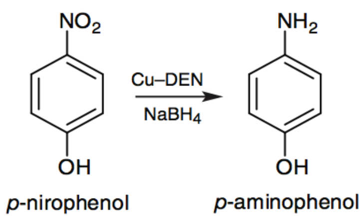
Department of Chemistry
University of Texas at Austin

Name:________________

**Kinetics Unit Activity – FRI Kinetics KEY**

The following is an examination of some data from the Nanoparticle research stream in the Freshman Research Initiative (FRI). This group of students is working to understand the effect that size and composition of metal nanoparticles has on catalytic rates.




They are studying the kinetics of a model chemical reaction to test the performance of metal catalyst. The model system is the reaction of p-nitrophenol with sodium borohydride ($NaBH_4$) to generate p-aminophenol. The reaction is shown at the left, where the Cu-DEN is a Copper Dendrimer Encapsulated Nanoparticle that is the catalyst for the reaction. The metal can be varied to test the performance of different metals and alloys.

The reaction is 2nd order overall: First order with respect to the p-nitrophenol and first order with respect to the $NaBH_4$.

The reaction kinetics can be monitored since the p-nitrophenol (NP) compound absorbs blue light ~400 nm (making the solution appear yellow). The absorbance of the p-aminophenol (AP) is in the ultraviolet (so the solution appears clear). Therefore, as the reaction proceeds the color changes from yellow to clear.

The conditions used for the reaction are typically around 40 μM for NP and 4 mM for $NaBH_4$ along with a fixed concentration of catalyst.

1. Given these conditions what would you expect for the $NaBH_4$ concentration during the course of the reaction? (If the two species react in a 1:1 ratio, what would the concentration of each reactant be at completion?)

The concentration of $NaBH_4$ is 100 times greater than that of the NP.

Multiplying the NP concentration by 100 gives us the $NaBH_4$ concentration:

(40 μM)*(100) = 4 mM Or $(40\times10^{-6}M)\times(100) = (4\times10^{-3}M)$

Thus, this reaction could be considered pseudo first-order and the concentration of $NaBH_4$ will remain relatively unchanged. If all of the NP reacted away then the RICE table would look like:

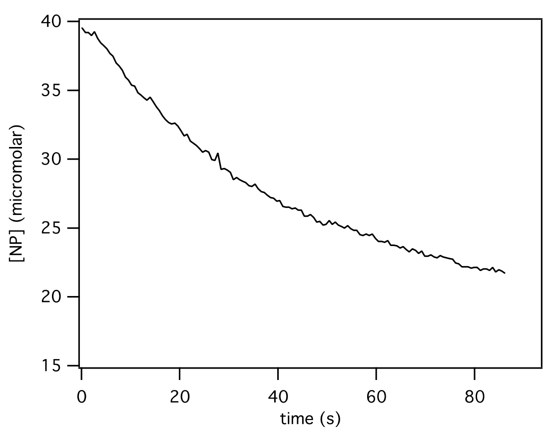
| | | | |
|---|---|---|---|
| R. | NP + | $NaBH_4$ --> | Products |
| I. | $40\times10^{-6}M$ | $4\times10^{-3}M$ | 0 |
| C. | $-40\times10^{-6}M$ | $-40\times10^{-6}M$ | $+40\times10^{-6}M$ |
| E. | 0 | $3.96\times10^{-3}M$ | $40\times10^{-6}M$ |

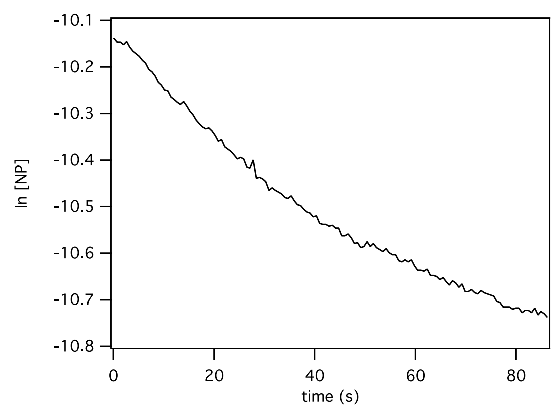
We can see that the concentration of $NaBH_4$ remains close to its original value even after all the NP has reacted away.

2. What implications do these concentrations have for the order of the reaction kinetics?

This means that we will have pseudo first-order kinetics. Since only one concentration is really changing, the rate will only depend on one reactant.

Below are two graphs of the concentration of NP and natural log of the concentration of NP as a function of time for the reaction using gold nanoparticles as catalysts.



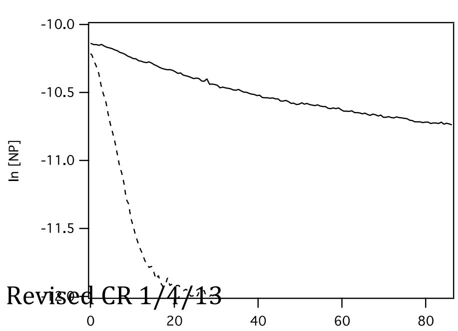

3. Do you think the kinetics appear overall zero order in NP or first order in NP?

It is first-order in NP. We can see that the plot of ln[NP] vs. time appears more linear than the plot of [NP] vs. time and thus we conjecture that the kinetics are first-order.

4. Do these plots meet with you expectations for the kinetics based on your answer to question 1? Explain

Yes! We expected pseudo first-order kinetics and graphically we see first-order.

5. This graph is a comparison of two different catalysts under identical conditions. The solid line plot is for gold nanoparticles and the dotted line is for palladium nanoparticles. Which type of particle is the better catalyst? Why? Can you estimate how much better a catalyst it is?



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The palladium is a better catalyst because we can see that the concentration of NP decreases faster and more completely in a given time period than gold when the palladium is the catalyst.

About 6 times as fast. It takes about 60 seconds for the gold to reach a certain concentration, and the palladium reaches the same concentration in 10 seconds. (Look at the y-coordinate point of -10.5 and trace a horizontal line out to both lines. Now look at the x-coordinate, aka time, associated with this y-coordinate for both graphs. You get about 10 seconds for the palladium and about 60 seconds for the gold).

Additionally, the slopes of these lines are the negative rate constants, k, for each reaction. The k value for the palladium would be larger and therefore the rate of reaction using palladium would be greater for the same given concentrations of reactants.

Slope for palladium:
$(-10.5 - -10.7) \div (0-10) = -0.0200\ s^{-1}$ Thus, the rate constant, k, is $0.0200\ s^{-1}$

Slope for gold:
$(-10.5 - -10.7) \div (0-60) = -0.0033\ s^{-1}$ Thus, the rate constant, k, is $0.0033\ s^{-1}$

How much greater is the palladium rate constant:
$(k_{gold})*6 = (k_{palladium})$ $(0.0033\ s^{-1})*6 = 0.0200\ s^{-1}$

So, the palladium catalyst will allow the reaction to occur about six times faster than the reaction with the gold catalyst.