Question Set 20

MECHANISM OF REACTIONS

Q. Explain the mechanism of the following : ***(2 to 3 marks)***

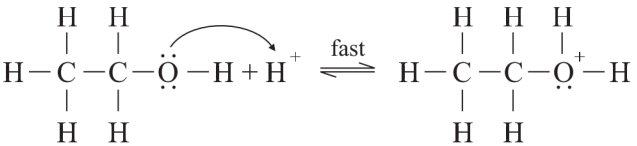
[**Note :** The questions on mechanisms of the reactions may be from the chapters 10 to 15 carrying 2 to 3 marks.]

Chapter 11. Alcohols, Phenols and Ethers

Q. 1. Mechanism of acid catalyzed dehydration of ethanol to give ethene.

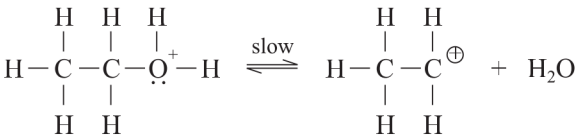
Ans. The mechanism of dehydration of ethanol involves the following order :

Step 1 : Formation of protonated alcohols : Initially ethyl alcohol gets protonated to form ethyl oxonium ion.



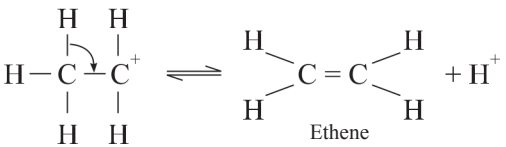
Ethanol — protonated alcohol (ethyl oxonium ion)

Step 2 : Formation of carbocation : It is the slowest step and hence, the rate determining step of the reaction.



Oxonium ion — Carbocation

Step 3 : Formation of ethene : Removal of a proton (H^+) from carbocation.



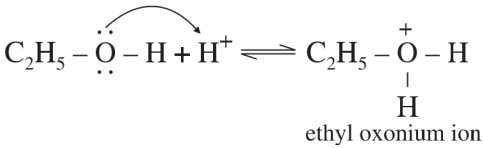
Ethene

The acid used in step 1 is released in step 3, the equilibrium is shifted to the right, ethene is removed as it is formed.

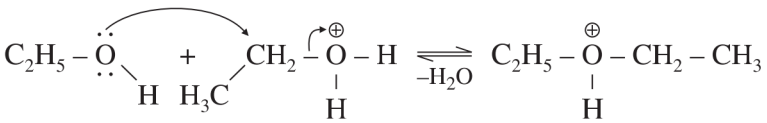
Q. 2. Write the mechanism of dehydration of alcohol to give ether.

Ans. Dehydration of alcohols to form ether is S_N2 reaction. The mechanism of dehydration of ethanol involves the following steps :

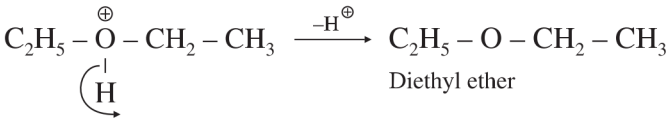
Step 1 (Protonation) : Initially ethyl alcohol gets protonated in the presence of acid to form ethyl oxonium ion.



Step 2 (S_N2 mechanism) : Protonated alcohol species undergoes a backside attack by second molecule of alcohol is a slow step.



Step 3 (Deprotonation) : Formation of diethyl ether by elimination of proton.

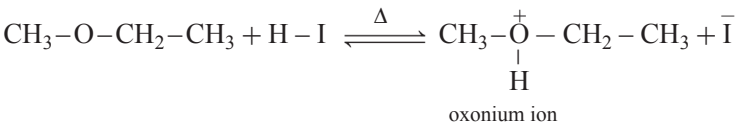


Q. 3. The mechanism of the reaction of HI with methoxy ethane.

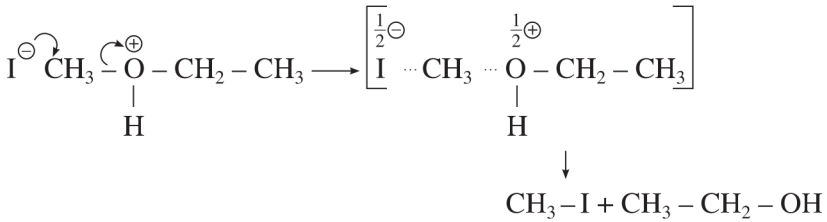
Ans. The reaction mechanism takes place as follows :

Step 1 : Protonation of ether :

Initially the ether molecule (methoxy ethane) protonated by conc. HI to form oxonium ion.



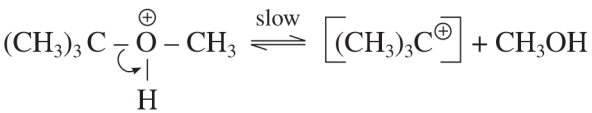
Step 2 : Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by S_N2 mechanism.



For example :

- Use of excess HI converts the alcohol into alkyl iodide.
- In case of ether having one tertiary alkyl group the reaction with hot HI follows S_N1 mechanism and tertiary iodide is formed rather than tertiary alcohol.

Step 1 :

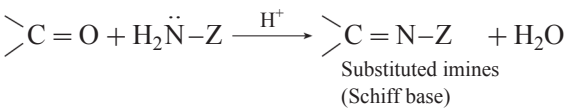


Step 2 : $(CH_3)\,C^+ + I^- \xrightarrow[\text{fast}]{} (CH_3)_3\,C - I$

Q. 4. Explain the mechanism of addition reactions of ammonia derivatives H_2N-Z with carbonyl compounds (aldehydes or ketones).

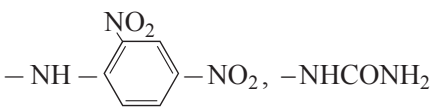
Ans. Derivatives of ammonia H_2N-Z reacts with carbonyl compounds (aldehydes or ketones) in weakly acidic medium to give addition products, which loses a water molecule to give a final product imine derivatives. A substituted imine is called a Schiff base. Schiff bases are solids and have sharp melting points.

General reaction :

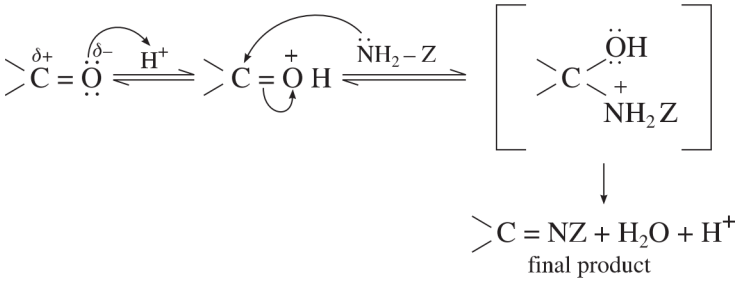


Various ammonia derivatives :

$Z = \text{alkyl}, -NH_2, OH, -NHC_6H_5$



General mechanism :



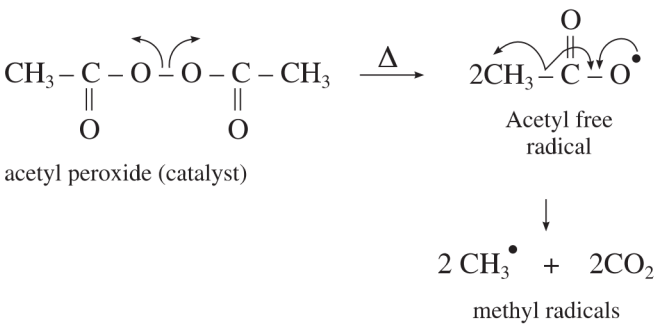
Q. 5. Write the steps involved in the free radical mechanism in polymerisation of ethylene. *OR*

Explain the free radical mechanism for the polymerisation of ethylene. *OR*

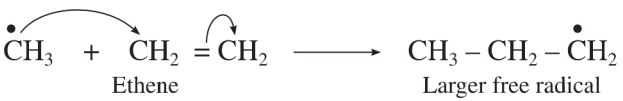
Explain in detail free radical mechanism involved during the preparation of addition polymer.

Ans. Polymerisation of ethylene is carried out at high temperature and at high pressure in presence of small amount of acetyl peroxide as initiator.

(1) Formation of free radicals : The first step involves clevage of acetyl peroxide to form two carboxy radicals. These carboxy radicals immediately undergo decarboxylation to give methyl initiator free radicals.



(2) Chain initiating step : The methyl radical thus formed adds to ethylene to form a new larger free radical.



(3) Chain propagation step : The larger free radical formed in the chain initiating step reacts with another molecule of ethene to form another big size free radicals and chain grows. This is called chain propagation step.

$$CH_3-CH_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow \underset{\text{Bigger free radical}}{CH_3-CH_2-CH_2-CH_2-\dot{C}H_2}$$

The chain reaction continues till thousands of ethylene molecules are added.

(4) Chain terminating step : The continuous chain reaction can be terminated by the combination of free radicals to form polyethene.

$$2CH_3-(CH_2-CH_2)_n-CH_2-\dot{C}H_2 \longrightarrow$$

$$CH_3-(CH_2-CH_2)_n-CH_2-CH_2-CH_2-CH_2-(CH_2-CH_2)_n-CH_3$$

Polythene (polymer)