B.SC PART I PAPER ORGANIC

TOPIC:- Reaction Mechanism Part-1

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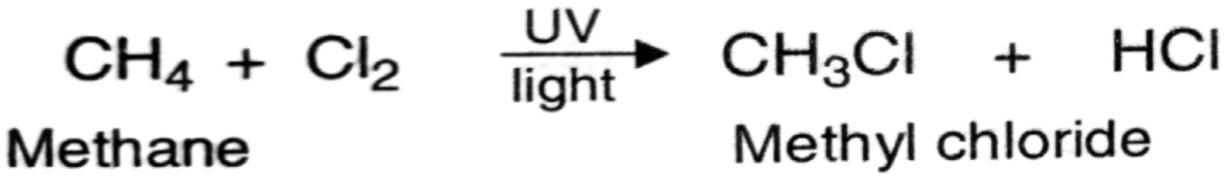
MECHANISMS OF SUBSTITUTION REACTIONS

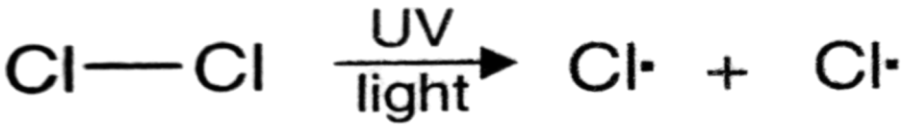
Reaction which involve the replacement or substitution of one or more atoms or groups of a compound by other atoms or groups are known as substitution reactions. These reactions may be initiated by a nucleophile, electrophile or free radical.

Free-Radical Substitution Reaction:- These reaction are initiated by free radicals. The chlorination of methane in the presence of ultraviolet light is an example of free-radical substitution.



The mechanism of the above reaction involves the following steps:

(1) Initiation Step:- A chlorine molecule undergoes hemolytic fission in the presence of ultraviolet light to give chlorine free radicals.



(2) **Propagation Steps:-** A chlorine atom attacks the methane molecule to give methyl free radicals and hydrogen chloride.

$$Cl\cdot + CH_4 \longrightarrow \underset{\text{Methyl free radical}}{\cdot CH_3} + HCl$$

The methyl free radical attacks a chlorine molecule to yield methyl chloride and Chlorine atom.

$$CH_3\cdot + Cl{-}Cl \longrightarrow CH_3{-}Cl + Cl\cdot$$

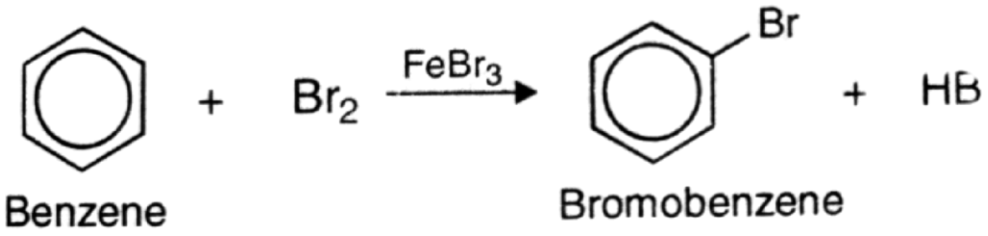
These propagation steps are repeated again and again.

(3) **Termination Steps:-** These involve the formation of stable molecule by combination of free radicals.

$$Cl\cdot + \cdot Cl \longrightarrow Cl{-}Cl$$
$$CH_3\cdot + \cdot Cl \longrightarrow CH_3{-}Cl$$
$$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3{-}CH_3$$

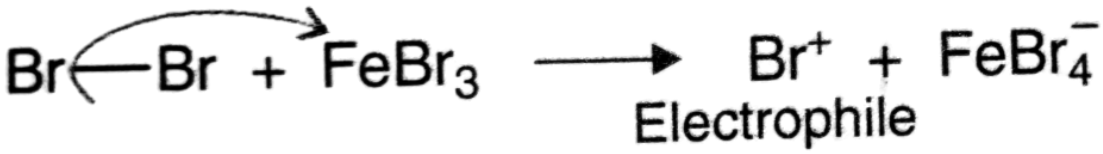
Electrophilic Substitution Reaction:- When a substitution reaction involves the attack by an electrophile, the reaction is referred to as electrophilic substitution. The bromination of

benzene in the presense of $FeBr_3$ is an example of Electrophilic substitution.

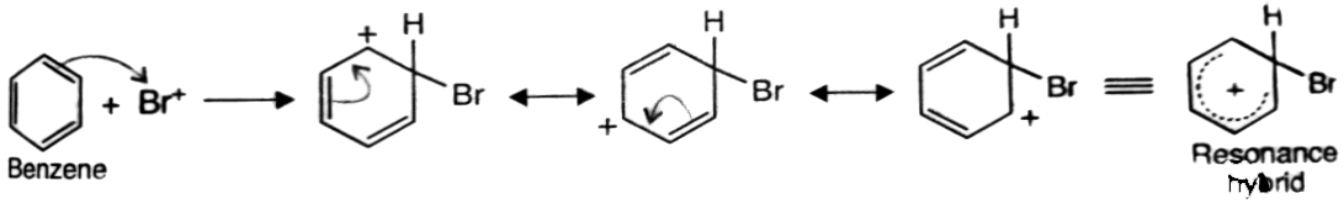


The mechanism of the above reaction involves the following steps:

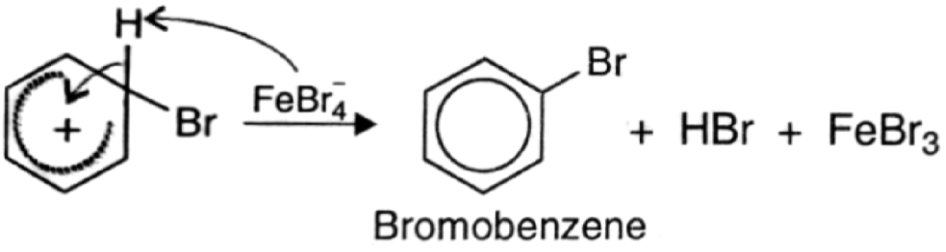
Step 1 – Formation of the electrophile.



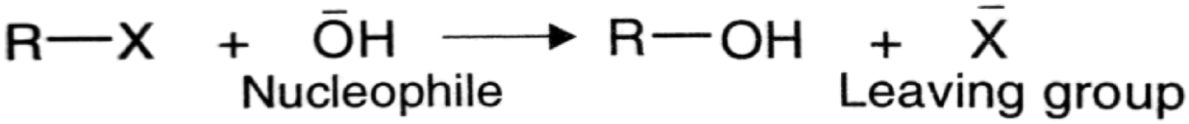
Step 2 – The electrophile(Br^+) attacks the benzene ring to form a resonsance stabilized carbonium



Step 3- Elimination of proton to give the substitution product.



Nucleophilic Substitution Reactions:- When a substitution reaction involves the attack by a nucleophile, the reaction is referred to as S_N (S stands for substitution and N for a nucleophile). The hydrolysis of alkyl halides by aqueous NaOH is an example of nucleophilic substitution.



The nucleophilic substitution reactions are divided into two classes:

(1) S_N2 Reactions

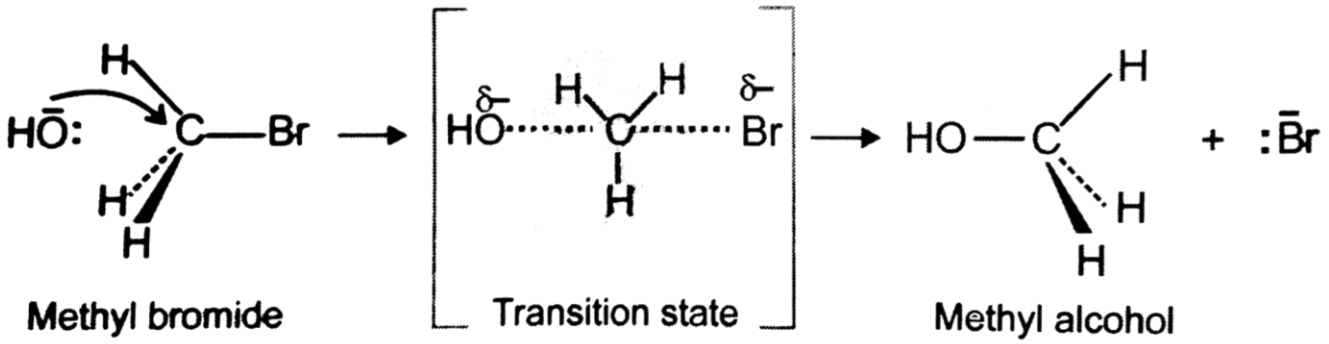
(2) **S_N1 Reactions**

S_N2 Reactions- S_N2 Stands for bimolecular nucleophilic substitution. When the rate a nucleophilic substitution reaction depends on the concentration of both the substrate and the nucleophile, the reaction is of second order and is represented as S_N2.

Rate α [Substrate] [nucleophile]

Evidently, the rate-determining step involves the participation of both the substrate and the nucleophile.

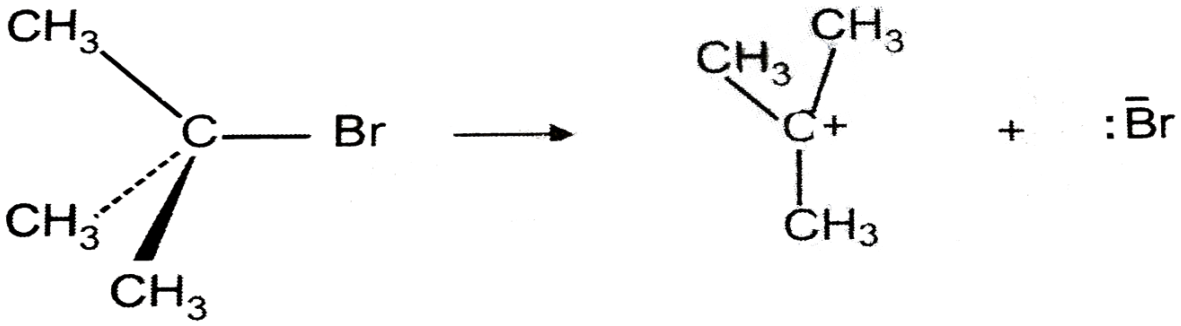
Consider the hydrolysis of methyl bromide by aqueous NaOH. The reaction and the transistion state are represented in fig



Nucleophilic substitution by S_N2 mechanism.

S_N1 Reaction:- S_N1 Stands for unimolecular nucleophilic substitution. When the rate of the nucleophilic substitution reaction depends only on the concentration of the alkyl halide, the reaction consider the hydrolysis of t-butyl bromide. The reaction consists of two steps:

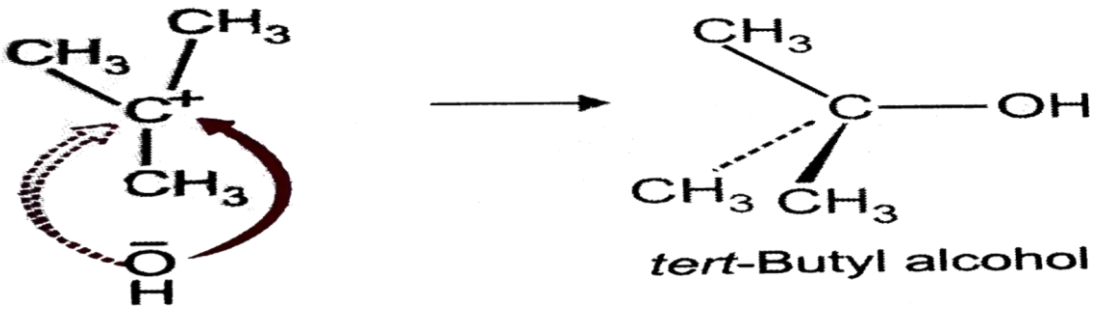
Step 1. The alkyl halide ionizes to give the carbonium ion.This is the rate determining step.



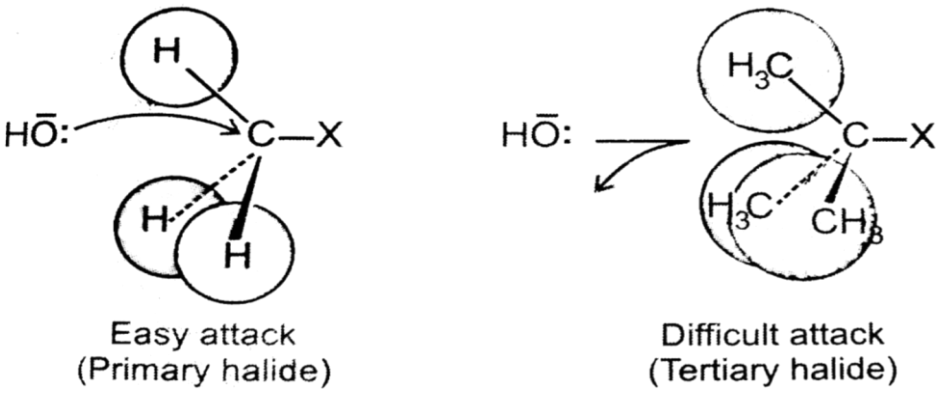
tert-Butyl bromide Carbonium ion

The carbonium ion is planar. This is because the central positively charged carbon atom is sp^2 hybridized.

Step 2. The nucleophile can attack the planer carbonium ion from either side to give t-butyl alcohol.



Remember that the primary alkyl halides undergo hydrolysis by S_N2 mechanism. The tertiary alkyl halides undergo hydrolysis by S_N2 mechanism. This is because the attack of the hydroxide ion on the crowded tertiary alkyl halides is quite difficult.



Secondary alkyl halides may undergo hydrolysis by either S_N1 or S_N2 mechanism


Thank You