Determination of rate of reaction and rate constant of the hydrolysis of ester (ethyl acetate) with alkali(sodium hydroxide)

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Abstract

*The rate of reaction is defined as the change in the number of molecules of reacting species per unit volume per unit time. Hydrolysis is the decomposition reaction involving breaking of a bond and the addition of water elements. In this hydrolysis of ethyl acetate with sodium hydroxide, hydrochloric acid was used as catalyst to accelerate the reaction mixture. 1ml and 2ml of ethyl acetate was injected separately into the 500 ml conical flask which contains 0.05N of sodium hydroxide and thoroughly mixed. At regular time interval, 0, 10, 20, 30, 40, and 90 minutes, 25ml of each of the samples were withdrawn into a 250 ml conical flask containing 0.05N hydrochloric acid, and titrated against 0.05N sodium hydroxide solution using phenolphthalein as an indicator. From the value of sodium hydroxide, the hydrolysis involving the 1ml ethyl acetate was faster than that of the 2ml ethyl acetate, indicating that the higher the concentration the faster the rate of reaction. The rate constant after calculation from the graphs was approximately 0.003*$min^{-1}cm^{-3}$*for the 1ml and 2ml of ethyl acetate, signifying that while the rate of reaction is concentration dependent but the rate constant is notconcentration dependent.*

Keywords: *concentration, hydrolysis, rate constant, ester, alkali*

I. Introduction

The chemical kinetics is the quantitativedetermination of rate of chemical reactions and of the factors upon which therates depend.Chemical reaction takes place when a certain number of molecules of one or more than one species have lost their identity and assumed a new form by a change in the kind or number of atoms in the compound and by a change in structure or configuration of these atoms. In this classical approach to chemical reaction, it is assumed that the total mass is neither created nor destroyed when a chemical reaction occurs. Chemical kinetics is the part of physical chemistry that studies rate of reaction and rate constant. The rate of reaction for a reactant or product in a particular reaction is intuitively defined as how fast a reaction takes place. For example, oxidation of iron under the atmosphere is a slow reaction which can take years, but the combustion of butane in a fire is a reaction that takes place in seconds.

A. Rate of reaction:The rate or velocity of a reaction may be expressed in terms of any one of the reactants or any one of the products of the reaction.The rate of reaction is defined as the change in the number of molecules of reacting species per unit volume per unit time. It is also defined to be proportional to the concentration of reacting species raised to a power called the order of reaction. It is usually taken as the rate at which the reactant disappear or the rate at which the product is formed. The rate at which the reactant 'a' is disappearing is proportional to its concentration at any instance,

i.e. Rateα (a - x)

Rate = k (a - x)

where k = rate constant

The concept of rate of reaction is very important to determining chemical reacting systems. It is the core factor in the development of performance models to stimulate reactor functional parameters.In place of concentration of reactant or product any physical property, which is directly related with concentration, such as viscosity, surface tension,refractive index, absorbance etc. can be measured for the determination ofthe rate of reaction.

B. Factors determining the rate of reaction

a. Surface area of the reactants: greater the surface area of a solid, greater the rate of reaction.

b. Concentration: increase in concentration increase the rate of reaction.

c. Pressure: increase in pressure results in an increase in the rate of reaction, if the reactants and products are gaseous.

d. Catalyst: presence of a catalyst increases the rate of reaction. There are however, negative catalysts that lower the rate of reactions.

e. Temperature: increase in temperature increase rate of reaction.

C. Rate Constant:For any general reaction

$aA + bB \rightarrow cC + dD$

the rate is proportional to $[A]^a \times [B]^b$, i.e.

$\text{Rate} = k[A]^a\,[B]^b$

where proportionality constant k, relating rate with concentration terms, isknown as rate constant or velocity constant at a given temperature.When the reactants are present at their unit concentrations,

Rate = k

Thus, the rate constant is the rate of reaction when concentrations of thereactants are unity. The rate constant under these conditions is also known asthe specific rate or the rate coefficient. The rate constant for any reaction canbe determined

(a) either by measuring the rate of the reaction at unit concentrations ofthe reactants.

(b) or by knowing the rate at any concentration of reactant using therelation

$\text{Rate constant} = \text{Rate}/\,[A]^a\,[B]^b$

The case where the reaction is slow enough, the thermal equilibrium willbe maintained due to constant collisions between the molecules and k remainsconstant at a given temperature. However, if the reaction is very fast the tailpart of the Maxwell-Boltzmann distribution will be depleted so rapidly thatthermal equilibrium will not be re-established. In such cases rate constantwill not truly be constant and it should be called a rate coefficient.

Therefore, the kinetics of the reaction can be determined by taking a known quantity of ethyl acetate (ester) and mixing it with a relatively large quantity of HCl. An aliquot of the reaction mixture is withdrawn at different intervals of time and titrated against a standard alkali (sodium hydroxide). Obviously, as the reaction proceeds, the value of alkali required to neutralize the acid (HCl present as catalyst + CH_3COOH produced by hydrolysis of the ester) progressively increases.

The fact that this is a first order reaction is established by substituting the results in the first order rate expression;

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

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As the reaction proceeds, each hydroxide ion (OH^-) removed in the formation of ethanol removes one molecule of ethyl acetate, being the number of moles of either hydroxide ion or ethyl acetate so removed the concentration of the reactants decreases. If we start with equal concentrations of the reactants, the concentration of sodium hydroxide can be conveniently followed at different time intervals by withdrawing an aliquot from the reaction mixture and determining the sodium hydroxide measure the rate of reaction, so the greater the value of the rate constant, the faster the reaction. Each reaction has a certain value of the rate constant at a particular temperature and the value of the rate constant for the same reaction changes with temperature and the values do not depend upon the concentration of reaction but depend upon order of reaction.

D. Hydrolysis of an ester (ethyl acetate) in presence of a mineral acid:Hydrolysis is a chemical decomposition involving breaking of a bond and the addition of water element. The use of an acid catalyst accelerates the hydrolysis. The reaction rate is expressed in terms of chemical composition of the reacting species.

a. The hydrolysis of an ester such as ethyl acetate in the presence of a mineral acid gives acetic acid and ethyl alcohol.

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

And verifying the constancy of the value of rate constant, k or in this case,$(a - x) \propto (V\infty - V0)$ and $a \propto (Vt - V0)$

$$k = \frac{2.303}{t} \log \frac{(V\infty - V0)}{(Vt - V0)}$$

2Where, Vo = initial titre value

$V\infty$= final titre value at the end of the experiment and

Vt = titre value at the various time intervals chosen

As the hydrolysis proceeds, there will be proportional increase in the concentration of acetic acid formed.

b. The hydrolysis of an ester such as ethyl acetate illustrates a bimolecular reaction that gives sodium acetate and ethanol as the product from which second order rate constant can be calculated:

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

present in it direct or indirect titration with a standard solution of an acid. The hydrolysis of ester in presence of alkaliis second order being first order with respect to both ester and NaOH. The second order reaction can be established by the consistency of the values of rate constant (k) determined by substituting the titration results at different time intervals in the second order rate equation as follows:

$$k = \frac{1}{t} \times \frac{(V0 - Vt)}{V0.Vt}$$

3

Where Vo = volume of the acid equivalent to the alkali present at initial stage of experiment

Vt= volume of the acid equivalent to the alkali present at any selected time interval

Obviously, Vt is proportional to $(a - x)$ and $Vo$is proportional to 'a' in the original rate equation for the second order reaction of type I.

$$k = \frac{1}{t} \times \frac{x}{a(a - x)}$$

4If we start with different concentrations of the reactants, the second order rate equation type II should be used for establishing the reaction to be of second order.

A + B → Products

$$k = \frac{2.303}{t\ (a - b)} \times \log \frac{b(a - x)}{a(b - x)}$$

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If 'b' moles of ester and 'a' moles of NaOH are taken initially, then

'a' α Vo (the volume of acid equivalent to the amount of NaOH present initially)

$(a - x)\ \alpha\ Vt$(the volume of acid equivalent to the amount of NaOH present at time, t)

$(a - b)\ \alpha\ V\infty$(the volume of acid equivalent to the amount of NaOH present at the end of the reaction)

$$x = a - (a - x) = V0 - Vt$$

$$b = a - (a - b) = V0 - V\infty$$

Therefore

$$(b - x) = a - (a - b) - [a - (a - x)]$$

$$= a - (a - b) - a + (a - x)$$

$$= (a - x) - (a - b) = Vt - V\infty$$

by substitution equation 5 become

$$k = \frac{2.303}{t.V\infty} \times \log \frac{(V0 - V\infty)Vt}{(Vt - V\infty)V0}$$

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$$k = \frac{2.303}{t.V\infty}\ [\log \frac{(V0 - V\infty)}{(Vt - V\infty)} - \log \frac{V0}{Vt}]$$

$$\log \frac{V0 - V\infty}{Vt - V\infty} = \frac{k.V\infty.t}{2.303} + log \frac{V0}{Vt}$$

7

Since this equation is of the form: y = mx + c, this represents an equation for a straight line.

Therefore, a plot oflog $\frac{V0 - V\infty}{Vt - V\infty}$vs. t gives a straight line with a slope equal to$\frac{k.V\infty}{2.303}$. From the value of theslope, the value of the rate constant, k can be calculated.

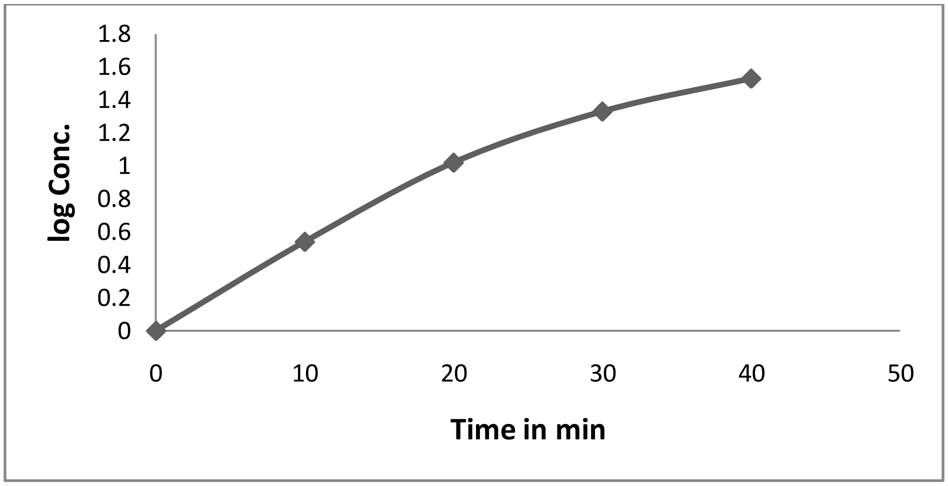
II. Experimental procedure: 25ml of 0.05N HCl was measured accurately with a pipette into each of six numbered 250ml conical flasks. 500ml of 0.05N NaOH solution was placed in a thermostatic water bath set at 27°C.At time zero, 1ml of ethyl acetate was also measured with a syringe into the reaction vessel and the mixture thoroughly shaken for ten to fifteen seconds. 25 ml of the sample was withdrawn and discharged as rapidly as possible into the respective 250ml conical flask containing the 25ml 0.05N HCl already and titrated against 0.05N of NaOH solution using two or three drops phenolphthalein as an indicator. The experiment was repeated with the volume of 2 ml of ethyl acetate at the same temperature. All reagents used in this experiment are of analytical grade.

III. Result and discussion

Table 1: Volume of 1 ml of ethyl acetate at 27^{0}C temperature

Time (min)	Volume of NaOH (ml)	$Vt - V\infty$	$Vo - V\infty$	$\frac{(Vo - V\infty)}{(Vt - V\infty)}$	$Log\,\frac{(Vo - V\infty)}{(Vt - V\infty)}$
0	6.50	-16.90	-16.90	1.00	0.00
10	18.50	-4.90	-16.90	3.45	0.54
20	21.80	-1.60	-16.90	10.56	1.02
30	22.60	-0.80	-16.90	21.13	1.33
40	22.90	-0.50	-16.90	33.80	1.53
90	23.40	0.00	-16.90	-	-

Figure 1: Plot (log conc. vs. time) for volume of 1 ml of ethyl acetate at 27^{0}C temperature



For the 1 ml of ethyl acetate at 27^{0}C temperature:

From equation 7,

$\log \frac{V0 - V\infty}{Vt - V\infty} = \frac{k.V\infty.t}{2.303} + \log \frac{V0}{Vt}$ using table 1, a plot of $\log \frac{(Vo - V\infty)}{(Vt - V\infty)}$ against time in figure 1, gives a slope which is equal to $\frac{k.V\infty}{2.303}$ from which k is evaluated.

Slope = $\frac{k.V\infty}{2.303}$ = 0.033 min^{-1}

Therefore,

$0.033 = \frac{k\ x\ 23.40}{2.303}$

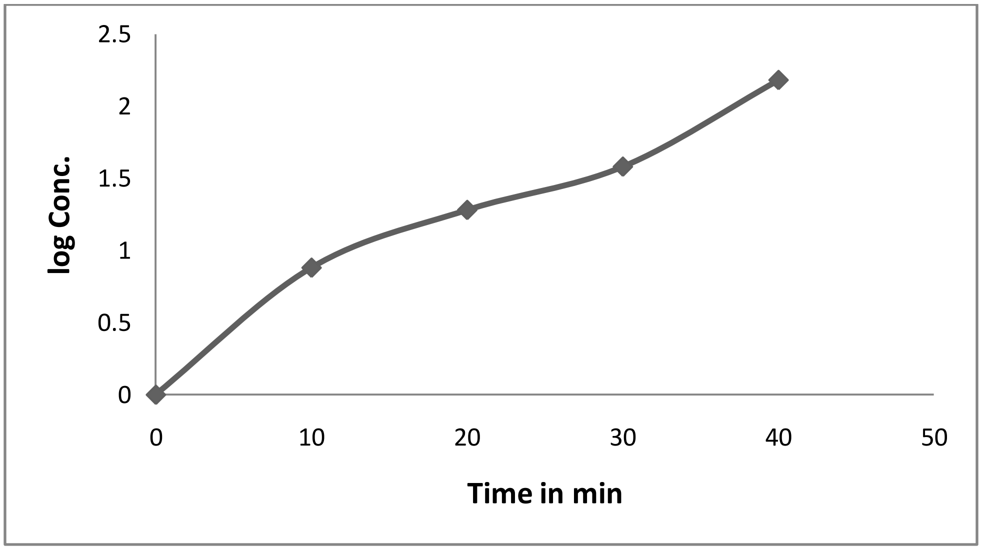
$k = \frac{0.033\ x\ 2.303}{23.40}$ = 0.00325 min^{-1}cm^{-3}

k≈ 0.003 min^{-1}cm^{-3}

Table 2: Volume of 2 ml of ethyl acetate at 27^{0}C temperature

Time (min)	Volume of NaOH (ml)	$Vt - V\infty$	$Vo - V\infty$	$\frac{(Vo - V\infty)}{(Vt - V\infty)}$	$Log\frac{(Vo - V\infty)}{(Vt - V\infty)}$
0	9.90	-15.20	-15.20	1.00	0.00
10	23.10	-2.00	-15.20	7.60	0.88
20	24.30	-0.80	-15.20	19.00	1.28
30	24.70	-0.40	-15.20	38.00	1.58
40	25.00	-0.10	-15.20	152.0	2.18
90	25.10	0.00	-15.20	-	-

Figure 2: Plot (log conc. vs. time) for volume of 2 ml of ethyl acetate at 27^{0}C temperature



For the 2 ml of ethyl acetate at 27^{0}C temperature:

From equation 7, log $\frac{V0-V\infty}{Vt-V\infty} = \frac{k.V\infty.t}{2.303} + log\frac{V0}{Vt}$ using table 2, a plot of $log\frac{(Vo-V\infty)}{(Vt-V\infty)}$ against time in figure 2, gives a slope which is equal to $\frac{k.V\infty}{2.303}$ from which k is evaluated.

Slope = $\frac{k.V\infty}{2.303}$= 0.043 min^{-1}

Therefore,

0.043 = $\frac{k\ x\ 25.10}{2.303}$

k = $\frac{0.043\ x\ 2.303}{25.10}$= 0.00395 min^{-1}cm^{-3}

k ≈ 0.003 min^{-1}cm^{-3}

IV. Conclusions

It can be concluded from this experiment that rate of reaction is concentration dependent whereas, rate constant does not concentration dependent. Also, that the rate constant for the hydrolysis of ethyl acetate with sodium hydroxide using hydrochloric acid as a catalyst at 27^{o}C is approximately 0.003 min^{-1}cm^{-3}.

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