Crystal Violet and Sodium Hydroxide Reaction Kinetics

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Introduction

Crystal Violet or hexamethyl pararosaniline chloride is a compound used in Grams stains. It has a vibrant purple color that decreases in intensity upon reaction with sodium hydroxide. Thus, Beer’s law can be used to determine the concentration of crystal violet at any point in time through a calibration curve. When measured across time, the reaction order and rate of hydroxide (OH-) and crystal violet cation (Vi+) can be determined. For the following reaction, the reaction rate is defined with k being the overall rate constant and a and b as the reaction orders with respect to crystal violet cation and hydroxide.

(1)

In large excess of sodium hydroxide, its respective term of the rate law is effectively constant. Therefore, making the following substitution results in a new rate law with pseudo-rate constant *k’*.

(2)

(3)

The reaction order *a* is solved by fitting the concentration of crystal violet at time *t* to the linear forms of the following possible integrated rate laws derived from eq. 3.

**Table 1:** Integrated rate laws. The laws are expressed in a form compatible with the linear equation (y=mx+b) where terms are easily exchanged.

|  |  |
| --- | --- |
| Zeroth order in *a* |  |
| First order in *a* |  |
| Second order in *a* |  |

The reaction order *b* is determined by selecting two concentrations of hydroxide [OH-]1 and [OH-]2 such that

(4)

Calculating the ratio of pseudo-rate constants at these concentrations results in the following expression

(5)

Since , determination of the reaction order with respect to hydroxide becomes trivial. Finally, the overall rate constant and rate law can be determined.

Methods

Six solutions of crystal violet were prepared by the lab instructor in advance. The solutions had the following concentrations: (1.5, 0.75, 0.325, 0.162, 0.081, 0.0405) x10-5 M. The 1.5x10-5M solution was placed in a cuvette and measured with the desktop UV-vis spectrometer (Spec-20) to determine its wavelength of maximum absorbance. DI-water was used as the blank. This wavelength was used as the standard by which all other measurements were made. The remaining five concentrations were used to determine the calibration curve. Each solutions absorbance was measured beginning with the lowest concentration with DI-water rinses between each measurement. Before beginning the kinetics runs, two graduated cylinders were prepared along with a 100-mL reaction vessel. One graduated cylinder was filled with 25 mL of 1.5x10-5M crystal violet solution. The other was filled with 25 mL of 0.2M sodium hydroxide solution. A stopwatch was started (t=0) when the two solutions were mixed. In quick succession the mixture was stirred, used to rinse a cuvette twice and finally placed in the cuvette for measurement in kinetics mode. The time at which measurement began was recorded and required to be less than t=25 seconds. The time at which the measurement ended was when absorbance reached 10% of its peak recorded value. Two trials for 0.2M NaOH and two trials for 0.4M NaOH (consistent with eq. 4) were conducted holding all other variables constant.

The calibration curve fit was used to translate absorbance for the four trials into concentration of crystal violet. One trial was chosen to be fitted to each of the three rate laws in table 1. The rate constant *a* corresponding to the most linear fit was used as the for each of the other trials. k' is determined for each plot, therefore *b* was also determined. Finally, the rate constant *k* was compared to literature values for the reaction.

Data and Results

**Figure 4:** Kinetic run two; second-order fit.

**Figure 1:** Beer’s law calibration plot. The slope was determined to be 1.6065E-5 M/AU.

**Figure 2:** Kinetic run two; zero-order fit.

**Figure 3:** Kinetic run two; first-order fit.

After testing the absorbance of the solution on the standard reaction concentration of 7.5E-6 M Vi, the wavelength of peak absorbance was visually identified and chosen to be 579 nm. Upon analysis of the data, the true peak was found to be 577nm.

The calibration curve as shown in figure 1 was made by plotting concentration over absorbance. This was done so that each absorbance in the data simply had to be multiplied by the slope of the calibration plot, 1.6065E-5 M/AU, to get the molarity of the solution at time *t*.

Next, the reaction order *a* was determined. The second trial 0.2M NaOH run was chosen to test the linearity of the three rate laws. The plots were generated by determining the substituted variables of the laws. For example, figure 3 plots the time versus the natural logarithm of the concentration of crystal violet, implying that the slope is equivalent to *-k’*.

The R2-value was maximized for the first order rate fit showing that a=1.

Next, the pseudo-rate constant was calculated for each of the trials. Figures 5 and 6 show the kinetic data for each of the trials grouped by concentration.

**Figure 1:** First-order fits for each four trials. The top left plot is trial one next to trial two on the top right. The bottom left plot is trial three next to trial four on the bottom right. Notice the similarity in the slopes of each fit.

The average of the pseudo rate constants were calculated as follows: *k1'*= ½( 0.00602+0.00656) ln(M)/s=0.00629 ln(M)/s and *k2'*= ½( 0.00910+0.00421) ln(M)/s =0.00666 ln(M)/s.

Using eq. 5, *b* was calculated to be 0*:*

Using eq. 2:

Compared to the literature, for the same reaction the overall rate constant is 0.054 M/s.1 Since these are on the same order of magnitude it is safe to assume that our results agree. It is difficult to determine uncertainty. Although first order was the best linear fit for trail two, trial four deviates strongly from the linear fit. It appears as though the reaction significantly slowed after 100 seconds creating a fit with large uncertainty.

Plugging all the calculated values back into eq. 2 we get our overall rate law as

Conclusion

The overall rate constant k was found to be 0.0315 ln M / Ms which on the same order of magnitude as the literature value. In our overall reaction rate, the hydroxide term fell out and we were left with .

Generally speaking, our approach to measuring kinetics works well when the time constraints are met. Obviously, if the reaction goes to completion before 20 seconds then this method will not work. Alternatively, if the reaction takes days to go to completion, any method without high precision would be far to unwieldy to use. It appears as though a half life of around one to fifteen minutes seems reasonable for this method. Also, it is necessary that the reaction obeys the integrated rate laws, which some reactions do not.

Safety

Sodium hydroxide is very corrosive and detrimental to skin and eyes.1 Crystal violet is harmful to the eyes and acutely toxic. It is also suspected to be carcinogenic.2

References

(1) Salahudeen, N.; Rasheed, A. A. Kinetics and Thermodynamics of Hydrolysis of Crystal Violet at Ambient and below Ambient Temperatures. *Sci Rep* **2020**, *10* (1), 21929. https://doi.org/10.1038/s41598-020-78937-4.

(2) *Sodium Hydroxide SDS (Safety Data Sheet) | Flinn Scientific*. https://www.flinnsci.com/sds\_734-sodium-hydroxide/sds\_734/ (accessed 2022-11-28).

(3) *Crystal Violet SDS (Safety Data Sheet) | Flinn Scientific*. https://www.flinnsci.com/sds\_276-crystal-violet/sds\_276/ (accessed 2022-11-28).