
- Chemistry Extended Essay -

**A spectrophotometric investigation into the effect of temperature on
the kinetics of a photochromic dye fading**

*What is the effect of decreasing the temperature on the reaction rate and rate constant of
fading of a photochromic dye?*

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1. INTRODUCTION

Background Knowledge:

The term photochromic originates from the Greek words “phos” (light) and “chroma” (color) and is used to describe a substance that changes color on exposure to light. More formally, photochromism is a reversible transformation of a chemical species, induced by the absorption of electromagnetic radiation, involving two forms, A (inactive) and B (active), each having different absorption spectra.¹ Generally, form A is colorless, while form B is a colored solution. Most dyes, inevitably return to their more stable form, the colorless state. Each dye is unique and varies greatly depending on the matrix in which it is dissolved.

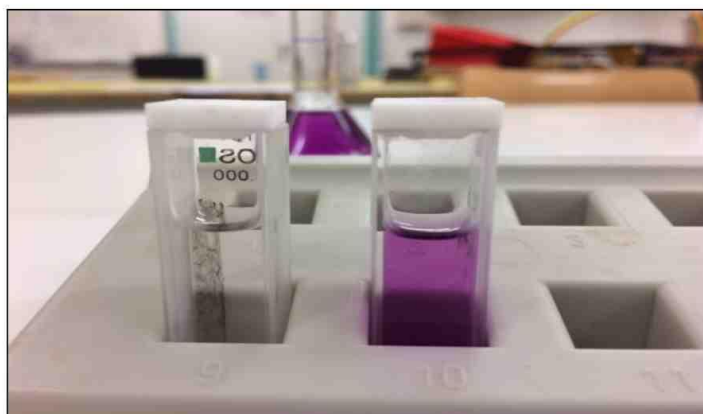


Figure 1 - Visual inspection of the two forms of a photochromic dye solution (on the left: form A, inactive and on the right: form B, active)

The practical applications of photochromism are far reaching. From something as familiar and mundane as color changing prescription glasses, to the innovative field of

¹ Heinz Dürr, Henri Bouas-Laurent eds., *Photochromism. Molecules and Systems Revised edition* (Gulf Professional Publishing, 2003) XXVII

supramolecular chemistry. The photochromic dye in normal glasses absorbs UV wavelengths from the sun, transforming to its activated state and consequently turning regular glasses into sunglasses. The possibility of attaching photochromic units to enzymes, thereby effectively creating an *on* and *off* switch for the enzyme, is a developing area of research. Further applications involve novel 3D optical data storage, where photochromic compounds could be used to potentially store petabytes² of information on a CD allowing us to keep up with the ever increasing amount of data produced in the world.

The unique physical properties of dyes stem from their particular chemical structure. There is a diverse range of chemical groups and reactions that give rise to the exquisite photochromic effect. For instance, *cis-trans* isomerizations or geometric isomerism, where the functional group of a molecule is rotated into a different position or orientation, retaining the same molecular formula. Then there are pericyclic reactions, following UV exposure, the molecule switches to form B by the rearrangement of bonds. The Spiropyrans, the most prevalent class of photochromes, are a good example. When exposed to high energy UV, the sp^3 -hybridized carbon-oxygen bond in a Spiropyran breaks and opens the ring such that the carbon becomes sp^2 hybridized. This process of bond rearrangement forms a colored compound called merocyanine³ (Figure 2). Once the UV source is removed and the dye is moved to a dark room at ambient temperature, the carbon-oxygen bond reforms and returns to its colorless state:

² Min Gu, Xiangping Li, Yaoyu Cao, "Optical storage arrays: a perspective for future big data storage" (*Light: Science & Applications* 23rd May 2014, DOI:10.1038/lsa.2014.58)

³ Eilmes, Andrzej, "Spiropyran to Merocyanine Conversion: Explicit versus Implicit Solvent" *Journal of Physical Chemistry* 2013, 117 (12) DOI: 10.1021/jp3117209

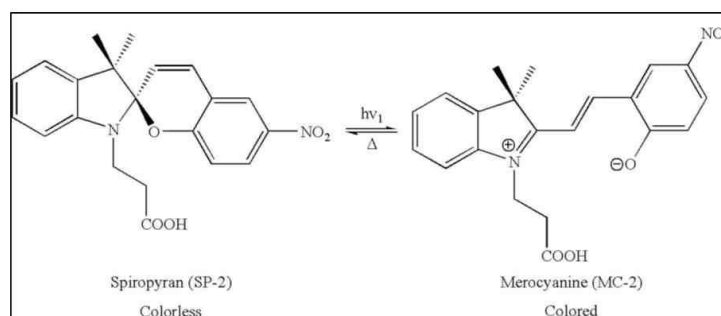


Figure 2 - Change in Spiropyran to Merocyanine rearrangement after exposure to high energy UV radiation.

The dye analyzed in this investigation is a proprietary aryl substituted heterocyclic organic compound. A heterocyclic compound is a cyclic compound with rings composed of at least two different elements⁴, while an aryl is a group obtained from an aromatic ring or arene by the removal of hydrogen from the carbon atom ring⁵. In a photochromic context, an aryl substituted heterocyclic compound could achieve greater thermal irreversibility, an increased reactivity or resistance to fatigue.⁶

Typical chemical kinetic parameters can be used to characterize the transformation of photochromic dyes.⁷ In this investigation, I aim to determine whether the fading of this proprietary dye transformation from form B back to form A follows first order kinetics. The defining feature of a first order kinetics curve is that the rate of reaction is directly proportional to the concentration of the reactants. For this to be turned into a rate expression

⁴ M. Nic, J. Jirat, B. Kosata, "Compendium of Chemical Terminology, 2nd ed. Gold Book" comp. A. D. McNaught and A. Wilkinson (Blackwell Scientific Publications, Oxford 1997), 1340

⁵ M. Nic, J. Jirat, B. Kosata, "Compendium of Chemical Terminology, 2nd ed. Gold Book", 1320

⁶ Masahiro Irie, Kingo Uchida, "Synthesis and Properties of Photochromic Diarylethenes with Heterocyclic Aryl Groups" Chemical Society of Japan Journals, 1998, Vol. 71, No. 5

⁷ David J. Mcgravey "Photochromism in View" Royal Society of Chemistry (2008): <https://eic.rsc.org/feature/photochromism-in-view/2020209.article>

or rate law, the rate constant, k , must be added and the concentration of the reactant is raised to the power of 1:

$$\text{Rate of Reaction} = k[\text{form B of photochromic dye}]$$

The rate constant, k , in the above expression is a fixed value at a specific temperature with units of s^{-1} in first order reactions. The Beer-Lambert law states that the amount of light absorbed by a substance dissolved completely is directly proportional to the concentration⁸. Therefore, the decrease in concentration of form B of the dye is directly proportional to the absorbance which means that the rate can be calculated and the order determined.

Another factor that affects kinetics is the activation energy. The fade rate from form B to A is dependant on the activation energy⁹, the higher the activation energy, the slower the rate of reaction. This leads to different applications for different types of photochromic compounds. Dyes with a high activation energy are used in optical memory devices as it is necessary for them to stay in form A. While dyes with a low activation energy are used in items such as prescription glasses as the transformation between the two dye forms needs to be quick.

The overall aim of this investigation is to describe the kinetic properties of a proprietary dye by measuring the photochromic reaction rate in a laboratory setting. Such properties can determine the practical applications of dyes and explain the complicated chemistry behind a simple observable color change.

⁸ Wikilectures, "Lambert-Beer Law", last modified 14 August 2016
http://www.wikilectures.eu/w/Lambert-Beer%27s_law

⁹ K. Horie, H. Ushiki, F.M Winnik, *Molecular Phototonics: Fundamentals and Practical Aspects* (Tokyo, Kodansha Ltd, 2000) 85.

Research Question:

What is the effect of decreasing the temperature on the reaction rate and rate constant of fading of a photochromic dye?

The Arrhenius equation can be used to show the effect of temperature on the rate constant. By decreasing the temperature, the rate of the transformation of the photochromic dye back to its colorless state is also likely to decrease. However, there are cases where reaction rates can be independent of temperature, this is called non-Arrhenius behavior, or in other cases where the rate constant decreases with increasing temperature, anti-Arrhenius.¹⁰

This investigation aims to explore the properties of a proprietary photochromic dye. This will be achieved by determining the order of the fading reaction, the effect of temperature on the rate constant (k) and the value of the activation energy by using the simultaneous form of the Arrhenius equation:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

The results will allow a profile of the unknown photochromic dye to be built and investigated. This information might be used to decide its potential applications in advancing technology or in everyday life.

¹⁰ Valter H.C. Silva, Vincenzo Aquilanti, Heibbe C.B. de Oliveira, Kleber C.Mundim "Uniform description of non-Arrhenius temperature dependence of reaction rates, and a heuristic criterion for quantum tunneling vs classical non-extensive distribution", *Chemical Physical Letters* 590, (2013):201-207 <https://doi.org/10.1016/j.cplett.2013.10.051>

Variables:

Independent Variables	
<i>Variable</i>	<i>How it will be changed</i>
Temperature	The first experiment will be performed with the photochromic dye at room temperature, then the sample will be cooled down by 10 - 15 degrees Celsius, using an ice water bath.

Table 1 - Independent variables

Dependent Variables	
<i>Variable</i>	<i>How the change will be measured</i>
Reaction rate	The reaction rate will be measured by the change in absorbance against time of the photochromic dye at two different temperatures. Then the rate constant will be derived from the plot of reaction rate vs time.
Activation energy	If the rate constants are different at the two temperatures measured, the activation energy will be calculated using the simultaneous form of the Arrhenius equation.

Table 2 - Dependent variables

Control Variables		
<i>Variable</i>	<i>Effect on experiment</i>	<i>How it will be controlled</i>
UV intensity/the time the sample is exposed	If the UV source is too intense or the sample is exposed for too long, it will cause the dye to degrade and decrease its colorability. This is known as dye fatigue and will affect the experiment by decreasing the absorbance reading of the dye and alter the absorbance - time curve and in turn the value of k.	The same UV lamp set at a relatively low wavelength (UV-B) will be used to only expose the sample for 5 seconds at a time before placing it in the spectrophotometer. Additionally, the volumetric flask containing the dye will be kept out of sunlight so as to further avoid dye fatigue.
The organic solvent used to dissolve the dye	If a different solvent were to be used it would likely alter	Only acetone will be used to dissolve the photochromic

	the properties of the dye which are known to be heavily dependent on the matrix. If the solvent were to be changed it would likely affect fading time and the absorption of the dye.	dye powder.
Dye reactivation by UV exposure	If the dye sample is exposed to even the smallest waves of UV radiation again it will reactivate the dye, slowing down the fading process and consequently slowing down the rate.	The experiment should be performed in a dark room with the blinds closed, or in a basement with no chance of UV radiation from the Sun interfering with data collection.

Table 3 - Control variables

2. MATERIALS & METHOD

In this investigation, spectrophotometry was used to detect the concentration of the active form of the dye and to measure its transformation to the inactive form against time. If the relationship follows first order decay, the rate constant will be measured by plotting the rate of reaction against absorbance and calculating the gradient of the linear line. This allows the rate of reaction and rate constant to be determined at two different temperatures of the dye and in turn the activation energy to be calculated - if there is a difference in rate constant.

The first step in this investigation was determining the suitable dye concentration (Trial Experiment 2). The initial dye concentration that was made up was colored dark purple even before exposure to the UV source. Henceforth, an ideal dye concentration was found by serial dilutions and exposing the sample to the UV lamp. The concentration with the longest fading rate and the greatest difference in absorbance between form B and A was chosen for the primary experiments.

Risk Assessment:

There were a few safety concerns that had to be taken into consideration. The first is that acetone is highly flammable and an irritant to eyes and skin. Moreover, acetone vapors can cause drowsiness or dizziness. Hence, this experiment should be performed in a fume cupboard. Furthermore, the dye powder is also an irritant. The dye solution should be properly disposed of, not in a sink, as it is potentially harmful to aquatic life.

Apparatus List:

- 1) Photochromic dye (LCR Hallcrest) there was no information on the composition as it is proprietary information.
- 2) Vernier SpectroVis Plus and the connecting cables (spectrophotometer)
- 3) Acetone in a squeeze bottle
- 4) Quartz cuvette set (one containing dye, the other containing acetone for the calibration of the SpectroVis Plus)
- 5) UV lamp (around 300 - 360 nm)
- 6) A data logger compatible with SpectroVis Plus downloaded on a computer such as LoggerPro
- 7) 50 ml volumetric flask
- 8) 20 ml volumetric flask
- 9) 10 ml pipette
- 10) Beaker containing ice and water
- 11) Temperature probe
- 12) Stopwatch

Method for Preliminary Experiment 1: *Determining the suitable concentration of the dye solution*

I noticed that if the solution is too concentrated, there would be no observable change between the activated and deactivated form of the dye, even when the UV source was removed making it impossible to determine the fall in absorbance at a certain wavelength. This showed that the concentration of the dye did affect the time it took for the dye to fade, so it had to be taken into account as a variable.

- 1) 0.2500 g of the photochromic powder was dissolved in 50 ml of acetone to make up a 0.0050 g ml⁻¹ solution in a volumetric flask.
- 2) The sample was activated by exposure to UV and the approximate time for the dye to fade back to the deactivated form was recorded in the table.
- 3) 1:2 dilutions were performed serially by taking 10 ml of the starting solution and adding 10 ml of acetone to make up 20 ml solution of dye in a volumetric flask.
- 4) Steps 3 was performed eight times, for each dilution, the approximate time for the dye to fade back to the deactivated form was recorded using a stopwatch while observing the absorbance fall in LoggerPro.

Method for Preliminary Experiment 2:

Generating absorption spectra and determining the maximum wavelength

- 1) The spectrophotometer was calibrated using a blank by pipetting 1 ml of acetone into a quartz cuvette.
- 2) Approximately 1 ml of the dye solution, at the concentration selected in preliminary experiment 1, was pipetted into the quartz cuvette and placed into the SpectroVis Plus to generate the absorption spectrum of the inactive form of the dye using LoggerPro.
- 3) The cuvette was exposed to UV for 5 seconds and then quickly placed into the SpectroVis Plus to generate the absorption spectrum of the activated form of the dye using LoggerPro.
- 4) The maximum wavelength of absorption was recorded by looking at the peak on the graph.

Method for Primary Experiment 1:

Sample at room temperature

- 1) The spectrophotometer was calibrated using the acetone as the blank.
- 2) The SpectroVis Plus was set to measure the decrease in absorbance at the wavelength determined in preliminary experiment 2 against time using LoggerPro.
- 3) The dye solution was prepared as detailed in preliminary experiment 1, 1 ml of dye at room temperature was pipetted into the quartz cuvette.
- 4) Using a temperature probe, the temperature of the dye sample was recorded.
- 5) The overhead lights were switched off and the UV lamp was turned on.
- 6) The dye sample was exposed for 5 seconds and then the activated dye was quickly placed in the spectrophotometer to record the decrease of absorbance against time using LoggerPro.

Method for Primary Experiment 2:
Sample at decreased temperature

Steps 1 - 2 and 4 - 6 were repeated as in primary experiment 1. In step 3, the volumetric flask containing the solution was placed in the ice bath for five minutes before being pipetted into the cuvette. The sides were wiped to remove condensation before placing in the spectrophotometer.

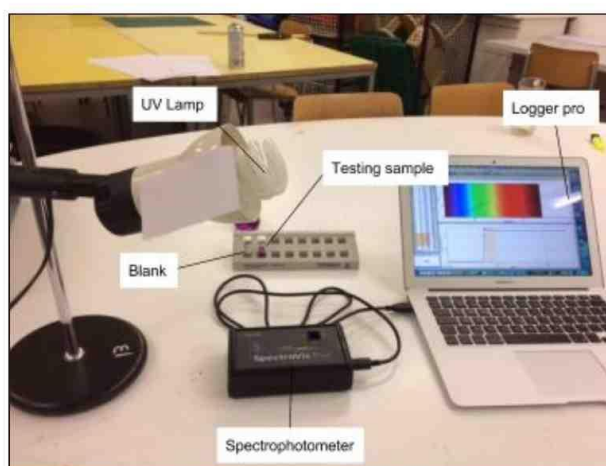


Figure 3 - Primary experiment setup

3. RESULTS

Preliminary Experiments

Experiment 1: Determining the ideal concentration of the dye solution

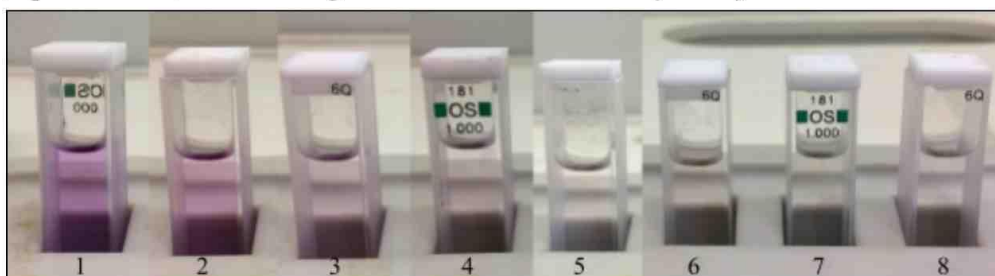


Figure 4 - Samples of the dye in quartz cuvettes after each dilution

	Recorded mass (g)	Dilution factor	Conc. (g ml ⁻¹)	%	Fade time (s)
Value	0.2527	0	0.0051	0.505	

Table 4 - Sample 1 dilution results

Sample 1 observations: The sample was colored in the inactive state. Once exposed to UV, it became marginally darker purple and faded almost immediately back to its original form. It would have been impossible to measure the fall in absorbance of this sample considering that by the time I could transfer the dye to the spectrophotometer, it would have already been in its original state.

Following the procedure detailed in Materials and Methods, I then performed several more dilutions until I reached the ideal concentration:

	Recorded mass (g)	Dilution factor	Conc. (g ml ⁻¹)	%	Fade time (s)
Values	0.2527	1/64	0.0002	0.016	10

Table 5 - Sample 7 dilution results

Sample 7 observations: The fading time was detectable and the absorbance difference between the two states maximal.

	Recorded mass	Dilution factor	Conc. (g ml ⁻¹)	%	Fade time (s)
Values	0.2527	1/128	0.0000	0.001	10

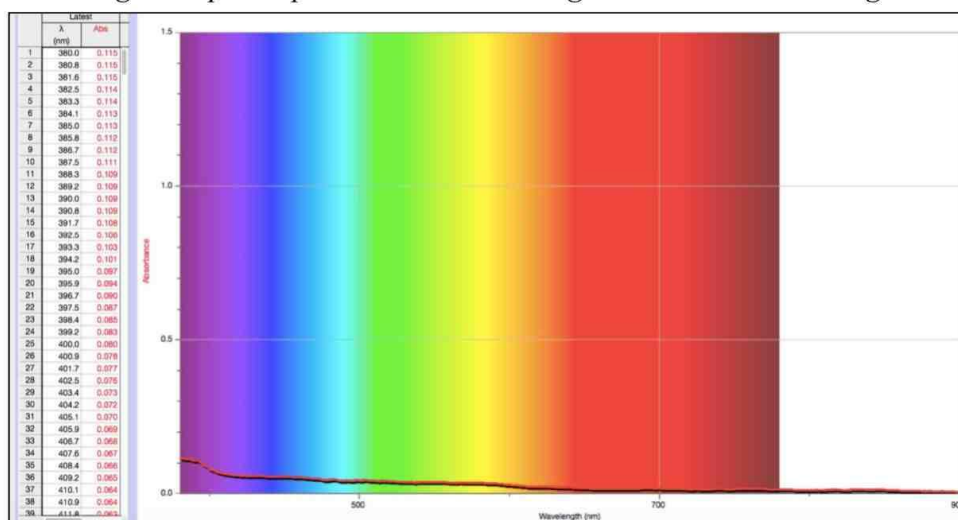
Table 6 - Sample 8 dilution results

Sample 8 observations: The fading time is the same as sample 7 but the absorbance difference between the two states of the dye was smaller.

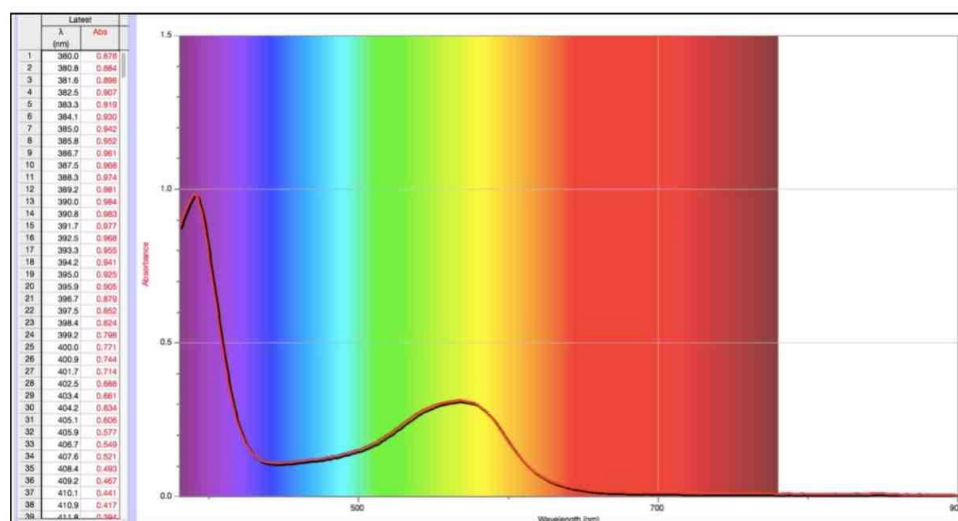
The concentration of sample 7 was used in the subsequent experiments. Results for samples 2 - 6 are available in the appendix.

Experiment 2:

Generating absorption spectra and determining the maximum wavelength



Graph 1 - Absorption spectrum of inactive sample before UV exposure



Graph 2 - Absorption spectrum of active sample after UV exposure

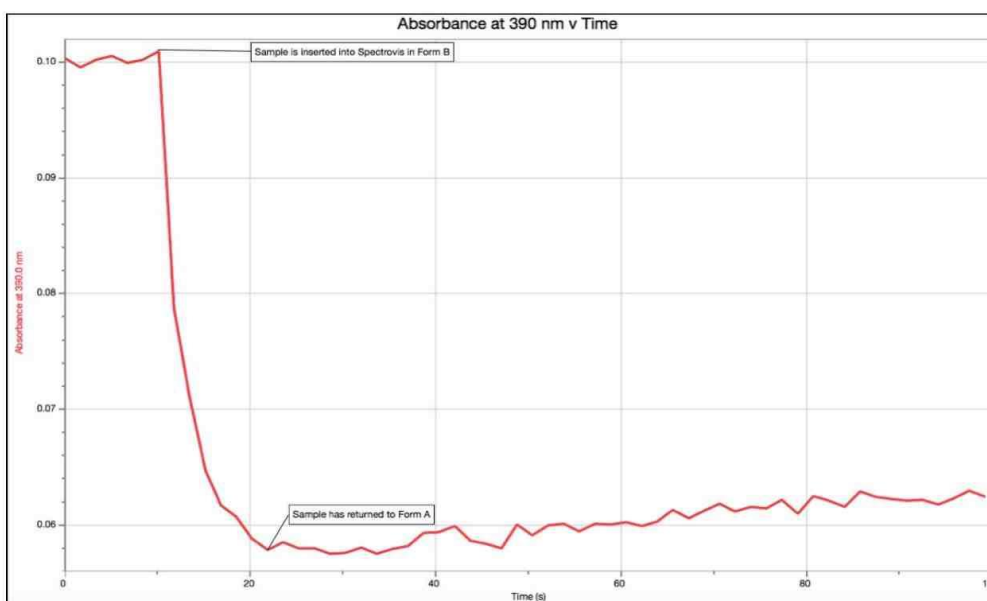
Sample 7 absorption spectrum shows a peak at 390 nm and at 560 nm. The peak at 390 nm gives a stronger signal. Therefore, it was chosen for the Primary Experiment 1 and 2

as the signal will be decreasing and needs to stay above the noise level for accurate data to be collected.

Primary Data Collection

Sample at Room Temperature (27.1 C): Run number 3

Despite the numerous runs I performed at the same wavelength, only run number 3 was successful. The other runs did not contain an appropriate data set that had more than 4 measurable points. This was mostly due to the fast reaction rate and partial data lost due to the transferring time of the cuvette to the spectrophotometer. The fading reaction proceeded for 12 seconds before the absorbance signal reached noise level (Graph 3):



Graph 3 - Change in absorbance over time due to the fading of the photochromic dye at 27.1 C, enlarged version in appendix

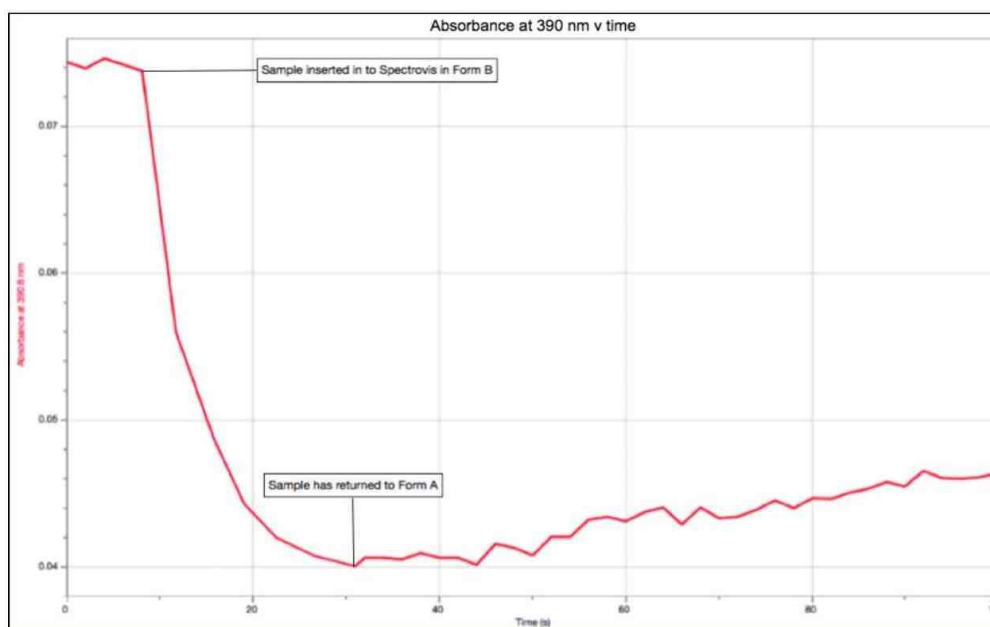
Time (s)	Absorption (at 390 nm)
12	0.097

14	0.071
16	0.065
18	0.062
20	0.061
22	0.059
24	0.058

Table 7 - Relevant data points from Graph 3

Sample at decreased temperature (10.7 C):

The issue with cooling the sample down in the ice bath was that condensation formed on the cuvette walls, affecting the absorbance reading which led to poor reproducibility, only one of the runs out of several had usable data that could be analyzed further. The fading reaction proceeded for 22 seconds before the absorbance signal reached noise level (Graph 4):



Graph 4 - Change in absorbance over time due to the fading of the photochromic dye at 10.7 C, enlarged version in the appendix

Time (s)	Absorption (at 390 nm)
8	0.074
10	0.069
12	0.058
14	0.053
16	0.050
18	0.046
20	0.044
22	0.042
24	0.041
26	0.040
28	0.040
30	0.040

Table 8 - Relevant data points from Graph 4

4. DATA ANALYSIS

To determine the fading reaction rate, I used the tangent tool on LoggerPro to obtain an accurate value for the relevant data points from Table 7 and 8 for each sample.

Sample at Room Temperature (27.1 C):

Time (s)	Absorbance (at 390 nm)	Slope (absorbance s ⁻¹)	Rate (absorbance s ⁻¹)
0	0.097	-0.018	0.018
2	0.071	-0.0086	0.0086
4	0.065	-0.0040	0.0040
6	0.062	-0.0017	0.0017

8	0.061	-0.0011	0.0011
10	0.059	-0.00090	0.00090
12	0.058	-0.00070	0.00070

Table 9 - Relevant absorption, slope and rate readings of the sample at room temperature. Time zero was assigned to the start of the absorbance decrease or time 12 second in Table 7.

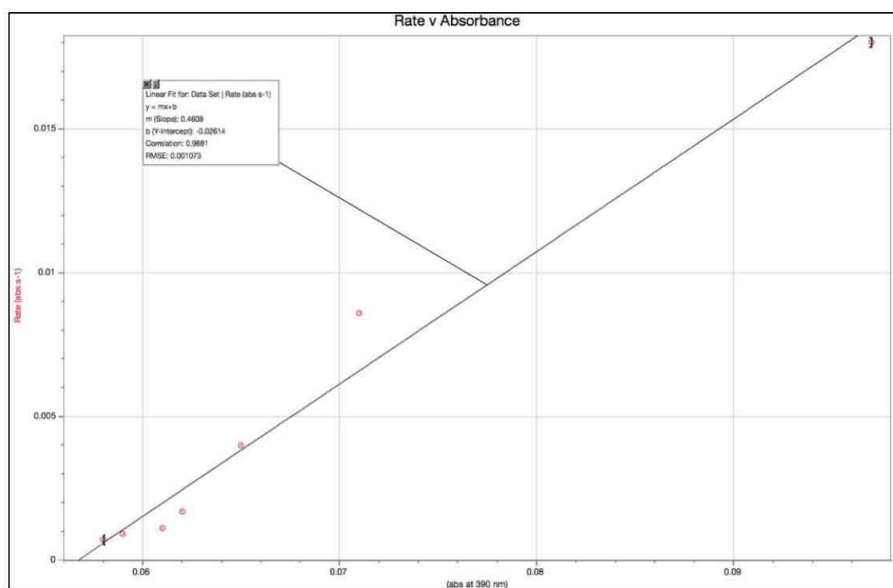
Calculating k at Room Temperature (27.1 C):

In making the assumption that the reaction is first order, a value for k will be determined by fitting the equation, Rate of Reaction = [form B of photochromic dye] to the linear function $y = mx + c$:

y	m	x	c
Rate of Reaction	k	[form B of photochromic dye]	0

Table 10 - Fitting the rate equation to line function $y = mx + c$

Hence, if the rate of reaction was plotted against the concentration or the absorbance (as per Beer-Lambert law) of the photochromic dye the gradient has to be equal to k . Furthermore, according to this relationship, the line should pass through the origin meaning the systematic error can be determined by the displacement in the y-axis.



Graph 5 - Rate of reaction against absorbance for the sample at room temperature, enlarged version in the appendix

$k = \text{gradient}$

$$k = 0.4608 \pm 0.0261 \text{ s}^{-1}$$

Sample at Decreased Temperature (10.7 C):

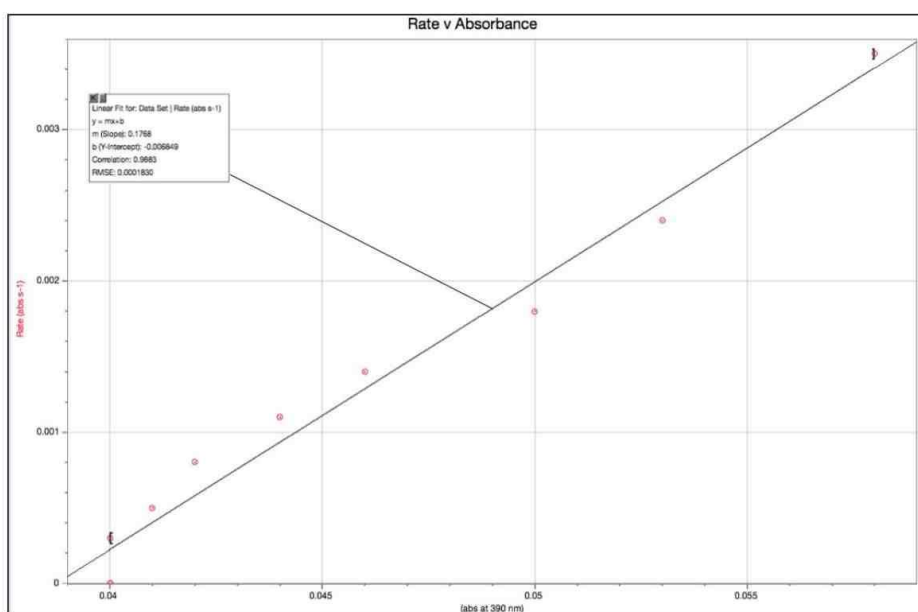
Time (s)	Absorption (at 390 nm)	Slope (absorbance s ⁻¹)	Rate (absorbance s ⁻¹)
0	0.074	-0.0032	0.0032
2	0.069	-0.0036	0.0036
4	0.058	-0.0035	0.0035
6	0.053	-0.0024	0.0024
8	0.050	-0.0018	0.0018
10	0.046	-0.0014	0.0014
12	0.044	-0.0011	0.0011
14	0.042	-0.0008	0.0008
16	0.041	-0.0005	0.0005
18	0.040	-0.0003	0.0003

20	0.040	-0.0000	0.0000
22	0.040	-0.0000	0.0000

Table 11 - Relevant absorption, slope and rate readings of the sample at the decreased temperature. Time zero was assigned to the start of the absorbance decrease or time 8 second in Table 8.

Calculating k at Decreased Temperature (10.7):

The first two data points from Table 11 were omitted from the graph below as they were outliers, see evaluation and discussion.



Graph 6 - Rate of reaction against absorbance for the sample at decreased temperature, enlarged version in the appendix

$k = \text{gradient}$

$$k = 0.1768 \pm 0.0068 \text{ s}^{-1}$$

The rate constant of the sample at decreased temperature is 2.6 fold smaller than k at room temperature, indicating that temperature does have a significant effect on the fading rate of the photochromic dye.

Calculating Activation Energy with the Simultaneous Arrhenius Equation:

The relationship between the rate of reaction and temperature is expressed by the Arrhenius equation¹¹:

$$k = Ae^{-E_a/RT}$$

There are two unknowns in this equation (Activation energy (E_a) and the pre-exponential factor (A)). In order to solve for activation energy, the simultaneous form of the Arrhenius equation will be used. Where k_1 is the rate constant of the reaction at room temperature and k_2 is the rate constant at the decreased temperature. T is expressed in degrees Kelvin and R is the universal gas constant.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{0.4608}{0.1768} = \frac{E_a}{8.31} \left(\frac{1}{247.7} - \frac{1}{258.7} \right)$$

$$E_a = 0.001367 \text{ J mol}^{-1}$$

5. CONCLUSIONS

The results of this investigation show that the overall dye fading reaction follows first order kinetics and that there was an observable and significant change in the value for k ($\Delta k = 0.4608 - 0.1768 = 0.2840$) as the temperature of the sample was decreased. This demonstrates that the fading rate is dependant on temperature, meaning that the fading reaction follows the Arrhenius relationship between temperature and rate constant. Therefore, a value for the activation energy was determined ($E_a = 0.001367 \text{ J mol}^{-1}$). This low value

¹¹ Chemistry LibreTexts library "Arrhenius Equation", last modified June 5th 2017
https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Kinetics/Modeling_Reaction_Kinetics/Temperature_Dependence_of_Reaction_Rates/The_Arrhenius_Law/Arrhenius_Equation

indicates that the proprietary dye was likely developed for applications that require a quick fading rate once no longer exposed to a UV source.

6. EVALUATION & DISCUSSION

The overall aim of this investigation, to describe the kinetic properties of a proprietary dye by measuring the photochromic fading rate in a laboratory setting, was achieved. However, the moderate percentage error of 10.25% in the final value for the activation energy, shown in Table 12 requires further discussion to supplement the interpretation of results.

Measurement	Value	Absolute Error (\pm)	Percentage Error (%)
k at room temperature / s^{-1}	0.4608	0.0261	6.40
k at decreased temperature / s^{-1}	0.1768	0.0068	3.85
Activation energy / $J mol^{-1}$	0.001367	0.000140	10.25

Table 12 - Systematic Error Analysis

$$\text{Activation energy} = 0.001367 \pm 0.000140 \text{ J mol}^{-1}$$

The most challenging aspect of this investigation and significant source of error was the dye itself. As a matter of fact, its properties were not ideally suited for kinetics experiments. The quick fading rate made it difficult to take accurate measurements in a relatively short period of time. Therefore, only a few data points were recorded and the ones directly after exposure to UV were lost due to the transfer time to the spectrophotometer. This

is when the rate of change in absorbance was at its largest, affecting the shape of the first order kinetic curve. Moreover, the dye had to be diluted for the fading reaction to be followed in the spectrophotometer, leading to a low absorbance reading. The low signal to noise ratio had a large effect on the accuracy of the data collected in this investigation. In addition, the Beer-Lambert law is only valid for a uniformly colored solution. When the dye was exposed to UV, instead of uniform coloration, certain segments of the solution were darker than others, forming column-like patterns due to local differences in concentration. This most likely led to further inaccuracy in the absorbance reading.

The concept of dye fatigue is also an important factor to take into consideration when investigating dye transformation. It is the root cause of the loss of the ability to convert between form A and B (Figure 5). There are numerous factors that contribute to fatigue, but the one that concerns this investigation the most is photodegradation or photobleaching.



Figure 5 - Dye fatigue, the same sample before (left) and after (right) following repeated exposure to UV

Dye fatigue causes the signal to noise ratio to decrease further as the starting absorbance signal of the dye is lower after repeated exposure.

The key element of this investigation was decreasing the temperature of the dye sample to measure its kinetic properties. Ideally, runs should have been repeated to generate reproducible curves that could then be averaged out. However, this was difficult as reproducing the decrease in temperature to the same degree was almost impossible using a rudimentary method such as the ice water bath. Additionally, the temperature of the cold sample was not perfectly maintained at 10.7 degrees celsius as it warmed up due to the higher room temperature. Albeit slowly, but still likely affecting the rate of reaction. Also, despite wiping the sides of the cuvette before placing it in the spectrophotometer, condensation still formed on the outside walls. Therefore, interfering with the absorbance reading in the spectrophotometer.

Despite all of the systematic errors described above, the data confirmed that the fading reaction was first order as the reaction rate plotted against absorbance was linear. However, two points had to be omitted in the decreased temperature data set to generate a linear curve (see Graph 7 in the appendix). These outliers could have been caused by any number of factors listed above. However, I think they are most likely attributed to the fluctuations in absorbance. Excluding these points from the analysis makes the error on the value of activation energy smaller. On the other hand, the one aspect of the results that doesn't change is the small value for the activation energy. This is likely because the dye was optimized to have a fast fading rate. LCR Hallcrest specializes in making photochromic dyes for novelty items¹², so a slow fading rate would have been undesirable.

¹² LCR Hallcrest, "Photochromic ink"
<http://www.lcrhallcrest.com/products/special-effect-coatings/inks/photochromic/photochromic-1>

Overall, if I were to repeat this experiment to improve the accuracy of the results, I would first make sure to use a different photochromic dye. The manufacturer did not provide any information on the dye other than it was an “aryl substituted heterocyclic photochromic organic compound”. Thus, I did not know the purity, the exact structural formula or even the molar mass. This limited my understanding of the dye properties. I could not draw its structure and hypothesize about the process that gave rise to the photochromic effect. The equipment used in this experiment was also another limiting factor. A spectrophotometer with a built-in temperature control, a faster sampling speed and an internal UV source would have been ideal for this experiment. This would improve the accuracy of the data collected and the final results by capturing the entire fading reaction curve. However, I think such equipment would be expensive and not realistic to purchase within the restrictions of my school’s laboratory budget.

8. BIBLIOGRAPHY

Chemistry LibreTexts library "Arrhenius Equation", last modified June 5th 2017
https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Kinetics/Modeling_Reaction_Kinetics/Temperature_Dependence_of_Reaction_Rates/The_Arrhenius_Law/Arrhenius_Equation

Dürr, Heinz, Bouas-Laurent, Henri eds., *Photochromism. Molecules and Systems Revised edition*. Gulf Professional Publishing, 2003

Eilmes, Andrzej, *Spiropyran to Merocyanine Conversion: Explicit versus Implicit Solvent*
 Journal of Physical Chemistry 2013, 117 (12) DOI: 10.1021/jp3117209

K. Horie, H. Ushiki, F.M Winnik, *Molecular Phototonics: Fundamentals and Practical Aspects*
 (Tokyo, Kodansha Ltd, 2000) 85.

Gu, Min, Li, Xiangping, Cao, Yaoyu, *Optical storage arrays: a perspective for future big data storage*
Light: Science & Applications, 2014

Irie, Masahiro, Uchida, Kingo, *Synthesis and Properties of Photochromic Diarylethenes with Heterocyclic Aryl Groups*
 Chemical Society of Japan Journals, 1998

LCR Hallcrest, "Photochromic ink"
<http://www.lcrhallcrest.com/products/special-effect-coatings/inks/photochromic/photochromic-1>

M. Nic, J. Jirat, B. Kosata, *Compendium of Chemical Terminology, 2nd ed. Gold Book* comp. A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford 1997

Mcgravey, David J., *Photochromism in View* Royal Society of Chemistry, 2008:
<https://eic.rsc.org/feature/photochromism-in-view/2020209.article>

Valter H.C. Silva, Vincenzo Aquilanti, Heibbe C.B. de Oliveira, Kleber C.Mundim "Uniform description of non-Arrhenius temperature dependence of reaction rates, and a heuristic criterion for quantum tunneling vs classical non-extensive distribution", *Chemical Physical Letters* 590, (2013):201-207 <https://doi.org/10.1016/j.cplett.2013.10.051>

Wikilectures, "Lambert-Beer Law", last modified 14 August 2016
http://www.wikilectures.eu/w/Lambert-Beer%27s_law

Works Consulted:

Irie, Masahiro, *Photochromism: Memories and Switches* Chemical Reviews 2000, 100 (5), pp 1683–1684 DOI: 10.1021/cr980068l

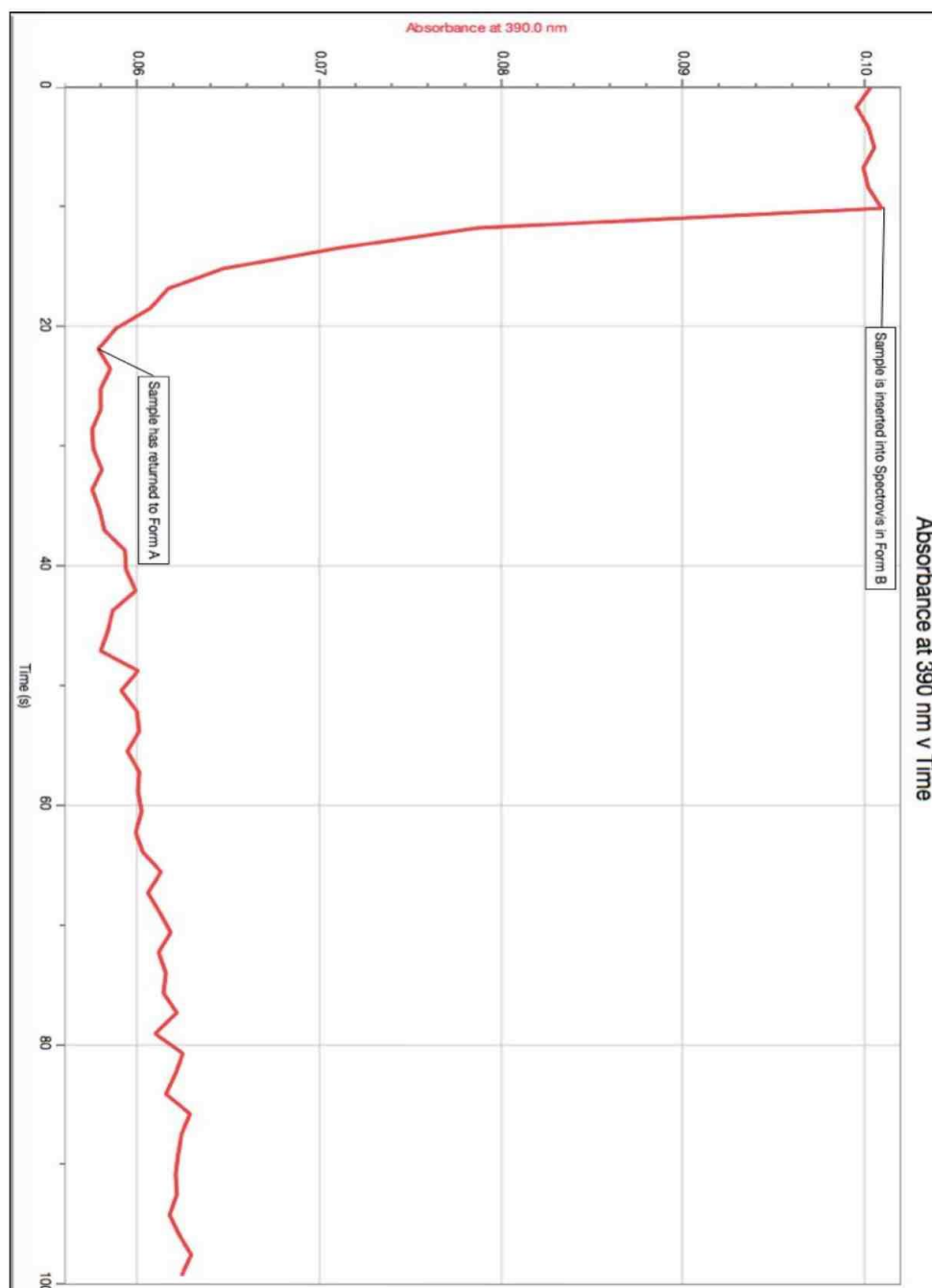
Photonics Wiki. "Photochromism" Last modified August, 2010.
<http://photonicswiki.org/index.php?title=Photochromism>. Accessed April 2017.

Mashiro Irie "Photochromism fundamentals and application", Department of Chemistry and Biochemistry Kyushu University, Fukuoka, Japan
<http://www.icmr.ucsb.edu/programs/archive/documents/Irie1.pdf>

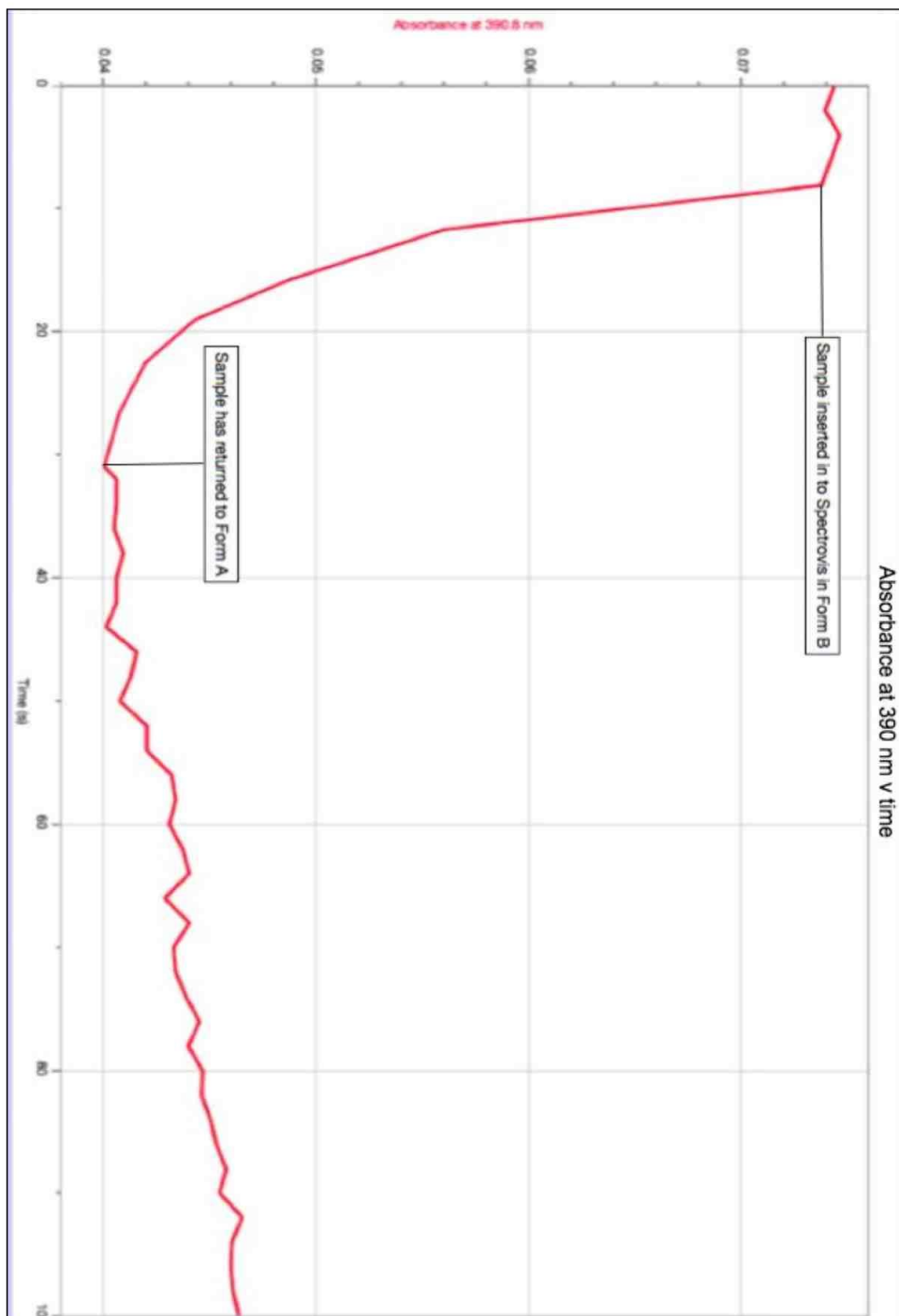
7. APPENDIX

Preliminary experiment 1 remaining data set:

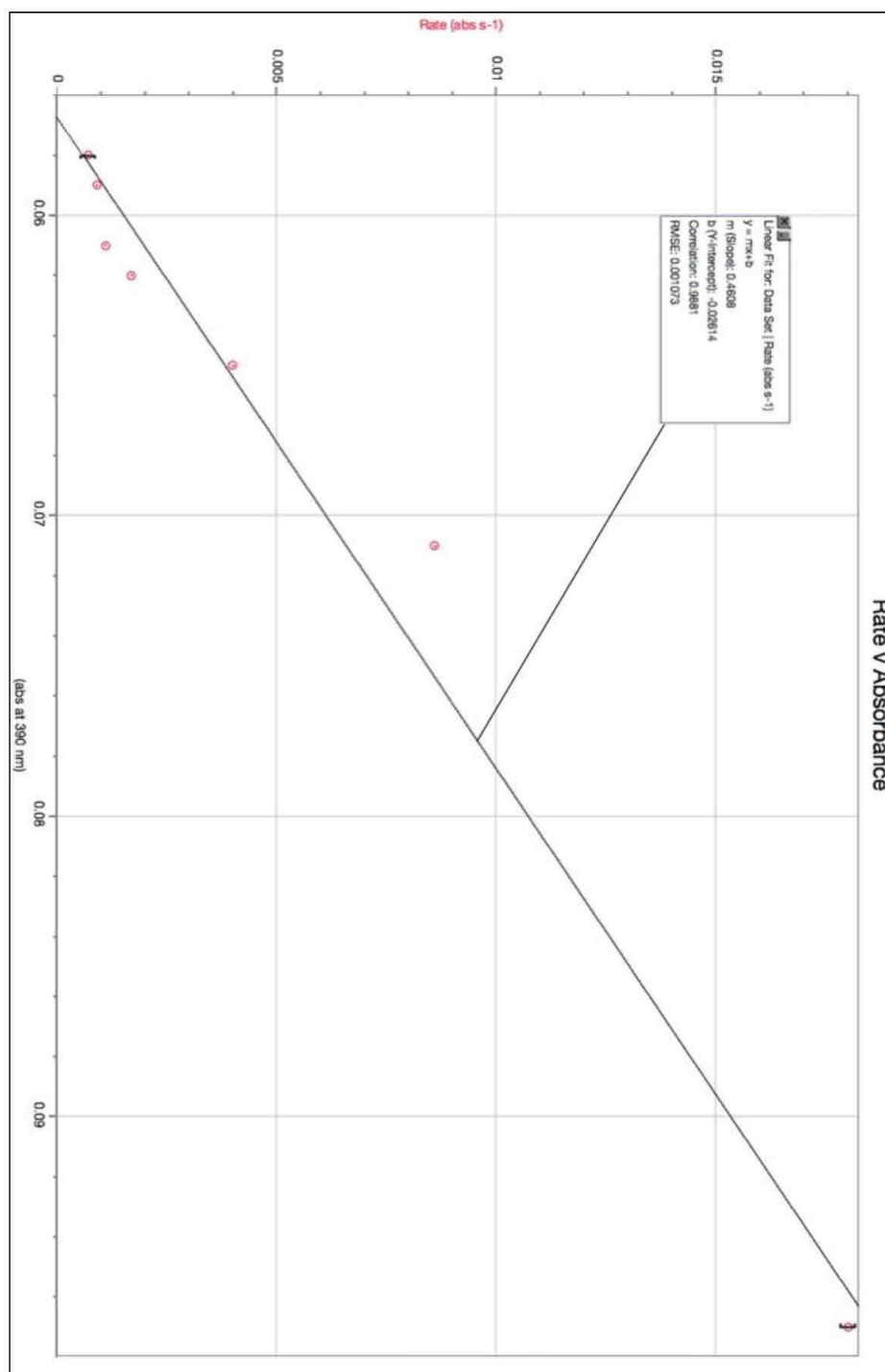
Trial 2				
Reading	Recorded mass	volume of acetone	Concentration (g/ml)	%
1	0.2527	100	0.0025	0.253
Trial 3				
Reading	Recorded mass	volume of acetone	Concentration (g/ml)	%
1	0.2527	200	0.0013	0.126
Trial 4				
Reading	Recorded mass	volume of acetone	Concentration (g/ml)	%
1	0.2527	200	0.0013	0.126
Trial 5				
Reading	Recorded mass	volume of acetone	Concentration (g/ml)	%
1	0.2527	400	0.0006	0.063
Trial 6				
Reading	Recorded mass	volume of acetone	Concentration (g/ml)	%
1	0.2527	600	0.0004	0.042



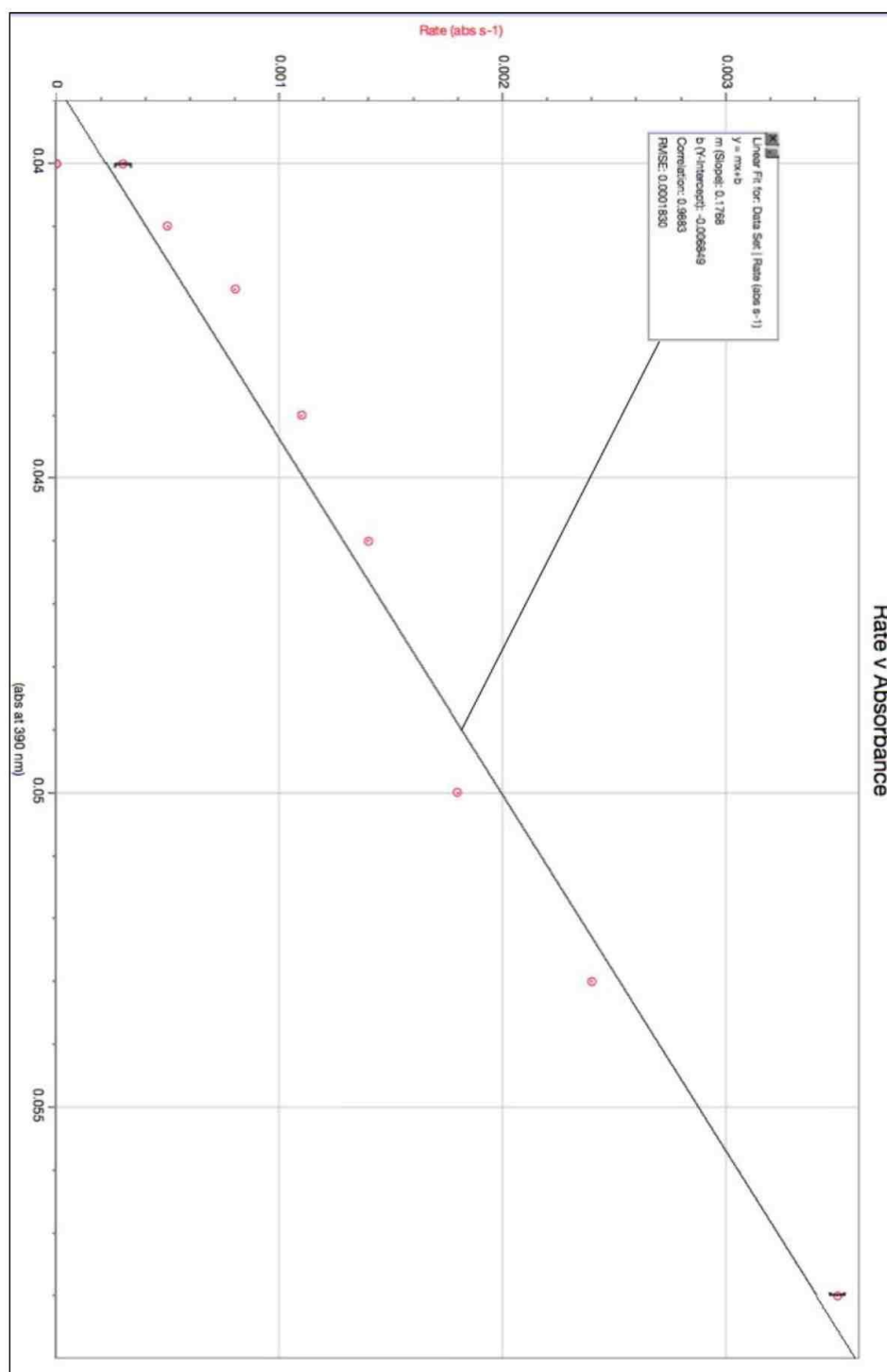
Graph 3 - Change in absorbance over time due to the fading of the photochromic dye at 27.1 C



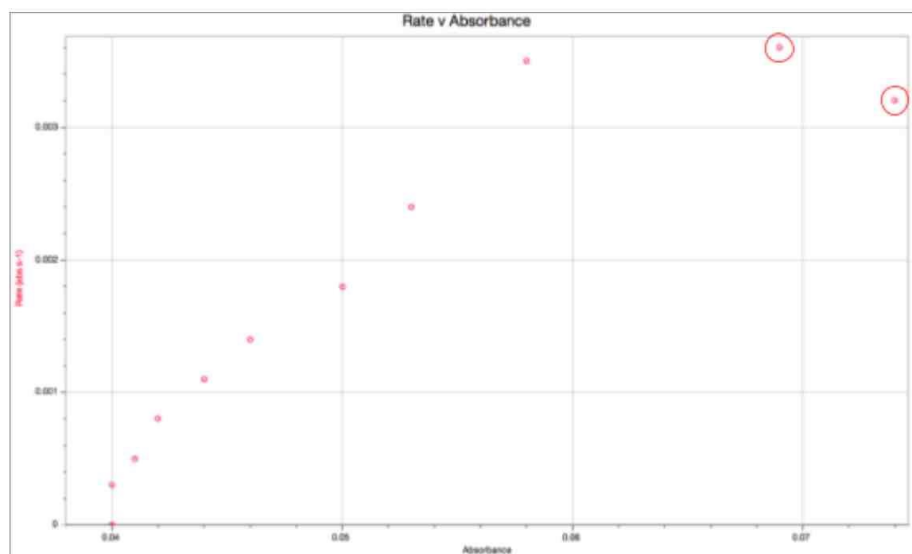
Graph 4 - Change in absorbance over time due to the fading of the photochromic dye at 10.7 C



Graph 5 - Rate of reaction against absorbance for the sample at room temperature



Graph 6 - Rate of reaction against absorbance for the sample at decreased temperature



Graph 7 - Plotting rate against absorbance at decreased temperature showing outliers that were omitted in data analysis