CHEMISTRY STUDY MATERIALS FOR CLASS 12
(NCERT BASED NOTES OF CHAPTER - 10)

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Haloalkanes and Haloarenes

Mechanism of Nucleophilic Substitution Reactions

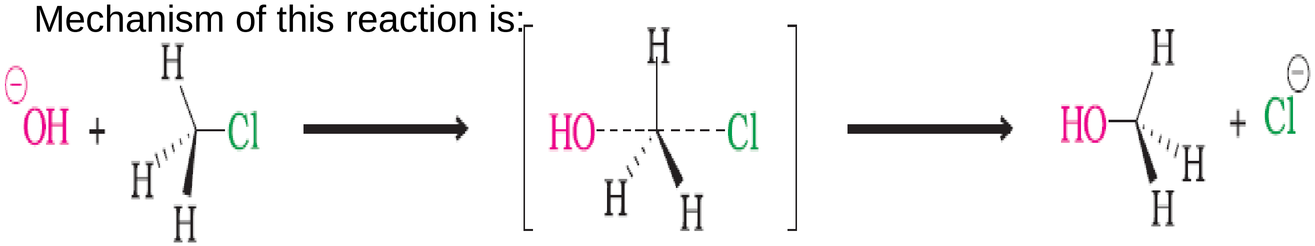
There are two types of mechanisms: Substitution Nucleophilic bimolecular (S_N2) and Substitution Nucleophilic unimolecular (S_N1)

1. Substitution Nucleophilic Bimolecular (S_N2) Mechanism:

Here the incoming nucleophile interacts with alkyl halide causing the carbon-halogen bond to break while forming a new carbon-OH bond. These two processes take place simultaneously in a single step and no intermediate is formed. As the reaction proceeds, the bond between the nucleophile and the carbon atom starts forming and the bond between carbon atom and leaving group (the halogen atom) weakens. In the case of optically active alkyl halides, during this process, the configuration of carbon atom inverts and hence this process is called as ***inversion of configuration***. In the transition state, the carbon atom is simultaneously bonded to five atoms and therefore is unstable.

An example is the reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion. This reaction follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants.

Mechanism of this reaction is:-



Since this mechanism requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom decreases the rate of this reaction.

Thus the order of reactivity of alkyl halides towards S_N2 reaction is:

Primary halide > Secondary halide > Tertiary halide.

2. Substitution Nucleophilic Unimolecular (S_N1):

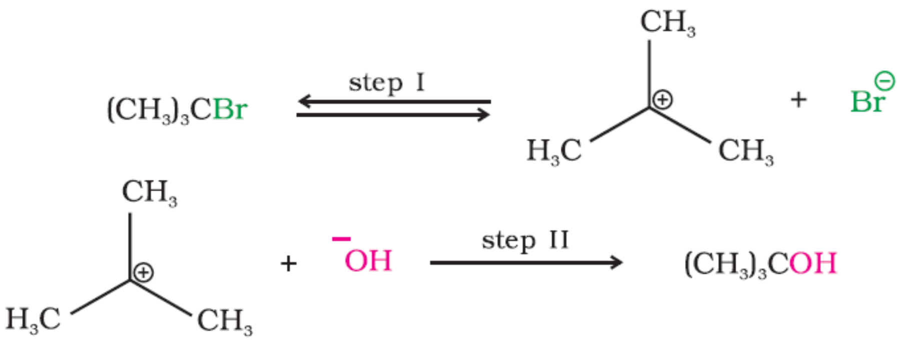
S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). Here the reaction occurs in two steps. In the first step, the C—X bond undergoes slow cleavage to produce a carbocation and a halide ion. In the second step, the carbocation is attacked by the nucleophile to form the product. Here first step is the slowest and reversible. So it is the rate determining step. Since this step contains only one reactant, it follows first order kinetics.

E.g.: The reaction between tert-butyl bromide and hydroxide ion to give tert-butyl alcohol.

$$(CH_3)_3CBr \quad + \quad {}^{-}OH \longrightarrow (CH_3)_3COH \quad + \quad Br^{-}$$

2-Bromo-2-methylpropane 2-Methylpropan-2-ol

This reaction occurs in two steps. In step I, the polarized C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to form the product.

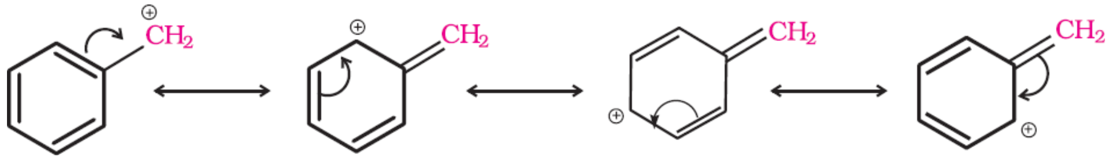


Thus in S_N1 reaction, there is an intermediate called carbocation. The greater the stability of the carbocation, the greater will be the rate of the reaction. In case of alkyl halides, 3^0 alkyl halides undergo S_N1 reaction very fast because of the high stability of 3^0 carbocations. So the order of reactivity of alkyl halides towards S_N1 reaction is: $3^0 > 2^0 > 1^0$.

Allylic and benzylic halides show high reactivity towards the S_N1 reaction. This is because of the higher stability of the carbocation formed. The allyl and benzyl halides are stabilized through resonance as follows:

Allyl carbocation

Benzyl Carbocation



For both the mechanisms, the reactivity of halides follows the order: R–I > R–Br > R–Cl > R–F.

Stereo chemical Aspects of Nucleophilic substitution Reactions

Plane Polarised light

It is a light beam in which the particles vibrate in only one direction. It is produced by passing ordinary light beam through a Nicol prism. When such a light beam is passed through solutions of certain compounds, they rotate the plane of polarisation. Such compounds are called ***optically active compounds***. The angle by which the plane polarised light is rotated is called *optical rotation*, which is measured by an instrument called polarimeter. If a compound rotates the plane polarised light towards *right* (i.e. clock-wise direction), it is called *dextro rotatory or d-form or + form* and if it rotates the plane polarised light towards *left* (i.e. anticlock-wise direction), it is called laevo *rotatory or l-form or – form*. The d and l form of a compound are called ***optical isomers*** and the phenomenon is called ***optical isomerism***.

Molecular asymmetry and Optical isomerism

Optical isomerism is due to molecular asymmetry. If all the 4 valencies of a carbon atom are satisfied by 4 different groups, it is called **asymmetric carbon or chiral carbon or stereo centre**. The resulting molecule is called asymmetric molecule. Such molecules are non-super imposable to their mirror images and are called **chiral molecules** and this property is known as **chirality**. The molecules which are super imposable to their mirror images are called achiral molecules. A chiral carbon is denoted by an asteric (*) mark.

e.g.: 2-Chlorobutane $[CH_3 – C^*HCl – CH_2 – CH_3]$

Here the 2nd C is chiral, since all the four valencies of this C are satisfied by 4 different groups.

Other examples:	2-butanol	$[CH_3 - C^*HOH - CH_2 - CH_3]$
	2-bromopropanoic acid	$[CH_3 - C^*HBr - COOH]$
	Lactic acid	$[CH_3 - C^*HOH - COOH]$

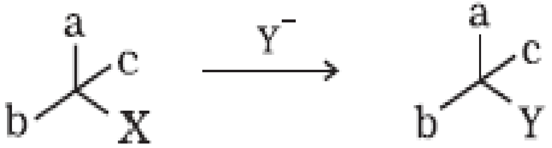
Enantiomers: *The stereo isomers related to each other as non-super imposable mirror images are called* ***enantiomers***. They have identical physical properties. They differ only in the direction of rotation of the plane polarised light. If one of the enantiomers is dextro rotatory, the other will be laevo rotatory.

Racemic mixture

A mixture containing d and l form of a compound in equal proportion has zero optical rotation and such a mixture is called ***racemic mixture or racemic modification***. It is denoted by dl or (±). Here the rotation due to one isomer is cancelled by the rotation due to the other isomer. The process of conversion of an enantiomer in to a racemic mixture is called **racemisation**.

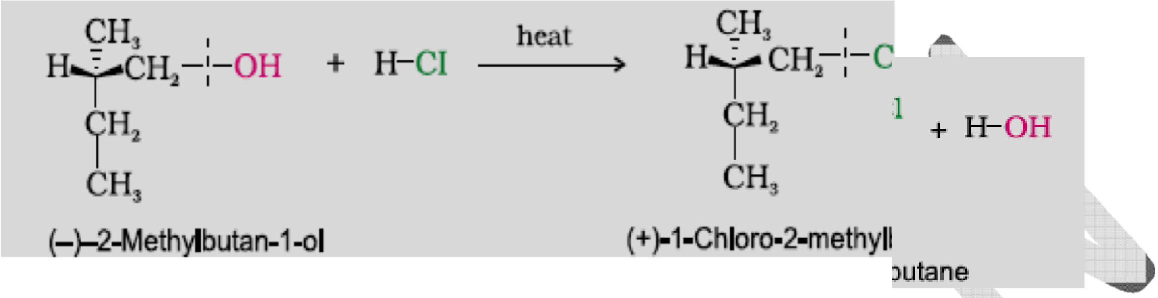
Retention and Inversion of configuration

If during a chemical reaction, there is no change in the spatial arrangement of bonds to an asymmetric centre, we can say that the reaction proceeds through *retention* of configuration. (Or, preservation of the integrity of configuration of a compound is termed as retention).

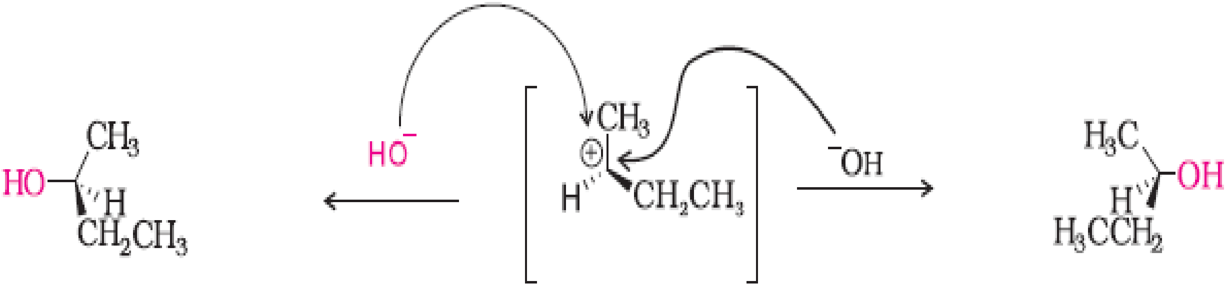


In general, if during a chemical reaction, no bond to the stereo centre is broken, the product will have the same configuration as that of the reactant. Such reactions always proceed through retention of configuration.

E.g. Reaction of 2-Methyl-1-butanol with HCl.



(+) – 1 Chloro-2- Methylbutanal is inverted and we can say that the reaction proceeds through inversion of configuration.



(-) 2-Butanol Planar carbocation (+) 2-butanol

Elimination Reactions

Alkyl halides having β-hydrogen atom when treated with alcoholic solution of KOH, they undergo elimination of one hydrogen halide molecule (dehydrohalogenation) to form alkenes. Since β-hydrogen atom is eliminated, the reaction is also called β-elimination.

e.g. : CH_3-CH_2-Br + KOH (alc) $\longrightarrow$ $CH_2 = CH_2$ + KBr + H_2O

If there is possibility of formation of more than one alkene during dehydrohalogenation reaction, the major product is selected by Zaitsev (Saytzeff) rule. The rule states that “in dehydrohalogenation reactions, if there is possibility of formation of more than one alkene the preferred product is that alkene which contains greater number of alkyl groups attached to the doubly bonded carbon atoms.”

So if 2-bromobutane is treated with alcoholic KOH, 2-butene is formed as the major product.

CH_3-CH_2-CHBr-CH_3 + KOH (alc) $\longrightarrow$ CH_3-CH_2-CH=CH_2 + CH_3-CH=CH-CH_3

2-Bromobutane 1-butene (minor) 2-butene (major)

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