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Determination of Activation Energy of Saponification Reaction through pH Analysis

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RESEARCH ARTICLE

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ABSTRACT

Saponification is a chemical reaction that produces surfactants and glycerol from fatty acid triglycerides from lye and oil. This investigation is interested in determining the activation energy of the Saponification reaction between the oleic acid triglyceride found in olive oil and sodium hydroxide solution. While the activation energy of the aforementioned reaction is theoretically known, current experimental values still deviate greatly. Since this investigation utilises a different method of rate determination, it is justied as a worthwhile investigation that may potentially provide a more accurate experimental value.

This research paper explains the methodology of using a Venirez pH probe to measure the rate of the Saponification reaction. The pKw values have to also be taken into consideration due to the changing temperature sat which the experiment occurs. The pH values can then be used to measure the concentration of hydroxide ions which can then be used to and the rate constant which subsequently enables the determination of the activation energy. The determined value of the activation energy of this investigation is 2.76 J/mol which suggests that this method of determining the activation energy is valid. However, due to long reaction times, only two temperatures could be tested throughout this investigation which is reacted in a low condense in the reliability of this result. This investigation does however introduce a new method of determining the activation energy of Saponification reactions.

The first draft of this paper was used as an extended essay for a higher level Chemistry course as part of an assignment. The publication of this research paper belongs solely to the Research and Reviews: Journal of Chemistry.

INTRODUCTION

Saponification Reaction Mechanism

Determining the activation energy of the Saponification reaction will require a method of measurement of the rate of reaction. The rate of reaction will then allow the rate constant of the rate expression to be determined. The natural logarithm of the rate constant and the reciprocal of die rent temperatures will then be plotted to identify the activation energy. In order to identify a method of measurement, the Saponification reaction mechanism mistrust be understood.

The Saponification reaction that is being investigated in this essay is primarily between the oleic-oleic-oleic triglyceride, $C_3H_5(C_{18}H_{33}O_2)$ and sodium hydroxide (NaOH). When both chemicals interact with each other, an exothermic hydrolysis equation occurs.

The actual reagents used in this experiment will be olive oil and a 5 M sodium hydroxide aqueous solution therefore the other constituent compounds in olive oil have to also be considered. Based on the Second Edition of Olive Oil published by Science Direct, olive oil is composed of monounsaturated, poly unsaturated and saturated fatty acids: oleic, linoleic, palm tic and stearic acid respectively. However, approximately 99% of the olive oil is composed of triacylglycerol or triglycerides such that a very small portion of the olive oil contains free moving fatty acids and an array of lipids such as hydrocarbons, sterols, aliphatic alcohols, tocopherols, and pigments [2].

The main constituent compound in olive oil is typically the oleic-oleic-oleic triacylglycerol. The olive oil that was used for this investigation is Bosco Pure and Natural 100% Pure Olive Oil and the content of oleic acid is listed as 10 g for 14 g serving of olive oil. This approximates the oleic acid triglyceride to 70% of the total mass of olive. While side reactions between sodium hydroxide and the remaining triacylglycerol are will likely occurs, this investigation will focus solely on the reaction between the oleic-oleic-oleic triacylglycerol and the sodium hydroxide.

$C_3H_5(C_{18}H_{33}O_2)_3(l)+3\ NaOH\ (aq) \rightarrow C_3H_5(OH)_3(l)+3\ C_7H_{33}COONa(s)$

The chemical equation explains the reaction between the aqueous sodium hydroxide solution and the triglyceride to ultimately form the sodium oleate polyatomic ionic compound and glycerol. This reaction is known as the alkaline ester hydrolysis which forms sodium oleate which is soap and hence is also known as Saponification. This Saponification reaction includes the hydrolysis of the triacylglycerol by the sodium hydroxide by splits the ester into three oleate ions. The three hydroxide acts as the three hydroxyl groups that bond covalently to form glycerol. The three negative oleate ions bond ironically with the positive sodium ion to form the polyatomic ionic compound: sodium oleate.

Understanding this alkaline hydrolysis reaction allows us to determine a method of measuring the rate of reaction as it can be inferred that the pH at the beginning and the end of the experiment differs. This is because more and more of the hydroxide ions will be become the hydroxyl group of the glycerol and no longer free moving. Even though the sodium oleate is still alkaline, the rate of reaction can then be determined by calculating the change in pH. The change in pH can then be converted into the change in concentration of hydroxide ions. More information about how this method of rate determination was developed can be found further. Measuring rate of reaction is an interesting note is that the hydrophobic and hydrophilic ends of the sodium oleate compound allows it make water and oil miscible.

Calculating the Rate of Reaction based on pH Values

Determining the activation energy of a reaction typically requires the plotting of the Arrhenius equation in the natural log form. Calculating the rate of reaction for this particular reaction cannot be done through a change in mass or volume of gas emitted but can be determined by the change of concentration of sodium hydroxide solution. Baghdad University carried out a similar experiment to identify the kinetics of the Saponification reaction by taking samples every 5 to 10 min which is then titrated against hydrochloric acid to determine the remaining concentration of sodium hydroxide. However, I personally thought measuring the change in pH using Vernier pH probes would prevent doing many titrations.

The pH value throughout the experiment can be measured and can then be converted to pH to then nd out the concentration of hydroxide ions. The decrease in the pH value reacts in a decrease in free moving hydroxide ions. It can then be inferred that the decrease in hydroxide ions is also equal to the rate of formation of sodium oleate as the mole ratio between the two compounds is 1:1 based on the chemical equation. However, since the temperature will be varied, the change in the water ionization constant, or Kw, of the water at different temperatures has to be considered when converting the pH value into the pOH value.

Since the pH value is simply a function of calculating the concentration of free moving hydrogen or hydroxide ions, it is erected by the factors erecting the equilibrium constant. As the temperature increases, the equilibrium constant shifts toward the left side of reaction and the net concentration of hydroxide ions decreases. Therefore, the pH calculated based on the pH has to take the Kw of the water at different temperatures into consideration and it cannot be assumed that water is at pH 7.

The European Physical Journal D has a list of water ionisation constants at different temperatures that can be used to calculate the pH values [1].

The following equation will then be used to determine the pOH value:

pOH=pKw-pH

Once the pOH value is determined throughout the reaction time, the average rate of reaction can then be determined **(Table 1)**.

Order of Saponification Reaction

It can be inferred based on the literature obtained from Dr. Raghdads results in his published paper in the Journal of Engineering that the order of reaction between olefin, otherwise known as the oleic acid triglyceride, and sodium hydroxide is 2 (150). The discussion of his results revealed that the order with respect to olein and sodium hydroxide are both 1 respectively. The results of his experiments that explain the order of the reaction will be used as the basis of calculating the rate constant for this investigation. The following equation will be used to calculate the rate constant, k.

k = Rate of Reaction/[NaOH][C_3H_5(C_18H_33O_2)_3]

A literature value for the rate constant will be used as the procedure to create different concentrations of olein is not defined.

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Since it is an organic compound, the olive oil used is insoluble in water and dissolving it in different organic compounds might risk unwanted side reactions.

The natural logarithm of the rate constant can then be plotted against the reciprocal of temperature in order to and the activation energy as well as the Arrhenius constant.

DEVELOPMENT OF METHOD

The method is loosely based of Dr. Raghads procedure but uses a change in pH instead of several titrations in order to measure the rate of reaction (149).

Measuring Temperature

The initial experimental setup used a magnetic heating stirrer to initially heat up the sodium hydroxide solution before adding the olive oil. A mercury thermometer was then used in order to monitor the temperature of the mixture. However, this method of temperature control was deemed to be inaccurate due to the fact that the temperature of the mixture is very likely to actuate and increasing the volume of substances will cause the temperature to drop because more energy will be required to get a larger volume at a specific temperature. This can be explained with the concept of specie heat capacity. Therefore, instead of using mercury thermometers to control the temperature, a Vernier temperature probe is used instead.

Using the Vernier temperature probe reduces the percentage uncertainty as the temperature can be measured even more precisely with a temperature probe instead of a mercury thermometer. Instead of using the initial temperature of the sodium hydroxide as a reading for the whole experiment, the temperature pro le of the whole reaction can be recorded. The stabilised temperature can then be used as the reading for the Arrhenius equation.

Measuring Rate of Reaction

This method of rate of reaction through change in pH was achieved through several experimental redesigns. I initially thought that the rate of reaction could be calculated based on the time taken for phenolphthalein to change from colour-less to pink. The intention behind the rest experimental design was to utilise the colour change of phenolphthalein that would turn colourless at high pH values, approximately 10-14 but would become pink when moderately basic, 7-10. However, the golden yellow colour of the olive oil makes it difficult to discern the change in colour and requires a high amount of qualitative observation. Using a Vernier spectrophotometer would allow the observation to be more quantitative but the change in colour cannot be accurately attributed toward the rate of change in moles of reactants or products.

After several redesigns using phenolphthalein, I then decided to use the Vernier pH probe instead to measure the change in concentration of hydroxide ions. The pH probe will measure pH of the sodium hydroxide at the beginning of the experiment at approximately pH 14 and should show a gradual decrease in pH as the reaction progresses. This method proved to be the best way to calculate the rate of reaction of this Saponification reaction.

The pH at the beginning and at the end of the experiment is then used to calculate the average rate of reaction. The pH is then converted into pOH by taking the pKw of water at different temperatures into consideration.

Controlling Non-Temperature Rate Factors

It is incredibly important in this investigation to control the other non-temperature rate of reaction factors such that the change in the rate can be solely attributed toward the change in temperature.

Since the order of the reaction is based on the results of Dr. Raghdads experiment, manipulating the concentration is not necessary. The concentration of the sodium hydroxide solution has to be kept consistent throughout all trials at 5.00 M. However, based on previous experiments, highly concentrated solutions of sodium hydroxide have a tendency to precipitate at the mouths of the volumetric ask. Therefore, it is not recommended to use a sodium hydroxide solution that has been shelved for a long period of time. To prevent a change in concentration due to precipitation, sodium hydroxide solution should be made immediately before being used to measure the rate of reaction. The concentration of the oleic acid triglyceride in the olive oil can be kept constant by consistently using the same olive oil and in this case Bosco Pure & Natural 100% Pure Olive Oil.

In initial experiments, the amount of excess sodium hydroxide was not con-trolled as it was assumed that volume of reactants does not affect the rate of reactions. However, the results showed calculations which could have been possibly attributed to the fact that the sodium oleate starts to solidify. Therefore, the amount of excess olive oil has to be controlled to prevent calculations in the contacting surface area that will influence the rate of reaction. The mass of olive oil is controlled up to two decimal places to ensure that the contact surface area of the sodium oleate can be controlled as well.

The rate of stirring of the olive oil and sodium hydroxide mixture also has to be controlled as the rate of stirring directly affects the amount of surface area contact between the two compounds. The rate of stirring is controlled at 100 rpm or rates per minutes. The size of the magnetises across all trials have to also be consistent to minimise its effect on the rate.

RESULTS AND DISCUSSION

Due to the extensive amount of time used for several experimental redesigns and the long reaction time of the experiment, only two temperatures were able to be tested **(Figures 1 and 2).**

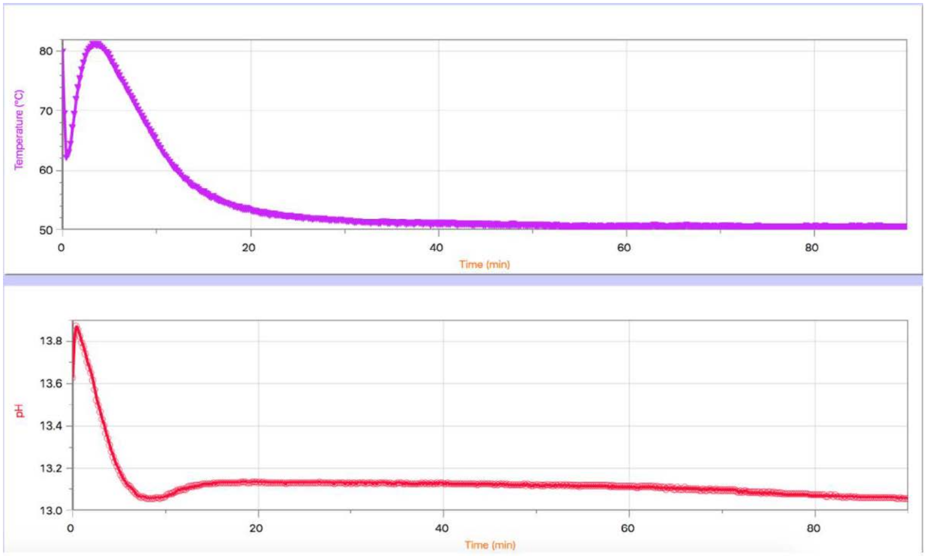

Figure 1. Temperature and pH against time at 50ºC.

Table 1. Median Temperature and Rate Constant.

Rate of Reaction	Median Temperature	Average Rate	Rate Constant
0.0554	119.8	0.00092	0.24
0.0486	51.0	0.00081	0.21

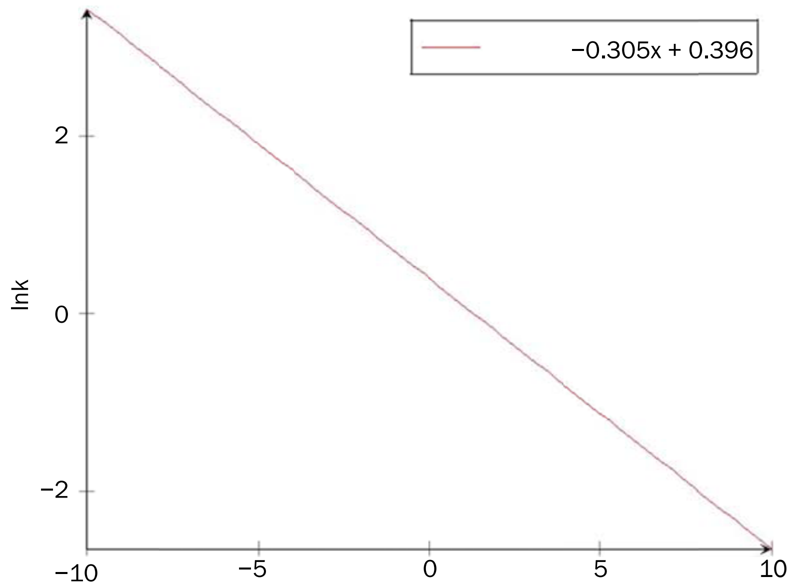

Figure 2. Arrhenius Equation.

Calculation of Activation Energy and Arrhenius Constant

InK = InA - Ea/RT

Ea = 2.53Jmol^-1

A = 1.485mol^-1dm^3s^-1

Discussion of Arrhenius Constant and Activation Energy Values

The determined activation energy of the Saponification reaction between olein and sodium hydroxide is 2.53 J mol^{-1}. However, there are a few interesting inferences that can be drawn from the results obtained.

Figure 1 show that the pH value increased at approximately 7 to 10 min during the reaction during the period when the temperature of the mixture was decreasing. This result is particularly interesting because the free moving hydroxide ion concentration should be reduced throughout the reaction. However, in this case, the increase in pH value can be attributed due to the change in equilibrium because of the decreasing temperature. The decreasing temperature then causes the equilibrium constant toward the right which then causes the pH value to increase. This also seen in Figure from 7 to 10 min but is appears more as a short plateau.

The Arrhenius constant was also identified at 1.485 mol^{-1} dm^3 s^{-1} which shows that the rate of stirring and the amount of excess olive oil will have a significant affect the rate of reaction. It can then be inferred that manipulating the surface area in contact between the reactant particles plays a big role in this Saponification reaction.

EVALUATIONS

Despite the fact that the results obtained answered the research question, there are many experimental was that had to be evaluated and accounted for. Each of the possible errors can be categorised into random or systematic errors. The experimental value obtained by Dr. Raghdad is determined to be 4.67 J/mol while his theoretical value that was calculated was 20.44 $Jmol^{-1}$. He based the discrepancy on experimental error (151). The percentage discrepancy was calculated based on Dr. Raghdads experimental value and is estimated at 85%.

Random Error

Every measurement that was conducted in this experiment produced a percentage uncertainty which ultimately led to the overall percentage uncertainty of the activation energy at approximately 2%. This produces a near negligible percentage uncertainty contribution to the overall percentage discrepancy. How-ever, due to the only two data points available, there is a low condense in the reliability of this experiment. The total amount of random error in this experiment could be reduced by increasing the amount of measured temperatures and trials per temperature.

Systematic Error

The systematic error of this experiment is expected to have a near 100% contribution to the overall percentage discrepancy and is main error that should be considered to improve the experimental procedure. The systematic error differs from the random error such that is it due to an experimental law that pushes the direction of the data points in one specific direction.

A possible experimental aw with this experiment is due to the inadequate calibration of the pH probes that may possibly show a lower rates of reactions at higher temperatures which may reflect on a less steep slope which ultimately leads to a lower reported activation energy which corresponds to the data points obtained. This experimental aw could be overcome by calibrating the pH probes with pH buffer solutions of pH values greater than 14. This would allow the measure pH values to be within the calibrated values

CONCLUSION

This investigation ultimately provides an alternative method for activation energy determination of Saponification reactions through pH analyses.

There is a low condense in the reliability of this experiment as only two temperatures were tested with one trial each but a much higher condense in the methodology's ability to discern the activation energy. This is due to the result being within a 40% discrepancy from the previously obtained practical values. The result of this experiment therefore provides evidence for the validity of the pH analysis method. The reliability of this experiment, however, could be greatly improved with a higher number of trials and tested temperatures.

An implication of this investigation is that the use of this methodology, to determine activation energies, can also be used for other reactions that undergo a change in pH during its reaction.

Further Investigation

While this experiment answers the research question, there are still many questions about the soap-making process that remains unanswered. The question would be to be identifying the systematic errors in the experiment that would cause both this investigations and Dr. Raghdads experimental value to have such a high percentage of discrepancy of 300%. The problem with both experimental setups is that it rate of reaction is too low at high temperatures and the rate of reaction is too high at low temperatures which creates a batter slope and lower subsequent activation energy. By possibly exploring different experimental methods, a more accurate method of activation energy determination can be achieved.

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