CHEMISTRY STUDY MATERIALS FOR CLASS 12
(NCERT BASED NOTES OF CHAPTER - 10)
GANESH KUMAR DATE:- 13/09/2020

Haloalkanes and Haloarenes

Mechanism of Nucleophilic Substitution Reactions

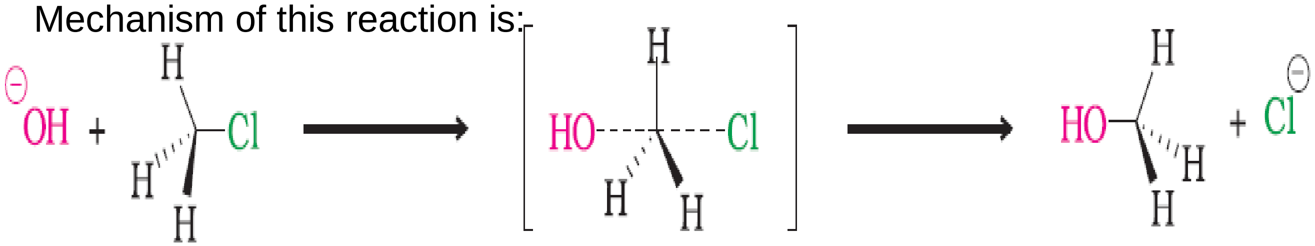
There are two types of mechanisms: Substitution Nucleophilic bimolecular (S_N2) and Substitution Nucleophilic unimolecular (S_N1)

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)*:

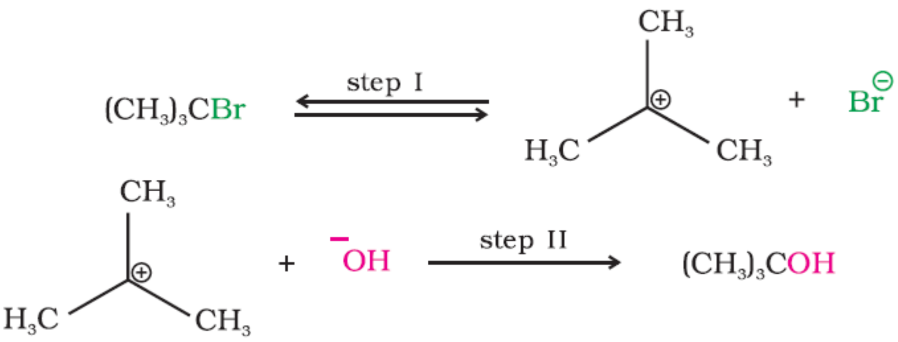
S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). Here the reaction occurs in two steps. In the first step, the C—X bond undergoes slow cleavage to produce a carbocation and a halide ion. In the second step, the carbocation is attacked by the 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.

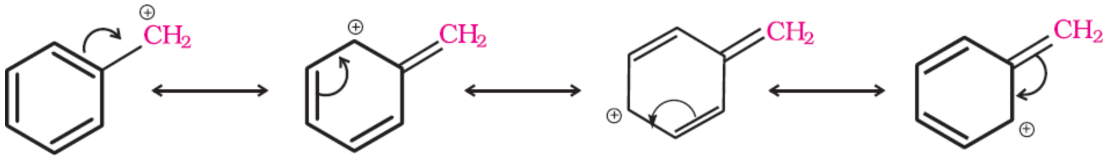


Thus in S_N1 reaction, there is an intermediate called carbocation. The greater the stability of the carbocation, the greater will be the rate of the reaction. In case of alkyl halides, 3^0 alkyl halides undergo S_N1 reaction very fast because of the high stability of 3^0 carbocations. So the order of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

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