Optional Readings


Assignment – Part I

1. For many years, Reed students determined the rate law for acid-catalyzed formation of 2-iodocyclohexanone from cyclohexanone and iodine.

   \[
   \text{rate} = k_{\text{obsd}}[\text{H}_3\text{O}^+][\text{cyclohexanone}]
   \]

   When the reaction was set up so that the initial concentration of the product was zero, the law governing the initial rate was governed by the rate law given above.
   a. What is the overall order of the rate law?
   b. Draw a mechanism that is consistent with this rate law.
   c. Label the forward and backward rate constants of each elementary step in your mechanism \( k_1, k_2, \) etc., and show how your mechanism fits the observed rate law. What is \( k_{\text{obsd}} \) in terms of the elementary rate constants, \( k_1, k_2, \) etc.? Clearly identify any assumptions that are needed for your derivation.

2. Recall from Chem 201/202 that alkyl groups are ortho-para directing in electrophilic aromatic substitution. Why, then, does 1,3,5-triethylbenzene form as the major product of the reaction of excess EtBr and AlCl₃ with benzene after extended reaction times?

3. Tropanes react with \(^{13}\text{CH}_3\text{I}\) as shown below (the • indicates the location of the \(^{13}\text{C}\)-labeled groups):

   \[
   \text{MINOR PRODUCT} \xrightleftharpoons[k_{\text{eq}}]{} \text{MORE STABLE} \xrightarrow{K} \text{LESS STABLE} \xleftarrow{k_{\text{eq}}} \text{MAJOR PRODUCT}
   \]
a. Draw a reaction coordinate diagram that reflects the observations in the figure. Pay careful attention to compound and transition state energies.

b. What, if anything, can you infer from these data regarding the steric requirements of a methyl group covalently bonded to N versus a methyl group being transferred from I to N?

4. The following questions refer to $\sigma$ values listed in Table 8.2
   a. Is Br more electron-withdrawing as a meta or para substituent? Why?
   b. Is CN more electron-withdrawing as a meta or para substituent? Why?
   c. The $\sigma^+$ value for $-$NHC(O)CH$_3$ is very negative. Draw a resonance form for the para isomer of CH$_3$C(O)NHC$_6$H$_4$C(CH$_3$)$_2^+$ that can account for this value.

5. Which reaction should exhibit a larger $\rho$ value when log($k_X$) is plotted against $\sigma_X$? Why?

![Diagram](attachment:reaction_coordinates.png)

Assignment – Part II

Universities use graduate students to teach laboratory sections. These students not only supervise and grade lab work, they also teach short pre-lab sessions analogous to our lab lectures. This assignment will simulate this teaching experience.

3-6 minute oral presentation + drawing on board. This assignment involves teaching your “lab section” how to purify the reaction product from a reaction that they are about to perform. You should briefly describe the reaction that is being performed (allow no more than 30 seconds for this), and then describe the purification procedure in some detail. Since your goal is to teach, you should present information about any physical and/or chemical transformations that will occur, and how the procedure manages to separate one compound from another. Your overall presentation will be limited to 6 minutes, so plan your presentation carefully. You will not be able to go into great depth, but try to do as much quality teaching as you can manage. I will be looking for teaching effectiveness.

Suitable reactions and purification procedures. Find a reaction in the journal literature that has a sufficiently (but not overly) complicated workup. (Note: it will be necessary to find the experimental details for the purification procedure. Journals like Organic Letters display this information in the supplementary information, which is available on-line free of charge.) To be satisfactory, a workup should include, at the very least, 1) the use of a separatory funnel to perform washes and/or extractions, and 2) a subsequent purification involving recrystallization, distillation, or chromatography. Additional steps, such as filtration, drying, and so on, may also appear.