

## Natubhai V. Patel College of Pure &amp; Applied Sciences

## T. Y. B.Sc. (Industrial chemistry)

## IC – 302: Unit Process, Synthetic dyes and Pharmaceuticals

## UNIT – 2D

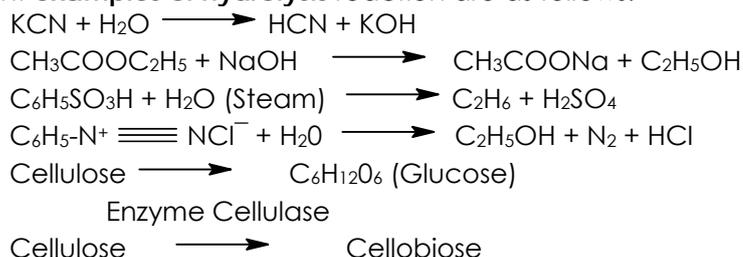
Syllabus

**Hydrolysis:** Introduction, hydrolyzing agents and different mechanism of Hydrolysis

HYDROLYSIS2.20 INTRODUCTION

The term **hydrolysis** is applied to the reaction in which **water effects a double decomposition** with **another compound**, **hydrogen** goes to **one of the product**, **hydroxyl** to the **other**. Breaking down of proteins, the saponification of fats and other esters are the examples of hydrolysis. It is **very difficult to** carry out effective **hydrolysis** with **water alone** even at high temperature and pressure. For completion and speedy hydrolysis an accelerating agent of some kind is always added. The most important **accelerating agents** are **alkali**, **acid** and **hydrolyzing enzyme**, although **ion-exchange resins** have also been used. The enzymes (organic catalyst) are of surpassing importance in vital processes, both animal and plant.

Different **examples of hydrolysis** reaction are as follows.

2.21 DIFFERENT HYDROLYZING AGENTS USED FOR HYDROLYSIS

The important hydrolysis agents are

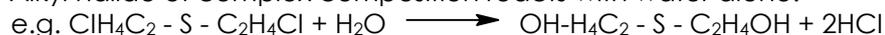
- Water
- Water - acid (acid hydrolysis)
- Water-alkali (alkali hydrolysis)
- Enzymes (enzymatic hydrolysis)

2.21.1 Water

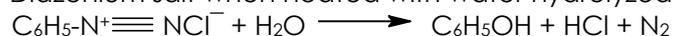
Although the word **hydrolysis** means **decomposition by water**, cases in which **water** unaided brings about **effective hydrolysis** are **rare**, but are there few specific reaction where water alone acting as effective hydrolysis agent.

Hydrolysis of **Grignard reagent** takes place completely and quickly by water alone. The acid anhydrides, lactones, lactides and other internal anhydrides such as ethylene oxide are readily hydrolyzed by water.

Alkyl halide of complex composition reacts with water alone.



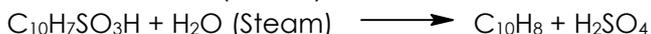
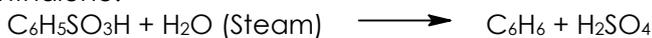
Diazonium salt when heated with water hydrolyzed completely.



Ethyl hydrogen sulfate, sodium salt of acetoacetic ester can be completely hydrolyzed by water.

A slight degree of hydrolysis seems to occur with numerous materials such as esters carbohydrates etc, but it should be noted that water by itself is able to bring about complete and rapid hydrolysis of only very few substances.

The **use of steam** rather than water has brought **good result**. Benzene sulfonic acid with steam yields benzene and sulfuric acid similarly  $\alpha$ -naphthalene sulfonic acid hydrolyzes to naphthalene.



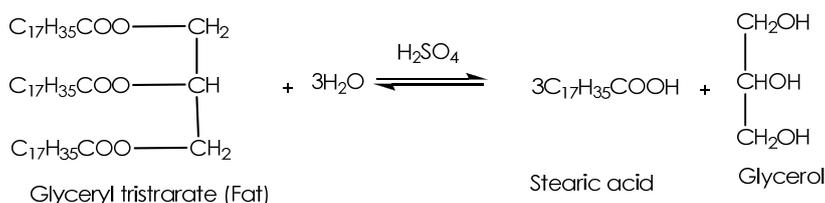
### 2.21.2 Acid hydrolysis

The use of **acid** in **hydrolysis** is rapidly extended to **organic materials** such as esters, sugar, amide etc. it was found that **acid accelerates** the **reaction**. It also initiates the reaction where water alone fails to complete the hydrolysis. This effect is **due to hydrogen ion content of acid**.

**Hydrochloric** and **sulfuric acids** are the most commonly used. Formic acid and trichloro acetic acid appears to be lower in activity whereas oxalic and benzenesulfonic acid are more active.

**Sulfuric acid** is **particularly useful** because it forms, with many types of organic substances, intermediate compound that themselves readily undergo hydrolysis; sulfuric acid exhibits a specific action, distinct from its hydrogen ion concentration, and cannot be replaced by other acids.

Organic esters of all kinds, including the esters of carbohydrates are quite subject to hydrolysis with acid.



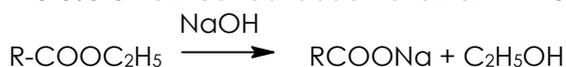
### 2.21.3 Alkali hydrolysis

**Sodium hydroxide** is most commonly used, but **alkali carbonates** and **bicarbonates** as well as the **alkaline earth hydroxides** all find occasional application. Potassium hydroxide shows no advantage over other hydroxides except in some case permits the use of a lower temperature. Ammonium hydroxide and ammonium salts are rarely used.

**Hydroxyl ion** catalyzes the hydrolysis. Acid is one of the products of hydrolysis that immediately reacts with hydroxyl ion.

Alkali hydrolysis is **distinguished into three cases**.

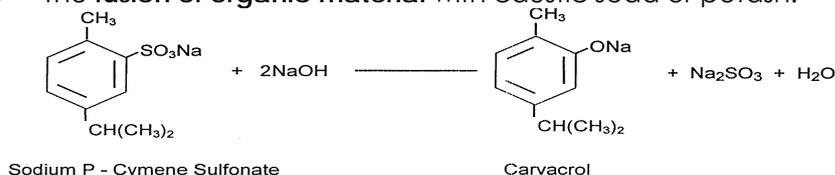
- The use of **low concentration of alkali** in the hydrolysis of esters and similar material.



- The **use of sufficient caustic** under pressure and in high concentrations to unite with all the acid produced.



- The **fusion of organic material** with caustic soda or potash.



### 2.21.4 Enzymatic hydrolysis

Very **few enzymes** are used for **hydrolysis** on large scale. Molasses is converted by invertase in the manufacture of industrial alcohol. Conversion of starch into glucose and maltose by amylase enzyme. Carbohydrate to cellobiose by enzyme cellulase are the few examples of enzymatic hydrolysis where enzymes are used.

### 2.22 THERMODYNAMICS OF HYDROLYSIS

The **extent** to which a **chemical reaction** may proceed under a given set of condition is given by the **equilibrium state**. The **driving force** of the reaction is the change in **free energy**, which is related to the equilibrium constant (K) by

$$\Delta F^\circ = -RT \ln K$$

Where, superscript ° indicates that all reactant and products are in the same standard state.

Thermodynamics relations relates the change in free energy to the heat of reaction

$$\text{Also: } \Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where,  $\Delta H^\circ$  is the heat of the reaction

$\Delta S^\circ$  is the entropy change.

If **free energy change** ( $\Delta F^\circ$ ) is **-ve**, the **reaction** is **spontaneous** and **favorable** and if free energy change is **+ve** and **greater than 10 kcal/mole** then the reaction is **not suitable** for **practical application**. **E.g.** Hydration of Ethyne



It is seen that long k and thus  $\Delta F^\circ$  becomes zero at approximately 70°C (experimental) or 90°C (calculated). At temperature below these value the formation of alcohol is favored ( $k > 1$ ) and at higher temperature the dehydration to ethylene takes place ( $k < 1$ ).

### 2.23 KINETICS OF HYDROLYSIS

In commercial processes, it is very important whether reactions goes fast or slow, if the **reaction** is **thermodynamically possible** but **proceeds** with **slow** rate then it is **modified** by changing temperature pressure and concentration ratios, a catalyst may be employed to bring about the desired results.

The **data** obtained on reaction rates may be **interpreted** through either the **collision theory** or the **theory of absolute reaction rate**. The collision theory emphasis on the energy of activation as the rate-determining factor, which may be related to temperature (T) and the rate constant (K) by **Arrhenius equation**

$$K = PZe^{-E/RT}$$

Where, E = Activation energy,

Z = frequency of collision at unit concentration of reactant,

R = Gas constant

P = probability factor

The newer theory, called **transition state theory**, places emphases on the free energy of activation and is concern with thermodynamic probability of attaining an activated complex, one form of rate constant expression is

$$k = \frac{k'T}{h} e^{-\Delta F/RT} = \frac{k'T}{h} K$$

$$k = \frac{k'T}{h} e^{-\Delta F/RT} e^{-\Delta S/R}$$

Where,  $\Delta H^\circ$  = heat of the reaction

$\Delta S^\circ$  = entropy change

### 2.24 MECHANISM OF HYDROLYSIS

#### 2.24.1 Hydrolysis of Ester

Extensive study of the hydrolysis of ester has shown that **reaction** is **reversible** and **catalyzed** by **both**  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions. The addition of acid speeds up the reaction but

scarcely shift the equilibrium position, where, the addition of sufficient base not only increase the rate but also causes the reaction to go completion by neutralization of the acid product.

**Ingold** has proposed eight possible **mechanisms** for **ester hydrolysis** B<sub>AC</sub>1, B<sub>AC</sub>2, B<sub>AL</sub>1, B<sub>AL</sub>2, A<sub>AC</sub>1, A<sub>AC</sub>2, A<sub>AL</sub>1 and A<sub>AL</sub>2

B =Basic hydrolysis

A =Acidic hydrolysis

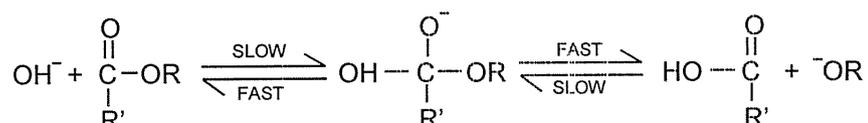
AC= Acyl oxygen fission

AL=Alkyl oxygen fission

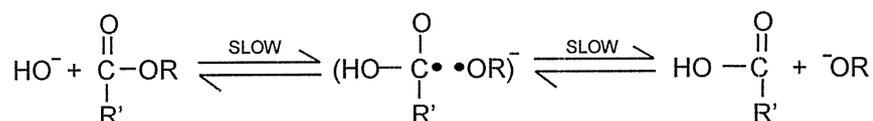
1=unimolecular process,

2=bimolecular process

The most common case of **basic hydrolysis** follows **B<sub>AC</sub>2** mechanism, which is represented as follows



or considering the intermediate to be transition state of nucleophilic substitution.



## 2.25 EXERCISE

Sr. No.	Question	Marks	Exam/year
1.	Explain sulfonation and sulfation. State the principle sulfonating and sulphating agents	03	SPU 2005
2.	Give an account of different type of oxidising agents and oxidative reaction	08	SPU 2005
3.	With the help of flow diagram describe the manufacture of vinyl acetate	05	SPU 2006
4.	Write manufacture of acetic acid from acetaldehyde	05	SPU 2006, 2007
5.	Explain the term sulphonation and sulfation giving suitable examples	03	SPU 2006
6.	Write note on various oxidative reactions	06	SPU 2006
7.	Write manufacture of benzoic acid	04	SPU 2006
8.	Write note on different hydrolysing agents used for hydrolysis	03	SPU 2006
9.	With the help of flow diagram describe the continuous partial sulfonation of benzene	05	SPU 2007
10.	Describe manufacture of benzoic acid from toluene	04	SPU 2007
11.	Define the term hydrolysis. Write note on alkali hydrolysis	04	SPU 2007
12.	Using neat flow diagram describe the manufacture of ethyl acetate	05	SPU 2007
13.	Define term sulfonation and sulfation giving suitable examples. Also write various sulfonating and sulphating agents used for sulfonation and sulfation	04	SPU 2007

## 2.26 FURTHER READING

- Unit Processes in Organic Synthesis by P. H. Groves.