

Solution Kinetics of a S_N2 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

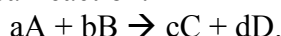
1. Halpern, A. M. "Experimental Physical Chemistry: A Laboratory Textbook." 2nd Ed. Prentice Hall: Upper Saddle River, NJ. [Available in Nobel 107]
2. McQuarrie, D.A., Simon, J.D., "Physical Chemistry: A Molecular Approach." University Science Books: Sausalito, CA. Chapter 28.

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 application, and gain some understanding of the mechanism of the reaction.

Consider a general chemical reaction:



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

$$v = k[A]^a[B]^b[C]^c[D]^d[Y]^e$$

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 not related 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 only be gained by experiment.

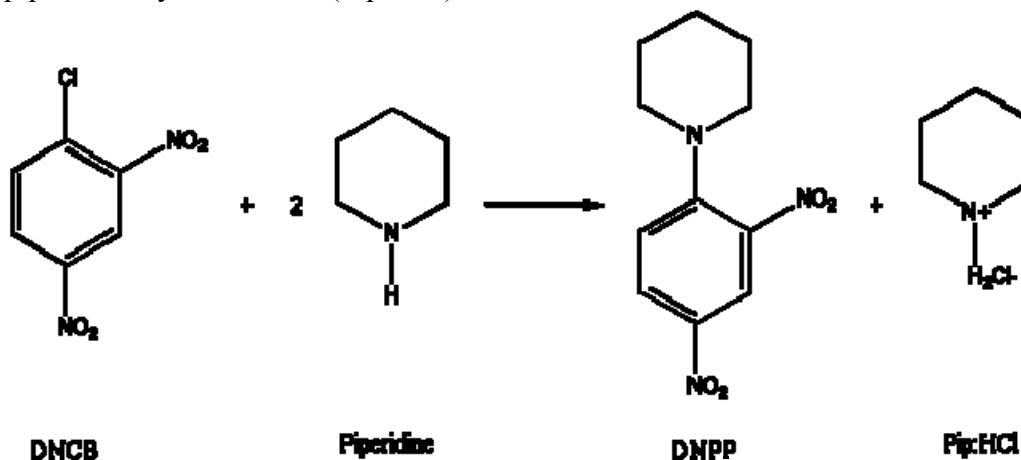
Reaction rates are generally temperature dependent. Often, this temperature dependence follows the Arrhenius equation:

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

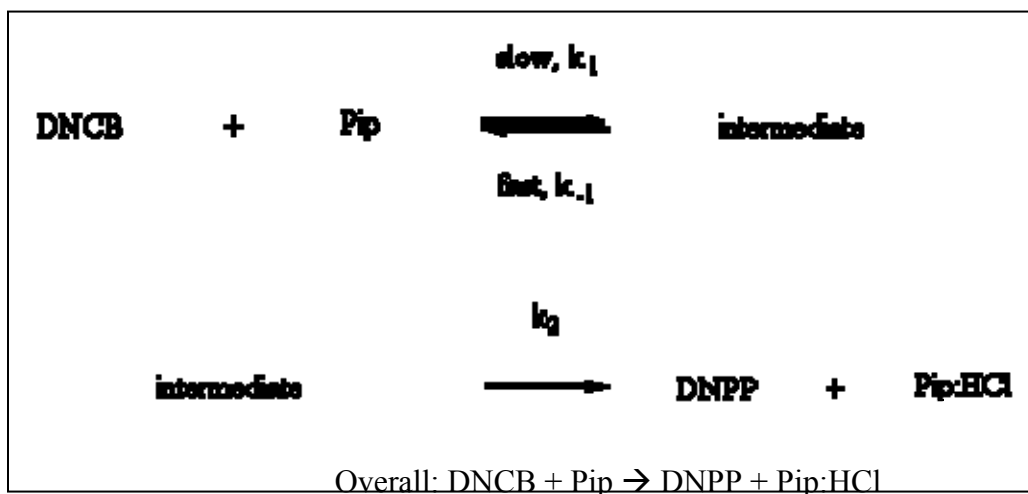
In this equation, A is the preexponential term and E_a is the activation energy (the potential energy barrier that must be surmounted in converting products to reactants).

DNCB + Pip – The reaction of interest: The reaction that will be examined in this experiment involves the S_N2 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:



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,

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

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

$$[\text{DNCB}]_t = [\text{DNCB}]_0 - [\text{DNPP}]_t$$

$$[\text{Pip}]_t = [\text{Pip}]_0 - [\text{Pip}]_t$$

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:

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

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 these integrated rate laws to find k_1).

1. Simple second order: $[\text{Pip}]_0 = 2 [\text{DNCB}]_0$

Integrated rate law:

$$\frac{1}{[\text{DNCB}]_0 - [\text{DNPP}]} = \frac{1}{[\text{DNCB}]_0} + 2k_1t$$

2. Pseudo first order: $[\text{Pip}]_0 \gg [\text{DNCB}]_0$

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

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 $[\text{DNPP}]_t$. Note: You'll do these for a series of time points. At each time, record absorbance at a particular wavelength, λ . Beer's Law:

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

where A_λ is the absorbance at a given wavelength, ϵ_λ is the molar absorptivity for DNPP, and l is the pathlength. For DNPP: $\epsilon_{472 \text{ nm}} = 360 \text{ dm}^3/\text{mole cm}$ and $\epsilon_{372 \text{ nm}} = 17,000$

dm³/mole cm. Using the integrated rate laws given above, you will find k_f for one of the limiting cases. The temperature of your system will be varied to find A and E_a .

General Steps:

1. Prepare stock solutions that will result in an appropriate absorption if we consider all of the DNCB converting into DNPP. Stock solutions of 0.620 M Piperidine in absolute ethanol and 0.0104 M DNCB in **absolute ethanol** can be made up and diluted for your work. (These stock MAY have been left by prior groups.)
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; start at 25 C). Use the Ocean Optics USB 2000 spectrometer for this. (There are instructions on the hardware/software needed next to the computer.)
3. Mix the reactants in accurately measured volumes (e.g, 2.0 mL each) and set aside for 5-10 minutes. Then record, store, and print the absorption spectrum of *product*; determine the proper detection wavelength. (You'll want to choose something in the 465-475 nm range.) 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. If time permit, try an experiment under the other set of conditions.

Report/Analysis

Follow the general lab report guidelines. In the experimental section, add a discussion 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 .
- Compare the values of k_1 obtained from the two limiting cases.
- 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." 2nd Ed. Prentice Hall: Upper Saddle River, NJ. [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).