The Isomerization of 4-anilino-4’-nitroazobenzene
Pre-Lab Assignment

Introduction

The ability to accurately and efficiently determine time-dependent properties of a reaction is of fundamental importance to all aspects of science. Flash photolysis is one such method which can be used in combination with simple spectroscopic techniques to monitor the kinetic processes of a reaction. This technique has applications in a wide variety of fields. For example, El-Khouly at Tanta University is using laser flash photolysis to study the intermolecular electron transfer processes of C$_{60}$\(^1\) while Feng et al. from the University of New Mexico are using the technique to study intraprotein electron transfer in the neural synthase of rats.\(^2\)

The kinetics of the photo-induced isomerization of 4-anilino-4’-nitroazobenzene were studied by a simple flash photolysis. 4-anilino-4’-nitroazobenzene usually exists in its thermodynamically preferred trans- isomer shown in Figure 1. Upon excitation by light, the N-N bond becomes more facile and rotation is allowed about it, generating the cis- isomer shown in Figure 2. Once the light source is removed, the cis- isomer will begin to back convert to the thermodynamic form.

![Figure 1: Structure of trans-4-anilino-4’-nitroazobenzene](image)

In the flash photolysis used in this experiment, a sample is exposed to a simple camera flash, exciting the 4-anilino-4’-nitroazobenzene. Because the trans- isomer greatly absorbs in the wavelength range of the flash, the change in absorbance of the sample can be detected by a simple UV-Vis spectrometer. To study the kinetics of this isomerization reaction, however, the change in concentration of a sample with time is needed.

This is accomplished by relating the time-coupled absorbance data to concentration data through the use of Beer’s law shown in Equation 1 where $A$ is the absorbance, $\varepsilon$ is the molar absorptivity constant, $b$ is the cell pathlength (in this case, 1 cm), and $C$ is the concentration of the sample, in this case the trans- isomer.

$$A = \varepsilon b C$$

(1)

Using this information, a number of other properties of the reaction can be determined. These include the rate constant, $k$, the enthalpy of activation $\Delta H^*$, the entropy of activation $\Delta S^*$, the activation energy $E_a$, and the frequency factor $A$.

After substituting $A$ in appropriately for the concentration of the trans- isomer in the rate equation, the rate constant can be expressed by the integrated rate law shown in Equation 2. Thus, a plot of $\ln(A_\infty - A_t)$ vs. time will allow for the determination of $k$ where $A_\infty$ is the absorbance at an infinite time (obtained from values before the flash), and $A_t$ is the absorbance at time $t$.

$$\ln(A_\infty - A_t) = \left[ \ln\left(\frac{k_b T}{h}\right) + \frac{\Delta S^* R}{h} \right] - \frac{\Delta H^*}{R T}$$

(2)

This equation can be rewritten as Equation 4. Thus, a plot of $\ln(k/T)$ vs. $1/T$ makes it possible to determine $\Delta H^*$ and $\Delta S^*$.

$$\ln(k/T) = \ln\left(\frac{k_b}{h}\right) + \left(\frac{\Delta S^*}{R}\right) - \frac{\Delta H^*}{RT}$$

(3)

Further, the Arrhenius equation, given in Equation 5 below, relates the rate constant to $E_a$ and $A$. The equation can be rewritten as Equation 6 to allow a graph of $\ln(k)$ vs. $1/T$ to easily determine $E_a$ and $A$.

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

(4)
\[
ln(k) = ln(A) - \frac{E_a}{RT}
\]  

(5)

Materials and Methods

Table 1: Physical properties of reagents

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Formula</th>
<th>MM (g·mol(^{-1}))</th>
<th>Density (g·cm(^{-3}))</th>
<th>Misc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>C(_2)H(_6)O</td>
<td>46.068</td>
<td>0.7893</td>
<td>Flammable</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>C(_2)H(_3)N</td>
<td>41.052</td>
<td>0.7857</td>
<td>Flammable</td>
</tr>
<tr>
<td>Aluminum Borohydride</td>
<td>Al(BH(_4))(_3)</td>
<td>71.510</td>
<td>-</td>
<td>Flammable</td>
</tr>
<tr>
<td>Hydrogen Fluoride</td>
<td>HF</td>
<td>20.006</td>
<td>0.818</td>
<td>-</td>
</tr>
</tbody>
</table>

All data obtained from the CRC Handbook of Chemistry and Physics.  
http://www.hbcpnetbase.com

The exact experimental procedures used to carry out this experiment can be found on pages 1-8 of reference [3].

- Here you should list your procedure.
- It should be the procedure from the lab manual written in your own words.
- Feel free to add any extra hints or tips you want to remember.
- But please, write in complete sentences.
- Trust me, it will save you time later when you have to change the list to prose.
- Don’t brush this off - you should be using this list instead of your lab manual in lab.
- Chem 203 lab is cool.
- I’m running out of things to say.
- “I’ve got an idea–an idea so smart that my head would explode if I even began to know what I’m talking about.” - Peter Griffin
- “When I stick this army guy with the sharp bayonet up my nose, it tickles my brain. Hah hah hah ... ow. Oh, now I don’t know math.” - Chris Griffin
- Anyone noticed yet that I’m just filling space to make this longer?
- “Cut my milk!” - Stewie Griffin
- “Woah, woah, woah, woah, woah, woah, woah, woah, woah, woah... Lois, this is not my Batman glass.” - Peter Griffin

• “Hey, mother, I come bearing a gift. I’ll give you a hint. It’s in my diaper and it’s not a toaster.” - Stewie Griffin

• Are you seriously still reading this?

• “I’m not going to call an ambulance this time because if I do you won’t learn anything.” - Brian

• Peter: Oh my god, Brian, there’s a message in my Alphabets. It says, “Oooooo.” Brian: Peter, those are Cheerios.

• Ok, enough of this - back to reading the real stuff! (Hope you enjoyed the break)

Questions to Consider

Here you should answer the “Pre-Lab Questions” and the “Questions to Consider” from the manual. There are not always “Questions to Consider” for each experiment. These should typically be 1-3 sentences if they require written answers, but some may require more exposition. Please try to be concise, however. Strive for clarity and answer the question completely, but not verbosely.

Any questions that require you to work out mathematical answers need to be done in Equation Editor or MathType and should have all work shown.