

Lab Report # 3: Second Order Reaction-Iodination of Aniline

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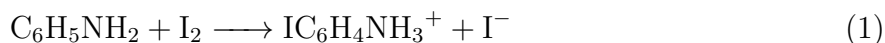
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Abstract

The kinetics of the iodination of aniline were studied in this experiment. Three solutions were made and the reactions progress was observed as absorbance over time using a spectrophotometer. From this, three data sets of the inverse of absorbance ($\frac{1}{A}$) versus time were gathered and using linear regression three lines of best fit were formed.

1 Overview

Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) is an organic compound that reacts with Iodine in the following manner:



To track the progress of this reaction, the absorbance of three solutions was measured in five minute intervals for approximately 1 hour. Each solution was prepared according to the following table:

Solution	mL of .04M Aniline	mL of .04M I_2	mL of 1.00M KH_2PO_4	mL of 1.00M NaOH
1	10	10	10	4
2	10	10	16	4
3	10	10	14	8

These values created solutions of initial concentrations shown below:

Solution	Init. Conc. Aniline (M)	Init. Conc. I_2 (M)	Init. Conc. KH_2PO_4 (M)	Init. Conc. NaOH (M)	Init. Conc. NaHPO_4 (M)
1	0.008	0.008	0.200	0.080	0.080
2	0.008	0.008	0.320	0.080	0.080
3	0.008	0.008	0.280	0.160	0.160

The NaOH, KH_2PO_4 , and aniline solutions were provided by the instructor. The I_2 solution was prepared by massing approximately .5023g of I_2 and diluting to 50mL with a 1.2M KI solution. The other table solutions were not diluted to 50mL until after the addition of the I_2 solution. Three stopwatches were prepared for each solution such that the time of measurement could be known for each. The reaction time started once the I_2 solution was added to the solution flask. Only then was the solution diluted to 50mL with DI water. Absorbance readings were taken approximately every five minutes for each solution. The times and measurements shown below:

Solution 1			Solution 2			Solution 3		
A	Time (s)	1/A	A	Time (s)	1/A	A	Time (s)	1/A
1.1720	391	0.8532	1.1628	437	0.8600	1.1456	391	0.8729
1.1551	600	0.8657	1.1405	650	0.8768	1.0980	600	0.9107
1.1295	928	0.8853	1.1159	924	0.8961	1.0606	928	0.9429
1.1091	1200	0.9016	1.0957	1200	0.9127	1.0230	1200	0.9775
1.0848	1500	0.9218	1.0734	1500	0.9316	0.9812	1500	1.0192
1.0620	1800	0.9416	1.0514	1800	0.9511	0.9486	1800	1.0542
1.0398	2100	0.9617	1.0301	2100	0.9708	0.9179	2100	1.0894
1.0205	2400	0.9799	1.0093	2400	0.9908	0.8904	2400	1.1231
1.0027	2700	0.9973	0.9908	2700	1.0093	0.8637	2700	1.1578
0.9834	3000	1.0169	0.9712	3000	1.0297	0.8403	3000	1.1901
0.9654	3300	1.0358	0.9539	3300	1.0483	0.8177	3300	1.2229
0.9493	3600	1.0534	0.9363	3600	1.0680	0.7972	3600	1.2544

2 Results and Analysis

To actually develop our relationship between the absorbance (A) and concentration (C) we look to Beer's Law, which states the absorbance has a linear relationship with the concentration of a substance:

$$A = bc \quad (2)$$

Where b is a constant made up of the molar absorptivity (ϵ) and the mean path length of the analyzed sample (l, which is 1 in most cases). Knowing the rate equation for a second order reaction:

$$rate = -\frac{dc}{dt} = k_2c^2 \quad (3)$$

Where c is the concentration of a sample, $\text{C}_6\text{H}_5\text{NH}_2$ in this case. I will denote the concentration of $\text{C}_6\text{H}_5\text{NH}_2$ as $[\text{C}_6\text{H}_5\text{NH}_2]$. Substituting into equation 3:

$$rate = -\frac{d[\text{C}_6\text{H}_5\text{NH}_2]}{dt} = k_2[\text{C}_6\text{H}_5\text{NH}_2]^2 \quad (4)$$

Now, the integration of this rate law will acquire a function of time for the concentration of our sample:

$$\frac{1}{[\text{C}_6\text{H}_5\text{NH}_2]} = k_2 t + \frac{1}{[\text{C}_6\text{H}_5\text{NH}_2]_0} \quad (5)$$

Writing equation 2 in a more suggestive manner:

$$\frac{1}{A} = \frac{1}{\epsilon} \frac{1}{[\text{C}_6\text{H}_5\text{NH}_2]} \quad (6)$$

substituting (5) into (6) and multiplying:

$$\frac{1}{A} = \frac{1}{\epsilon} k_2 t + \frac{1}{\epsilon [\text{C}_6\text{H}_5\text{NH}_2]_0} \quad (7)$$

So now we have established a linear equation with a relationship between the absorbance and time where we can extract k_2 , ϵ , and A_0 . Where A_0 is given by:

$$A_0 = \epsilon [\text{C}_6\text{H}_5\text{NH}_2]_0 \quad (8)$$

So once we have determined ϵ we can find A_0 .

The plots from the data gathered are shown below with the lines of best fit.

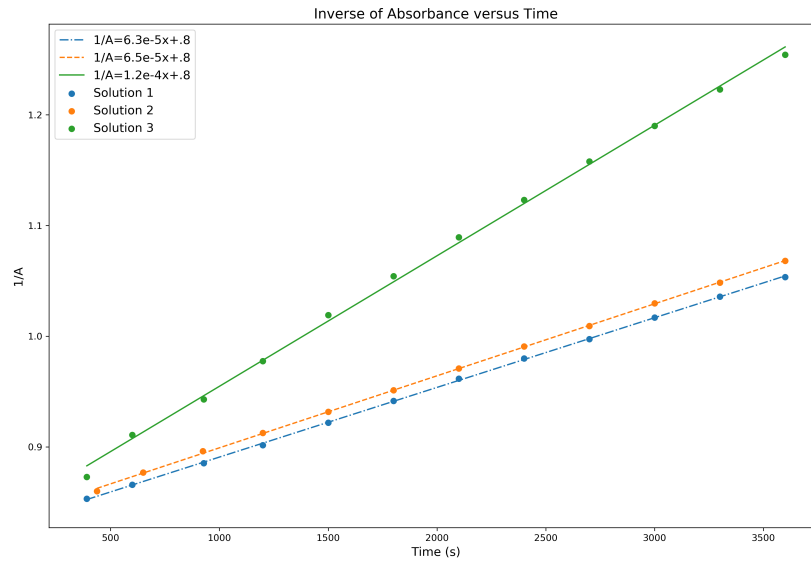
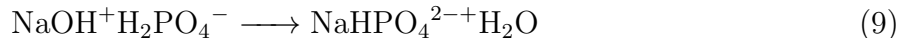


Figure 1: Inverse of absorbance versus time plots.

Some additional data that was extracted is displayed in the table below:

Solution	Initial pH	Slope	$1/\epsilon c_0$	k_2	Temp	Rate w/ IC
1	6.8	6.30E-05	0.8	9.37E-03	23	6.00E-07
2	6.6	6.50E-05	0.8	9.67E-03	23	6.19E-07
3	7.0	1.20E-04	0.8	1.79E-02	23	1.14E-06

Where the pH was found from the buffer solution:



and the pH equation is given by:

$$\text{pH} = -\log(K_a) + \log\left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}\right) \quad (10)$$

K_a is given to be 6.2×10^{-8} .

There is not evidence to support the pH has a noticeable affect on the reaction rate. There are several reasons for this. Primarily due to the lack of data. There are three pH values, each very close to the other. It is nonsensical to draw conclusions from this data set. This also means we cannot draw conclusions about the effect the concentration of H_2PO_4^- or HPO_4^{2-} . In fact we have no mathematical expressions that relate the rate of the primary reaction to the pH and any plots that can be made include three data points. The equation would be no different since the rate law is not affected by the stoichiometric coefficients.

3 References

E. Berliner, J. Amer. Chem. Soc. 72, 4003 (1950). L.K. Brice, J. Chem. Educ. 39, 632 (1962).