$$

$$\int_{[\mathbf{6}]_0}^{[\mathbf{6}]_t} \frac{\partial[\mathbf{6}]}{[\mathbf{6}]} = -\int_0^t k_{\text{obs}} \partial t$$

$$[\mathbf{6}]_t = [\mathbf{6}]_0 e^{-k_{\text{obs}} t}$$

*Rubric:*

5 points for *any* pseudo-order experiment (where the concentration of at least one species is large enough that it doesn't vary).

5 points for expression of re-evaluating instantaneous from part (c) consistent with this approximation.

5 points for integrating correctly.

-1 point for trivial math errors,

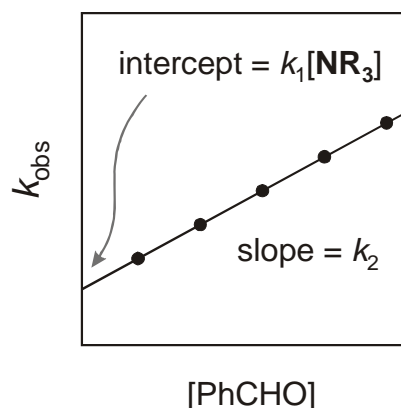
-2 points for small conceptual errors. (not integrating over space, etc.)

5 points for  $[\mathbf{6}]_t$  expression that it internally consistent with (c).

- e. The other part of a pseudo-order experiment is to set up multiple rate experiments that measure  $k_{\text{obs}}$ , and then use this data to determine component  $k$ 's. If you set up your answer the way I did, that could mean either or both of two sets of experiments:

one in which  $[\text{PhCHO}]$  is varied and  $[\text{NR}_3]$  is held constant to measure  $k_2$  as slope and  $k_1[\text{NR}_3]$  as intercept (which yields  $k_1$  by dividing out the known constant concentration  $[\text{NR}_3]$ ; see graph on the right);

and/or the other in which  $[\text{NR}_3]$  is varied and  $[\text{PhCHO}]$  is held constant to measure  $k_1$  as slope and  $k_2[\text{PhCHO}]$  as intercept (which yields  $k_2$  by dividing out the known constant concentration  $[\text{PhCHO}]$ ).



Regardless of how you answered the previous parts, however, your answer to this question has to contain a set of experiments in which  $k_{\text{obs}}$  is varied for different concentrations of a pseudo-order component, and then that data plotted to extract a slope and intercept that correspond to  $k_1$  and  $k_2$ .

*Rubric:*

5 points for describing how  $k_{\text{obs}}$  would be measured for different concentrations of excess reactant.

5 points for describing how plot of  $k_{\text{obs}}$  vs. reactant would yield some answers.