Effect of carbon chain on equilidruim and rate constants of esterification

Science, Chemistry

The reaction rate of the reaction plays an important role in the production of the ester which could affect the production of the ester. Esterification is a reversible reaction and thus this affects the amount of ester produced as ester hydrolysis changes it back to its reactants. Very little data is available on how does the carbon chain length of carboxylic acid and alcohol affects the rate constant and equilibrium constant of esterification.

Thus, the research topic of this investigation is: How does the carbon chain length of the alcohols and carboxylic acids affect the rate constants of the forward and backward reactions and equilibrium constant of the esterification reaction? The affect of the carbon chain length of carboxylic acid and alcohol was measured separately by first reacting carboxylic acids with ethanol and then alcohols with ethanoic acid. Each reaction was repeated four times and the amount of reactant and catalyst was varied. The initial rate was measured by plotting the graph of concentration of the carboxylic acid withrespectto time.

Thus, the order of reaction with respect to each reactant was measured. The reaction equation was then formed and the rate constant for each reaction was calculated. The rate constant of esterification decreased with the increase in the carbon chain length of both the carboxylic acid and alcohol. The amount of carboxylic acid present in the solution was calculated after the reactions had reached dynamic equilibrium. By using this value and the balanced equation of the reaction, the amount of other chemicals present in the solution was calculated. The equilibrium constant for each reaction was calculated using these values.

The equilibrium constant decreased with the increase in the carbon chain length of the reactants.

Research question:

How does the carbon chain length of the alcohols and carboxylic acids affect the rate constants of the forward and backward reactions and equilibrium constant of the esterification reaction?

Independent variable: Carbon chain length of alcohols and carboxylic acids

Dependent variables:

1. Rate constants of the forward and reverse reactions of esterification
2. Equilibrium constant of esterification reaction

Motivation: I have a special interest in organic chemistry. I have always been amazed by the special properties of esters such as the different fragrance that most of the esters have; and their wide industrial use.

Thus, after some research I realized that esterification is actually a reversible reaction. This created further interest in me to do my research on this topic as it relates to the recent chemistry topic that I have learnt. Therefore, through this topic I intend to gain a better knowledge of this segment of organic chemistry and also master the new chemistry concepts that I have learnt.

Background Information: Alcohol Alcohols are thefamilyof In the figure above, R represents any compounds that contain one length or type of hydrocarbon chain. 1 r more functional groups of It can contain any number of carbons Fig. 1 in the form of straight chain, branched hydroxyl (-OH) groups. chain or cyclic chain. Carboxylic acid the In the figure above, R represents any family of compounds which length or type of hydrocarbon chain. Carboxylic acids are contain one or more (-COOH) It can contain any number of carbons 2 Fig. 2 functional group. in the form of straight chain, branched chain or cyclic chain.

Ester In the figure above, R and R’ Esters are the family of represents any length or type of alkyl organic compounds which chain. It can contain any number of ontain one or 3 more Fig. 3 carbons in the form of straight chain, (RCOOR’) functional groups. branched chain or cyclic chain. 1 " Functional Groups. " Both Brains and Beauty. Web. 11 Nov. 2010. . 2 " Functional Groups. " Chemistry Tutorials & Drills. Web. 11 Nov. 2010. . 3 " Functional Groups. " Both Brains and Beauty. Web. 11 Nov. 2010. Esterification is a process in which an alcohol and a carboxylic acid react to form ester and water. 4 For esterification, concentrated sulfuric acid is used as a catalyst to increase the rate of reaction.

H+ ions act as a catalyst to provide an alternative pathway for reaction to occur. This new pathway has lower activation energy compared to the uncatalysed reaction. Thus more particles undergo effective collision and the rate of reaction increases. Due to the release of high concentration of H + ions in the complete dissociation of sulfuric acid in its aqueous form, it is used as a catalyst in this investigation. Rate equation: The rate of reaction is defined as the decrease in concentration of a reactant per unit time or the increase in concentration of a product per unit time.

The rate equation of a reaction is given by: In the above equation, the rate constant, k is defined as a constant of proportionality in the rate equation. 6 It is temperature dependent meaning its value only changes with a change in temperature. The symbols [A] and [B] represent the concentrations of the reactants A and B. The denotations ‘ m’ and ‘ n’ represent the order of reaction with respect to the reactants A and B respectively. The overall order of reaction is measured by adding the values of ‘ m’ and ‘ n’. 4 " Determining the Equilibrium Constant for an Esterification.

Web. 27 Oct. 2010. . 5 " Kinetics, Year 5 (2010) IBDP Chemistry HL. " Anglo-Chinese School (Independent). Web. 28 Oct. 2010. 6 " Kinetics, Year 5 (2010) IBDP Chemistry HL. " Anglo-Chinese School (Independent). Web. 28 Oct. 2010. A reversible reaction takes place in both forward reaction and backward directions simultaneously. When the rates of the forward and backward reactions are equal the reaction system reaches dynamic equilibrium and at this point, the concentration of reactants and products remain constant.

This hold s true until a change is made to the conditions of system because the position of equilibrium will readjust to counteract the change according to Le Chatelier’s principle. For a reaction: The equilibrium constant kc at a particular temperature is given by the equation: This equilibrium constant is also related to the rate constants of the forward and reverse reactions of . 7 esterification and it is given by the equation Esterification is a reversible reaction. Thus, when an alcohol and a carboxylic acid are react from ester and water as products; these products react to from the alcohol and carboxylic acid.

At the start of the reaction, the concentrations of the alcohol and carboxylic acid are much higher than the ester and water present in the container. Thus, the rate of forward reaction is higher than the backward reaction and hence, more products are formed than the reactants. As the concentration of the reactants decrease the rate of forward reaction decreases and as the concentration of the products increase the rate of backward reaction increases. Eventually the rates of forward reaction and backward reaction become equal and the system reaches dynamic equilibrium.

At this point the concentrations of the alcohol, carboxylic acid, ester and water remain constant. 8 7 " Equilibrium, Year 5 (2010) IBDP Chemistry HL. " Anglo-Chinese School (Independent). Web. 28 Oct. 2010. 8 " Equilibrium, Year 5 (2010) IBDP Chemistry HL. " Anglo-Chinese School (Independent). Web. 28 Oct. 2010. In gases and liquids the atoms and molecules move in random direction. However, the speed of the motion is not the same for each particle due to the continuous collisions which result s in a spread of speeds in the particles.

Thus, in liquids and gases exhibit a distribution of speeds and this distribution is called Maxwell Boltzmann distribution. Fig. 4 The above Maxwell Boltzmann distribution shows that at a particular temperature only the fast moving particles have energy higher than the activation energy of a reaction. In esterification, the particles of the carboxylic acid and alcohol with higher velocity will have higher energy than the activation energy of the reaction. Thus, only these few molecules will react when they collide. At a particular temperature, the average kinetic energy of the particles of any substance is same.

This can be referenced from the formula . Hence, as the carbon chain length of the carboxylic acid and alcohol increases the average kinetic energy of the particles remains constant. Therefore the increase in the molecular mass of the particles results in a lower velocity. Due to this lower velocity the frequency of the collisions of the particles decreases. Due to fewer collisions there are less effective collisions which result s in a slower rate of reaction. This claim is justified by an example of how the rate of escape of Hydrogen from Earth’s atmosphere is faster than the rate of escape of oxygen.

It is observed that the original hydrogen present in Earth’s atmosphere has disappeared whereas there is a comparatively little change in the volume of oxygen. Through the Maxwell Boltzmann distribution we know that of hydrogen particles, . Thus, the average speed . However, the molecular mass of an oxygen molecule is 16 times of a hydrogen molecule (1). Therefore the average speed of oxygen particles, Since, the average speed of the particles of hydrogen is times faster than the particles of oxygen, they can easily overcome the escape velocity of earth i. e. 11. 2km/s.

The escape velocity in this case can be seen as the activation energy of a reaction. Hence, the rate of escape of hydrogen is much higher than the rate of oxygen. 9 This example supports how the heavier particles i. e. the carboxylic acids and alcohols with bigger carbon chain lengths will result in a slower reaction rate. 9 " The Maxwell-Boltzmann Distribution. " Web. 27 Apr.

2011. . " An Introduction to the Collision Theory in Rates of Reaction. " Chemguide: Helping You to Understand Chemistry - Main Menu. Web. 28 Apr. 2011.

As the carbon chain of an organic compound increases, the size of the molecule increases. Thus, the mass of the molecule increases as well. The increase in the mass of the molecule will result in a slower velocity for the same kinetic energy. Hence, at the same temperature heavier molecules will move slower which will result in less number of effective collisions. This will decrease the rate of formation of ester i. e. the value of the rate constant for the forward reaction will decrease. The increase in the carbon chain of alcohol and carboxylic acid will result in a bigger molecule of ester.

With the bigger carbon chain lengths the ester will become less stable due to the weakening of the ester linkage. Thus, the ester will get hydrolyzed easily. This means that the rate constant of the reverse reaction will increase in value with the increase in the carbon chain length of both carboxylic acid and the alcohol. With the decrease in the rate constant of forward reaction and the increase in the rate constant of reverse reaction, the value of the equilibrium constant will decrease. Significance of the study: Esters are important organic compounds which have wide use as solvents, plasticizers, pharmaceuticals and intermediates.

All these uses make esters important industrial chemicals. Their fragrance provides even further uses in cosmetics andfoodindustries. Therefore, esters are produced at large quantities in today’s industry. The reaction of forming esters using acid catalyzed alcohols and carboxylic acids is called Fisher esterification. Therefore, this study aims to provide a better knowledge of the effects of carbon chain length on the kinetics and equilibrium properties of esterification reaction.

These properties greatly affect the production of esters. Hence, this study will provide data which can aid the choice of esters made by industries. 0 10 " Ester (chemical Compound) -- Britannica Online Encyclopedia. " Encyclopedia - Britannica Online Encyclopedia. Web. 27 Oct. 2010. .

Description of investigation (Methodology): Variables: Independent variable Carbon chain length of The carboxylic acids used are ethanoic acid, carboxylic acid alcohol and propanoic acid and butanoic acid. The alcohols used are ethanol, propanol and butanol. By using the carboxylic acids and alcohols with increasing chain length the carbon chain length is varied in this investigation. Dependent variable Rate constant esterification f A series of esterification reactions was carried out using the carboxylic acids and alcohols Equilibrium constant of mentioned above.

The rate constants and esterification equilibrium constants of these reactions are measured to determine the change in the two constants. Controlled variable Temperature Both rate constant and equilibrium constant are temperature dependent. Thus, it is necessary that temperature is kept constant. IT is assured by conducting the investigation in an air-conditioned laboratory. Carbon carboxylic chain of Carboxylic acid and alcohol can contain many acid nd types of carbon chain length like branched alcohol chain or cyclic chain.

This can greatly affect the results. Hence, only carboxylic acids and alcohols with straight carbon chain are used in this experiment. Catalyst There many types of catalyst that can be used to esterification reaction. The esterification reactions in this investigation are catalyzed by sulfuric acid. Indicator for titration Since weak acids are titrated against sodium hydroxide which is a strong base, the salt produced will have a higher pH value than 7. Thus, phenolphthalein is used as an indicator for this investigation as it changes color etween a high pH range of 8. 3-10. 0.

The materials required for the experiment: Apparatus Quantity Pipette – 1ml 2 Pipette – 5 ml 2 Pipette filler 1 Burette – 50 ml 1 Burette stand 1 Conical flask – 100 ml 1 Beaker – 100 ml 3 Measuring cylinder – 10 ml 2 Measuring cylinder – 50 ml 2 Mass balance 1 Reflux system 1 Ethanol – 95% 200 ml Propanol – 99% 150 ml Butanol – 99. 5% 150 ml Ethanoic acid – 99. 5% 200 ml Propanoic acid – 99% 150 ml Butanoic acid – 99 % 150 ml Sulfuric acid – 6. 0 moldm-3 100 ml Sodium hydroxide – 1. 0 moldm-3 3000 ml Phenolphthalein indicator 00 ml. Measurement of initial rate of reaction using the progressive curve method:

1. Measure 10 cm3 volumes of ethanol and ethanoic acid separately using measuring cylinders.
2. Add the ethanoic acid to a beaker followed by 2 cm3 of 6 moldm-3 sulfuric acid.
3. Add ethanol to the beaker to start the reaction and start the stopwatch.

4. Add 25 cm3 of deionised water and few drops of phenolphthalein indicator to a conical flask and pipette 1 cm3 of the reaction mixture into the conical flask in intervals of 5 minutes from the start point.
5. Titrate the solution with 1. moldm-3 aqueous sodium hydroxide until the color of the indicator changes from colorless to pink.
6. Repeat this step of titration every 5 minutes until there is no change in the amount of sodium hydroxide required to titrate.
7. Collect the data and plot the curve of concentration of ethanoic acid against time to calculate the initial rate of reaction.

Measurement of the rate equation of the forward reaction using the initial rate method:

1. Now vary the volume of ethanoic acid used and keep the volumes of ethanol and sulfuric acid constant.
2. Repeat the procedure of measuring the initial rate of reaction.
3. Repeat the steps 1 and 2 for ethanol and sulfuric acid respectively.
4. By analyzing the initial rates of reactions and the amount of reactants used, calculate the order of the reaction with respect to ethanol and ethanoic acid. Use the equation:
5. By using the order of reaction calculated from the rate equation:
6. Use the equation to find the value of the rate constant of the forward reaction of esterification. Replace ethanol and ethanoic acid in the above reaction with other alcohols and carboxylic acids and repeat the procedure for finding the initial rate and rate constant.

The temperature of the reactions is kept constant to ensure that the change in rate constant is solely dependent on the change in carbon chain length. 11 11 " Kinetics, Year 5 (2010) IBDP Chemistry HL. " Anglo -Chinese School (Independent). Web. 28 Oct. 2010.

Geert Hangx Et. Al. " REACTION KINETICS OF THE ESTERIFICATION OF ETHANOL AND ACE TIC ACID TOWARDS ETHYL ACETATE. " 24 Aug. 2001. Web. 27 Oct. 2010.

Measurement of equilibrium constant:

1. Using a pipette add 20 cm3 of ethanoic acid to a round bottom flask.
2. Pipette 5 cm3 of sulfuric acid of concentration 6 mol/dm3.
3. Pipette 20 cm3 of ethanol to the flask.
4. Set-up a reflux system with the round bottom flask containing the reaction mixture. Reflux system is used to ensure that no vapors escape from the reaction during heating. Heating is done to ensure that equilibrium is reached faster.
5. After 60 minutes, stop heating and put the flask in an ice water bath until the temperature of the mixture reaches the room temperature.
6. Pipette 1 cm3 of the reaction mixture into a conical flask and add 25 cm3 of deionised water to quench the reaction.
7. Titrate the solution with sodium hydroxide of concentration 1. 0mol/dm3.

Repeat the procedure twice with heating time of 15 minutes to ensure that equilibrium has been reached. 12 Fig. 5 By using the titration values measure the amount the carboxylic acid present at dynamic equilibrium. 13

Measure the amount of alcohol, ester and water present in the solution by using the reaction equation: Use these values to find the equilibrium constant kc. 12 " Missdeadlift in the Mouse Maze" JP Fitness Forums. Web. 30 Nov. 2010. . 13 " Determining the Equilibrium Constant for an Esterification. " Web. 27 Oct. 2010. . " Determination of an Equilibrium Constant. " HL IB Chemistry. Web. 27 Oct. 2010.

Arun Kumar 002329-179 Reaction mechanism for esterification: The steps of the mechanism:

1. Firstly the carboxylic acid molecule accepts a proton from sulfuric acid. The partially positively charged hydrogen atom on the sulfuric acid molecule is attracted to the lone pair of the oxygen atom from the carboxylic acid. This converts the double bond between carbon and oxygen into a single bond.
2. The positive charge is delocalized over the hydrophilic end of the molecule.

This can be shown by three resonance structures:

- The protonated carboxyl group reacts with the alcohol molecule in SN1 reaction to give a tetrahedral intermediate.
- The alcohol acts as a nucleophile and attacks the partially positively charged carbon in the carboxylic acid molecule. The oxygen atom forms a single bond with the carbon atom and the positive charge is transferred to the newly bonded oxygen atom.

- A proton is lost into the reaction mixture from the oxygen in the alcohol molecule and a proton is accepted by one of the oxygen from the carboxyl group from the reaction intermediate.
- The excess positive charge created on the oxygen molecule attracts bonded pair of electrons with the carbon atom.

This weakens the bond between the carbon atom and oxygen atom. Thus, a molecule of water is lost into the reaction solution from the reaction intermediate. 6. This creates a positive charge on the molecule which is delocalized over the molecule as shown by the resonance structures: 7. This creates a positive charge on the molecule which is delocalized over the molecule as shown by the resonance structures: 14 14 " Mechanism for the Esterification Reaction. " Chemguide: Helping You to Understand Chemistry Main Menu. Web. 27 Oct. 2010. . T. W. Graham Solomons Et. Al. Organic Chemistry. 9th ed. New Delhi: John Wiley & Sons, 2008.

Discussion of results: Sample calculations The calculations for the first esterification reaction are given below as sample calculations. The data for other reactions is given under appendix 1. Titration values of the reaction between ethanol and ethanoic acid: Reaction 1: Calculation of concentration of ethanol Mass/volume percentage given for ethanol = 95% Thus, in 1 dm3 of the ethanol solution = 950 g of ethanol No. of mol of ethanol = Therefore, the molar concentration of ethanol = 20. 62 moldm-3 Volume used/ml Concentration/moldm-3

Ethanol 10. 0±0. 1 20. 62

Ethanoic acid 10. 0±0. 17. 28

Sulfuric acid 1. 000±0. 001 6. 00

Initial rate in terms of concentration calculated from the graph = - (gradient of the tangent) = 0. 0722 moldm-3min-1

Reaction 2: Volume used/ml Concentration/moldm-3 Ethanol 10. 0±0. 1 20. 62 Ethanoic acid 10. 0±0. 1 17. 28 Sulfuric acid 2. 000±0. 001 6. 00 Chemical (Time±0. 01) /min (Initial volume ±0. 05)/cm3 (Final volume ±0. 05)/cm3

Graph 2 Initial rate calculated from the graph = - (Gradient of the tangent) = 0. 00260 molmin-1

No. of mol of thanoic acid remaining/mol ±? /% Arun Kumar 002329-179 Reaction 3: Volume used/ml Concentration/moldm-3 Ethanol 15. 0±0. 1 20. 62 Ethanoic acid 10. 0±0. 1 17. 28 Sulfuric acid 2. 000±0. 001 6. 00 Chemical (Time±0. 01) /min (Initial volume ±0. 05)/cm3 (Final volume ±0. 05)/cm3 (Total volume used ±0. 1)/cm3 No. of moles of NaOH used/mol ±? /%

Ethanoic acid 10. 0±0. 1 17. 28

Sulfuric acid 2. 000±0. 001 6. 00