Solution Kinetics of an Organic Reaction

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Abstract

In this lab, the S_N2 reaction between 2,4-dinitrochlorobenzene and piperidine is examined to determine the rate constant, test the reaction mechanism, and determine the Arrhenius parameters. The progress of the reaction (as a function of time) will be tracked using spectrophotometry.

Related Readings

1. Halpern, A. M. "Experimental Physical Chemistry: A Laboratory Textbook." 2nd Ed. Prentice Hall: Upper Saddle River, NJ. [Available on Moodle, Exp 20]
2. McQuarrie, D.A., Simon, J.D., "Physical Chemistry: A Molecular Approach." University Science Books: Sausalito, CA. Chapter 28.

Background

We won't be discussing kinetics in class until December. To help you with this lab, take advantage of the resources listed in "*Related Readings*". This background section will provide some basic ideas of kinetics and some particulars of the reaction to be investigated.

Kinetics: Thermodynamics is the study of the likelihood of a reaction (i.e., whether it will progress as written or not) whereas kinetics is the study of the rates of a reaction. We are specifically interested in how the rate of a reaction depends on the concentrations of all relevant chemical species and on the temperature. With this information, one can predict how a reaction will proceed, adjust conditions to make the reaction relevant for an application, and gain some understanding of the mechanism of the reaction.

Consider a general chemical reaction:

$$aA + bB \rightarrow cC + dD.$$

The rate of the reaction is given by the general rate law:

$$v = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}[D]^{\delta}[Y]^{\varepsilon}$$

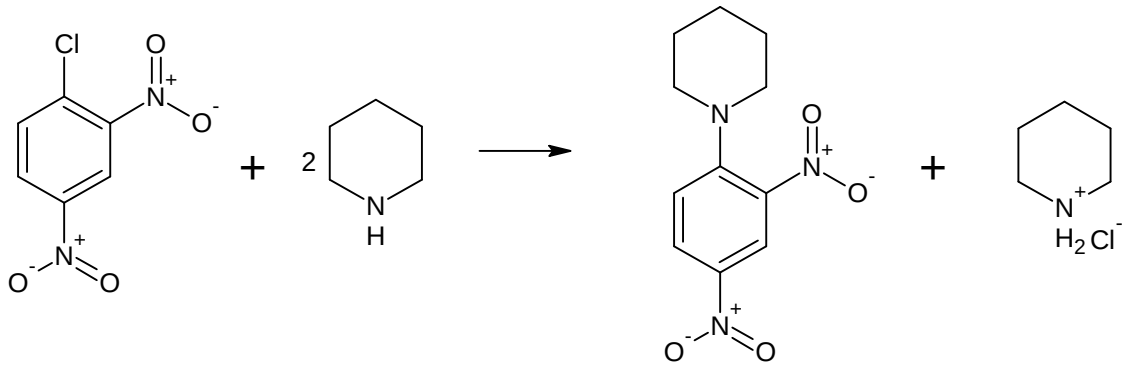
where k is the *rate constant*, [A], [B], … are the molar concentrations, and [Y] is the concentration of a species not represented in the balanced reaction but that still affects the rate (e.g., a spectator ion or a catalyst). The exponent to which a particular species concentrations are raised is called the *order* of reaction with respect to that species. The *overall order* of reaction is the sum of exponents. It is important to note that the exponents are <u>not related</u> to the stoichiometric coefficients of the balanced reaction and are not known in advance. We also do not know which of the species will or will not be present in the rate law. This information can <u>only be gained by experiment</u>.

Reaction rates are generally temperature dependent. Often, this temperature dependence follows the Arrhenius equation:

$$k(T) = A\exp\left(\frac{-E_a}{RT}\right)$$

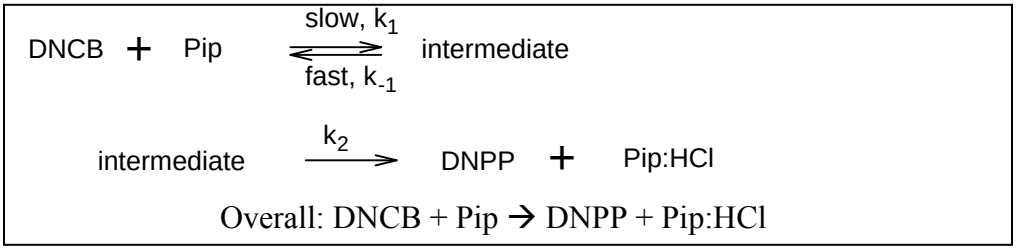
In this equation, A is the preexponential term (a measure of rate at which collisions occur) and E_a is the activation energy (the potential energy barrier that must be surmounted in converting products to reactants).

DNCB + Pip – The reaction of interest: The reaction that will be examined in this experiment involves the reaction of two organic molecules, 2,4-dinitrochlorobenzene (DNCB) and piperidine (Pip) to produce 2,4-dinitrophenylpiperidine (DNPP) and piperidine hydrochloride (Pip:HCl). This reaction is shown below:



DNCB Piperidine DNPP Pip:HCl

This reaction occurs by a two-step mechanism summarized here:



The elementary steps shown above can be used to derive a kinetic expression for the reaction. We propose that the rate of the reaction is approximately equal to the rate of the slow elementary step (i.e., apply the rate determining-step approximation). Then,

$$v = \frac{d[DNPP]}{dt} \cong k_1[DNCB][Pip]$$

If [DNPP] is zero at $t = 0$, the following equations hold true:

$$[DNCB]_t = [DNCB]_0 - [DNPP]_t$$

$$[Pip]_t = [Pip]_0 - [Pip]_t$$

where $[X]_t$ is the species concentration at some time t and $[X]_0$ is the species concentration at time $t = 0$. By substituting these expressions into the rate law, we get the differential rate law:

$$\frac{d[DNPP]}{dt} = k_1\{[DNCB]_0 - [DNPP]\}\{[Pip]_0 - 2[DNPP]\}$$

This equation holds true for all cases. We will examine two limiting sets of conditions in lab. These conditions are given below along with the integrated rate laws for each case. (Note for pre-lab, you will be showing how to use the pseudo-first order integrated rate law to find k_1).

1. Simple second order: $[Pip]_0 = 2\,[DNCB]_0$

   Integrated rate law:

$$\frac{1}{[DNCB]_0 - [DNPP]} = \frac{1}{[DNCB]_0} + 2k_1 t$$

2. Pseudo first order: $[Pip]_0 >> [DNCB]_0$

$$\ln\left\{1 - \frac{[DNPP]}{[DNCB]_0}\right\} = -\{[Pip]_0 k_1\} t$$

Each of these conditions permits determination of k_1 by using an appropriate plot vs. time and a linear regression. Once these conditions are examined experimentally, an additional experiment can be conducted at various temperatures in order to examine the temperature dependence of rate which should obey an Arrhenius relationship permitting determination of the activation energy.

Pre-Lab Exercises

See separate document for pre-lab questions. These will be turned in at the beginning of lab. In addition, read the appropriate chapter of Halpern to gain additional insight on the reaction of interest (book available in Nobel 107).

Safety Precautions

- Safety goggles must be worn at all times.
- It is recommended that a laboratory coat that covers clothes and arms be worn.
- All work MUST BE DONE IN THE HOOD.
- 1-chloro-2,4-dinitrobenzene (DNCB) is highly toxic irritant – wear gloves at all times and wash immediately with soap and water if any DNCB gets on your skin.
- Piperidine is a toxic and flammable liquid with an objectionable odor.
- Properly dispose of waste materials.

Procedure

Summary: Given that DNPP is a colored compound we can follow the reaction by using visible absorption. By using Beer's law, given below, we can find the $[DNPP]_t$.

$$[DNPP]_t = \frac{A_t}{\varepsilon_\lambda l}$$

where A_λ is the absorbance at a given wavelength, ε_λ is the molar aborptivity for DNPP, and l is the pathlength. For DNPP: $\varepsilon_{472\text{ nm}} = 360$ dm^3/mole cm and $\varepsilon_{372\text{ nm}} = 17{,}000$ dm^3/mole cm. Note: You'll do these calculations for a series of time points. At each time, record absorbance at a particular wavelength, λ and then convert the absorbance to $[DNPP]_t$. Using the pseudo-first order integrated rate law given above, you will find k_1. You will then vary the temperature of the system and determine k_1 at the different temperatures. From this, you can find A and E_a.

General Steps:

1. Prepare stock solutions of 0.620 M Piperidine in **absolute ethanol** and 0.0104 M DNCB in **absolute ethanol.** (These stock MAY have been left by prior groups, but you may want to make your own to ensure proper concentrations.)
2. Prior to running the experiment, scan the UV-Vis absorption spectrum of your *reactants* (after keeping them under isothermal conditions in the water bath; use 25 °C). Use the Ocean Optics USB 2000 spectrometer for this. (There are instructions on the hardware/software at the end of this document and on the course website.)
3. Mix the reactants and some absolute ethanol in accurately measured volumes (e.g, 1.0 mL each reactant and 2.0 mL absolute ethanol) and set aside for 5-10 minutes. Then record, store, and print the absorption spectrum of *product*; determine the proper detection wavelength. Determine the molar absorptivity of the product at this concentration (assume DNCB is the limiting reagent and that the experiment went to completion; *don't forget that you diluted when mixing*.)
4. For the kinetics experiments, we will focus on the pseudo-first order case outlined above, i.e., where [Pip] is in excess. Add 0.60 mL of DNCB and 2.00 mL of ethanol into the test tube. Prepare the instrument (i.e, get dark and reference, set-up up for kinetic study). When ready, add 0.5 mL of Pip, use probe to lightly mix, and start collection. Collect for 15 minutes.
5. Carry out the reactions at a second and third temperature. After finding the rate constants (see #6), use the Arrhenius equation to find E_a and A.
6. Use the equation outlined above for the pseudo-first order kinetics condition, determine the rate constant for each set of data.

Report/Analysis

Follow the general lab report guidelines – write in the style of a communication. In the experimental section, be sure to discuss on any deviations from your planned procedure. Your data (i.e., results section) should include UV-Vis spectra (one of each reactant, one of the product mixture, and any others you deem important), any plots used to determine the rate constant, preexponential, and activation energy, and a table(s) of those parameters. In the discussion, include the following (and any other thoughts you deem important…).

- Discuss the meaning and importance of k, A, and E_a.
- Consider what effect changing from piperidine to another amine might have on the reaction. Give two examples.
- How would steric bulkiness of the amine and the electron-donating ability of the amine affect the stability of the intermediate and the rates of reaction?

References

1. Halpern, A. M. "Experimental Physical Chemistry: A Laboratory Textbook, Exp 21." 2nd Ed. Prentice Hall: Upper Saddle River, NJ. Pg 341. [Available in Nobel 107]
2. McQuarrie, D.A., Simon, J.D., "Physical Chemistry: A Molecular Approach." University Science Books: Sausalito, CA. Chapter sections 23-3 and 23-4 (pp 935-944).

OOIChem Software for Ocean Optics UV-VIS Spectrometers

We will use OOIChem Software to collect UV-Vis spectra and kinetics information (i.e., Absorbance vs. Time). This software can be found on the lab machines under the Chemistry/Ocean Optics folder. The following notes will help you properly set up the software for use in the lab.

1. The software sometimes has problems recognizing the hardware. Lab instructors/TAs can help troubleshoot or you can try the following.
    a. Go to the Control Panel to Add Hardware. Step through each dialog box as they come up. When prompted, choose "I've already installed".
    b. Once you've added the hardware, you need to tell the software it is there. Open OOIChem, go to Configure/Hardware and choose USB under A/D convertor type. Click OK.
    c. Check that the software has recognized the hardware. Go to Configure/Spectrometer. Under "Serial #" there should be a recognizable value such as USB#### (not greek letters).
    d. Once the software and hardware are communication, continue on to #2.
2. Prior to obtaining data on your samples, you need to take a reference and dark sample to calibrate the spectrometer.
    a. Dark sample: Turn off the lamp (or unplug if there is no off switch). Click on "Dark" toggle button (bottom right hand side of screen). Turn lamp back on and let it warm up for 5-10 minutes.
    b. Reference: The reference is generally your solvent for the experiment. Prepare the reference in a cuvette for most experiments and in a large test tube for kinetics experiments (test tube must be large enough for probe). If using the probe, change your integration period to 5000 ms and your boxcar smooth to 10. When lamp is warm, put cuvette in holder (or put probe in test tube) and click on "Reference" toggle button (bottom right hand side of the screen).
3. Switch to Absorbance mode (using drop down menu on top left of screen). Change your axes (by clicking on the first and/or last value on axes) so you have a y-axis range of -0.2 to 1 and a x-axis range of 250-700 nm (or other appropriate values). Your baseline should be present and be nearly flat.
4. Collecting data…
    a. UV-Vis spectra: Fill cuvette and put in holder (alternatively, put probe into a test tube filled with sample). Use the "scan/stop" toggle button (bottom right) to collect spectra. Save spectra.
    b. Kinetic samples: First configure the software properly, and then collect data:
        i. Go to Configure/Kinetics. In box, change Preset Duration (total collection time) to appropriate time limit (~15-20 min). Change Sampling Interval (time between data points) to ~10 s. Set wavelength(s) of interest in right hand boxes. Click OK.
        ii. Go to Configure/Spectrometer. Choose the Display tab. Choose "Spectrum and kinetics" from bottom drop box.

iii. Choose “Chart Active” and “Continuous” at bottom right. Use “Scan/Stop” Toggle button to collect data. (Note: Time counts down under the plots.)

5. Saving data: Save the kinetics values to get data as wavelength vs. time. Save spectral values to save spectra. Both types will be saved as an ASCII (or text) file that can be opened and manipulated in Excel. See the lab instructors or TAs if you have questions – not saving data properly can cause you to repeat part of the experiment!