

Saponifacation of ethyl acetate and soldium hydroxide

Profession



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Ethyl Acetate - NaOH Reaction Kinetics Experiment Martin Novick Group 14, Chemical Engineering Laboratory Submitted to Prof. David B. Henthorn September 25, 2012 Summary The goal of this project was to determine the pre-exponential factor, k_0 , the activation energy, E , and the reaction rate constants, k , of the saponification process of ethyl acetate using sodium hydroxide (NaOH) at 5 temperature between 15 and 25 degrees Celsius. Two trials were performed at temperatures 16, 18, 20, 22, and 24 degrees Celsius. The main equipment of the project were the jacketed beaker batch reactor and the LabPro conductivity probe.

The solution's conductivity throughout the reaction was collected and plotted in a linearized plot against time to retrieve k value for each trial. The rate law was assumed to be $k = k_0 e^{-E/RT}$ = $k_0 e^{-E/RT}$ $[NaOH]^m [EtAc]^n$, where $[NaOH]$ and $[EtAc]$ are the concentrations of sodium hydroxide and ethyl acetate respectively. The $\ln(k)$ values were plotted against the inverse temperatures to (linearize the Arrhenius equation. The k_0 value and E value from the linearized Arrhenius plot were found to be $15 \pm 3M^{-1} s^{-1}$ and $6402 \pm 8191 J mol^{-1}$ respectively. The E value being negative suggests the reaction is exothermic. The large standard errors of the k_0 and E values were probably caused by the low number of data points collected or the assumed rate law was wrong.

Introduction The objective of this project was to determine the pre-exponential factor, k_0 , the activation energy, E , and the reaction rate constants, k , of the saponification process of ethyl acetate using sodium hydroxide (NaOH). Saponification is a chemical process heavily used in industry, especially in soap production.

Knowing the effects of temperature on the reaction rate allows better control over the reaction process and find the optimizing point of production. The right temperature maximizes production and minimizes reactants and heating or cooling energy, finding the maximum possible profit. 2 The saponification of ethyl acetate with sodium hydroxide (NaOH) is an equimolar reaction given as $\text{NaOH} + \text{CH}_3\text{COOCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{COONa} + \text{CH}_3\text{CH}_2\text{OH}$. [2] The rate was assumed to be second order overall, but first order relative to either reactant,[2] with the disappearance rate of sodium hydroxide given as:[4] $\frac{d[\text{COH}]}{dt} = -k[\text{COH}][\text{Cac}]$, (1) where COH is the NaOH concentration, Cac is the concentration of ethyl acetate, and k is the rate constant. COH is represented with x, and Cac is assumed to be in excess with a starting concentration of a. The concentration of ethyl acetate throughout the reaction was given as $\text{Cac} = a - x_0 + x$, where x_0 is the initial starting concentration of NaOH. Substituting the expressions for COH and Cac into Equation 1 results in: $\frac{dx}{dt} = -kx(a - x_0 + x)$. Equation 2 is then separated and integrated shown as the following: $\int \frac{dx}{x(a - x_0 + x)} = -k \int dt$. $\frac{1}{x_0} \ln \left(\frac{x_0 + x}{a - x_0 + x} \right) = -kt$ (2) (3)

The result of equation 3 would become: $\ln \left(\frac{x_0 + x}{a - x_0 + x} \right) = -kt \frac{a - x_0}{x_0}$. (4) Since a 20% excess ethyl acetate solution was used, the initial ethyl acetate concentration was 1.25 times of the initial starting concentration of NaOH, so $a = 1.25x_0$. After the substitution of $a = 1.25x_0$, Equation 4 was simplified to: $0.2x \ln \left(\frac{x_0 + x}{0.8x_0 + x} \right) = -kt$. The relationship between x_0 x (5) and conductivity of the solution was given as: [2] $\kappa = \kappa_0 + \alpha x$, (6) where κ_0 is the initial conductivity of NaOH before adding ethyl

acetate, σ is the conductivity after the reaction has reached completion, and σ_t is the conductivity at any point of time during the reaction process. Substituting Equation 6 into Equation 5 gives the following:

$$\ln \left(\frac{0.2 \sigma + 0.8 \sigma_0}{0.2 \sigma_t + 0.8 \sigma_0} \right) = kt \quad (7)$$

Since σ , σ_0 and σ_t are constants, the only variable in the left hand side of Equation 7 being t . Each t point can be substituted into the left hand side of Equation 7 and plotted against time to retrieve a linear plot with the slope being the k value. To find the value of the pre-exponential factor, k_0 and activation energy, E , would require linearizing the Arrhenius equation given as: $k = k_0 e^{-E/RT}$, where R is the gas constant and T is the temperature the given k is at in degrees Kelvin. Equation 8 is linearized by taking the natural log of both sides: $\ln(k) = \ln(k_0) - E/RT$ (8) (9) to retrieve a linear plot with Equation 9 shows a linear relationship between $\ln(k)$ and $1/T$ the y-intercept being $\ln(k_0)$ and the slope being $-E/R$. Hence: $k_0 = e^{\text{intercept}}$ (10) (11) $E = -R \times \text{slope}$

Equipment, Materials, and Method The equipment used were a jacketed batch reactor beaker, cooling water circulation system, computer, LabPro temperature probe and conductivity probe, mixing stand and magnetic stir bar. The materials used for this reaction were a 0.08M NaOH solution and a 0.1M ethyl acetate solution. A 20% excess Ethyl acetate was used to ensure NaOH was the limiting reactant. [1] NaOH was chosen for the limiting reactant because of its high conductivity relative to Ethyl acetate. The extent

of the reaction was monitored by measuring the conductivity throughout the reaction.

With NaOH being the limiting reactant, the change in conductivity is more visible, and the termination of the reaction can be more easily observed. The each experimental trail was setup as shown in Figures A1 and A2 of Appendix A. The temperature and conductivity probes were completely submerged under the surface of the reacting solution. One data reading was retrieved per second. Before the reaction process begun, the cooling water circulation system was set at desired temperature and the reactants were cooled to the target temperature to keep an 5 isothermal reactionenvironment.

In Equation 8, the k value was only a function of temperature; if temperature varied throughout the reaction, the k value would also vary throughout the reaction. The reaction was started once thermal equilibrium between the batch reactor beaker and cooling water was established. For about the first half a minute, only the conductivity of NaOH in the reactor was collected, to ensure the initial conductivity in conductivity was more easily observed. The initial conductivity was the first conductivity point after the major drop of conductivity due to the addition of ethyl acetate.

The reaction was started after about half a minute after the start of the data collection by adding the ethyl acetate. The solution was well mixed throughout the reaction to ensure a uniform temperature of the solution, to prevent any local k values being different from the overall k value. If there any temperature gradients throughout the system existed during the reaction process, there would be different local k values throughout the

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reactor. Data collection was terminated at least half a minute after the reaction had gone to completion, when no conductivity change was observed.

The final reaction completion conductivity, σ_{∞} , was the conductivity of the solution after the reaction has completed, and was used to find k value. Hysteresis effects were removed by using a random number generator to determine the order of trials.

6 Results and Discussion

1/T (T-1)	ln(k)
0.9	0.8
0.7	0.6
0.5	0.4
0.3	0.00335
0.00337	0.00339
0.00341	0.00343
0.00345	0.00347

Figure 1 the plot of the linearized Arrhenius equation where $\ln(k) = \ln(k_0) - \frac{E}{R(T-1)}$. The linearized Arrhenius equation plot shown in Figure 1 has a R^2 value of 0.383 suggesting the data does not have a good linear fit. The lack of data points may have been the cause of the low R^2 value. The $\ln(k)$ values of the same temperature mostly seem to have small variations, but overall has the predicted trend of decreasing in $\ln(k)$ value as $1/T$ increases. The plot has a negative overall trend with and hence retrieving a negative E value. The negative E value suggests the release of energy as the reaction proceeds. Table B1 in appendix B shows the retrieved values of k , k_0 and E . The positive k_0 value was expected according to Equation 8.

Since k values are linearly proportional to k_0 , for k values to be positive, k_0 must also be positive. The resulting negative E value was an expected result, since the reaction was said to be very spontaneous. The standard errors of k_0 and E being about 20% to 25% of the original value, suggests the data as imprecise. The imprecision of the data can also be observed from the low R^2

Conclusion and Recommendations The retrieved k_0 value and E value were 15 ± 0.3 and 36402 ± 8191 .

Since the standard errors of k_0 and E values were about 20% and 25% of the original value respectively, and the R^2 value was only 0.7383 for the plot in Figure 1, the data is concluded to be imprecise and that more data points should be collected to improve the precision. The assumption of the rate being second order overall, but first order relative to either reactant was concluded to be inappropriate. Though the R^2 value for all the trials were above 0.95, because a clear parabolic trend was observed in all the residual plots, Figures B6 to B14 of Appendix B, it was concluded that all the trial data do not have a linear relationship.

Since it has been concluded that the assumed rate equation, Equation 1, does not describe the reaction, a new rate equation is needed to describe the reaction. The low R^2 value in Figure 1 can be improved by increasing the amount of data collected. More trials can be done at each temperature and more temperatures can be tested within the given interval. One large bulk solution can be made and used for all the trials, but stored and isolated from the atmosphere. The error caused by the variation in concentrations of the reactants at different trails can be solved by using the one large bulk of reactants.

The problem of the reactants reacting with the atmosphere can be solved by isolating the reactants from the atmosphere during storage. 9 References [1]

Crismyre, Bobby, Do, Bryan, and Kronmiller, Mandy. "Ethyl Acetate - NaOH Reaction Kinetics Experiment Standard Operating Procedures," (2010) [2]

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Ethyl Acetate. Journal of the American Chemical Society, (2010), 124 (10), 2259-2262. [3] Keusch Fachdidaktik Chemie. "Reaction Second Order," Institute of Organic Chemistry, Universitat Regensburg. [4] Schmidt, Larry D. "The Engineering of Chemical Reactions," 2 Ed.

Press, New York (2005) Oxford University 10 APPENDIX A: Experimental Set

Up Figure A 1: Shows the theoretical setup and flow of each experiment.

Figure A 2: Shows the actual set up used for each experiment. 11 APPENDIX

B: Experimental Results and Data Table B 1 shows the result of the desired

information Set Temperature (oC) 16 (Trial 1) 16 (Trial 2) 18 (Trial 1) 20

(Trial 1) 20 (Trial 2) 22 (Trial 1) 22 (Trial 2) 24 (Trial 1) 24 (Trial

2) ????????????? (???????? 1 ?????? ? 1) ?????? (??????) ?????????????????????

Actual Temperature (oC) 16. 45 ± 0. 05 16. 44 ± 0. 04 18. 33 ± 0. 03 20. 30

± 0. 05 20. 30 ± 0. 5 22. 24 ± 0. 04 22. 25 ± 0. 05 16. 45 ± 0. 05 16. 45 ±

0. 05 15 ± 3 ? 36402 ± 8191 k-values (???????? 1 min? 1) 1. 674±0. 001 2.

023±0. 001 1. 921±0. 002 2. 241±0. 002 2. 247±0. 003 2. 244±0. 006 2.

169±0. 002 2. 572±0. 003 3. 140±0. 002 12 25 20 $y = 2. 0232x$ $R^2 = 0.$

9994 15 Y (L/mol) $y = 1. 6744x$ $R^2 = 0. 9972$ 10 5 0 0 2

$\ln(1 ????????????????????????????????????? (+1))$ 1. 25 ????????????????????????????????????? 4 6 Time (min) 8

$\ln(10 1 ????????????????????????????????????? (+1))$ 1. 25 ????????????????????????????????????? 12 Figuer B 1 Plot

of ????????????????????????????????????? 0. 25xo at 16 degrees Celsius, where ??????? = 0.

25xo . 16 14 12 10 8 6 4 2 0 0 -2 $\ln(1 ????????????????????????????????????? +1))$ 1.

25 ????????????????????????????????????? $y = 1. 9206x$ $R^2 = 0. 9974$ Series1 Linear (Series1) 1 2 3 4

5 6 7 8 Figuer B 2 Plot of ????????????????????????????????????? 0. 25xo at 18 degrees Celsius,

where ??????? = $\ln(1 ????????????????????????????????????? (+1))$ 1. 25 ????????????????????????????????????? 0.

25xo . 13 25 $y = 2. 247x$ $R^2 = 0. 9964$ $y = 2. 2407x$ $R^2 = 0. 9982$ Y (L/mol)

7 8 X Variable 1 Figure B 11 The residual plot for 22 degrees Celsius Trial 1.

X Variable 1 Residual Plot 0. 8 0. 6 Residuals 0. 4 0. 2 0 -0. 2 -0. 4 0 1 2 3 4 5

6 7 8 9 X Variable 1 Figure B 12 The residual plot for 22 degrees Celsius Trial

12 7 X Variable 1 Residual Plot 1 Residuals 0. 5 0 0 -0. 5 1 2 3 4 X Variable 1

5 6 7 8 Figure B 13 The residual plot for 24 degrees Celsius Trial 1. X

Variable 1 Residual Plot 0. 6 0. 4 Residuals 0. 2 0 -0. 2 -0. 4 0 1 2 3 4 X

Variable 1 5 6 7 8 Figure B 14 The residual plot for 24 degrees Celsius Trial 2.

140 120 100 Y (L/mol) 80 60 40 20 0 0 5 10 15 20 25 30 35 40 45 Time (min)

Figure B 15 The plot of all the data from 16oC trail 2 18 APPENDIX C: Sample

Calculations Volume of 1M NaOH solution needed to prepare 300mL 0. 08M

NaOH solution: $0.3 \text{ L} \times 0.08 \text{ M} = 0.024 \text{ mol} = 24 \text{ mL}$

Volume of ethyl acetate needed to prepare a 300mL

0. 1M ethyl acetate solution: $1000 \text{ mL} \times 0.1 \text{ M} = 100 \text{ mL}$

$0.001 \text{ L} \times 0.1 \text{ M} = 0.1 \text{ mol} = 10 \text{ mL}$

$0.897 \text{ L} \times 0.1 \text{ M} = 89.7 \text{ mL}$

Finding E value: Calculating the k value for time

being 1 minute in trial 2 of 16 degrees: $k = \frac{\ln(1 + 1)}{1.25} = 2904.9$

$= \frac{\ln(1 + 1)}{1.25} = 2904.9$

$1.25 \times 0.25 \times 1.6324$

$71 \times 4698.16 \ln(1 + 1) 1.25 8259.03 \times 4698.16 0.25(0.8) = kt = 14.8919$

89 19

APPENDIX D: Error Analysis If the result (R) is calculated by the following

equation: $R = a \times b^x$ where x is the exponent

of the independent variable, a . The standard error would be

calculated by the following equation: $2 \times \frac{R}{b^x} = \frac{2R}{b^x}$

($\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$) $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ (1) (2) where $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is taken from equation 5, $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the standard error of each individual independent variable. Since the equation used is the following: $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) = \frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} + 1 \right) + 0.25$ $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) = \frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} + 1 \right)$, 3) where $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the rate constant, $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the initial conductivity, $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the conductivity at the end of the reaction, $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the conductivity at any time, and $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the initial concentration of the NaOH solution. The error of the right hand side of equation 3 with $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) = 36.662$ is show as the follow: $36.662 \left(\frac{0.0339}{0.08} \right) = 15.536$. 0.08 ± 0.0339 was given the value of 0.08 with an uncertainty of ± 0.0339 . The reaction rate constant, k , were found by the best fit line of the plot, so the uncertainty of the k were found by taking the linear regression.

The rate constant was the slope of the best fit line making the calculation of the error with a 95% confidence level as: $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) = 1.96 \frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) \sqrt{\frac{1}{n-2}}$ Where $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the standard error of estimate, $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the x values of the plot, n being the number of points, and $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) = \frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) = 1$, (4). As for the y intercept, or the activation energy, the error with a 95% confidence level would be: $20 \frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) = 1.96 \frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) \sqrt{\frac{1}{n-2}}$ ($\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) + 2$, $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) \sqrt{\frac{1}{n-2}}$) (5) Where $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the standard error of estimate, $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right)$ is the x values of the plot, n being the number of points, and $\frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) = \frac{1}{k} \ln \left(\frac{a(x-b)}{b(x-a)} \right) = 1$. The standard error of

estimate, \bar{y} , seen in both equation 4 and equation 5 is given as: $\bar{y} = \frac{1}{n} \sum_{i=1}^n y_i$ (6) where y_i is the y value of the points, \hat{y}_i is the corresponding y value on the best fit line, and n is the number of data points.