Topic 20 Organic chemistry (HL)

Syllabus:

20.1 Types of organic reactions

Nucleophilic Substitution Reactions

S_N1 represents a unimolecular nucleophilic substitution reaction which involves a carbocation intermediate and S_N2 represents a bimolecular nucleophilic substitution which involves a concerted reaction with a transition state.

Tertiary halogenoalkanes favour S_N1 and primary halogenoalkanes favour S_N2. Both mechanisms occur for secondary halogenoalkanes.

The rate equation of S_N1 is rate = k[halogenoalkane]. The rate equation of S_N2 is rate = k[halogenoalkane][nucleophile]. S_N2 is stereospecific with an inversion of configuration at the carbon.

Polar, protic solvents favour S_N1. Polar, aprotic solvents favour S_N2.

Electrophilic Addition Reactions

An electrophile is an electro-deficient species that can accept electron pairs from a nucleophile. Electrophiles are Lewis acids.

Markovnikov's rule can be applied to predict the major product in electrophilic addition reactions of unsymmetrical alkanes with hydrogen halides and interhalogens.

Electrophilic Substitution Reactions

Benzene is the simplest organic aromatic hydrocarbon compound and has delocalized structure of π bonds around its ring. Each carbon to carbon bond has a bond order of 1.5. Benzene is susceptible to attack by electrophiles.

Reduction Reactions

Carboxylic acids can be reduced to primary alcohols. Ketone can be reduced to secondary alcohols. Typical reducing agents are lithium aluminium hydride and sodium borohydride.

20.2 Synthetic routes

The synthesis of an organic compound stems from a readily available starting material via a series of discrete steps. Functional group interconversions are the basis of such synthetic routes.

Retro-synthesis of organic compounds

20.3 Stereoisomerism

Stereoisomers are subdivided into two classes–conformational isomers, which interconvert by rotation about a α bond and configurational isomers that interconvert only by breaking and reforming a bond.

Configurational isomers are further subdivided into cis–trans and E/Z isomers and optical isomers.

Cis–trans isomers can occur in alkenes or cycloalkanes (or heteroanalogues) and differ in the positions of atoms relative to a reference plane. According to IUPAC, E/Z isomers refer to alkenes of the form R1R2C = CR3R4 (R1 ≠ R2, R3 ≠ R4) where neither R1 nor R2 need be different from R3 or R4.

A chiral carbon is a carbon joined to four different atoms or groups.

An optically active compound can rotate the plane of polarized light as it passes through a solution of the compound. Optical isomers are enantiomers. Enantiomers are non-superimposable mirror images of each other.

Diastereomers are not mirror of each other.

A racemic mixture (or racemate) is a mixture of two enantiomers in equal amounts and is optically inactive.

20.1 Types of organic reactions

(A) Nucleophilic substitution reaction

Alcohols can be formed via the nucleophilic substitution reactions of halogenoalkanes.

Nucleophile: OH^-

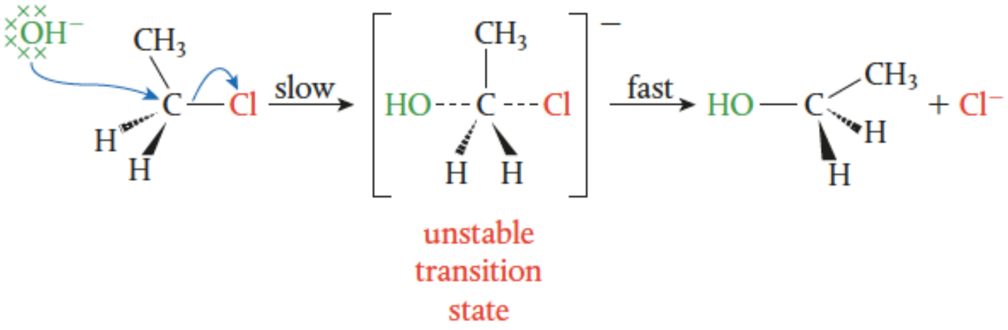
Halogenoalkane + OH^- → Alcohol + X^-

$CH_3Cl + NaOH \rightarrow CH_3OH + NaCl$

1. Bimolecular nucleophilic substitution (S_N2)

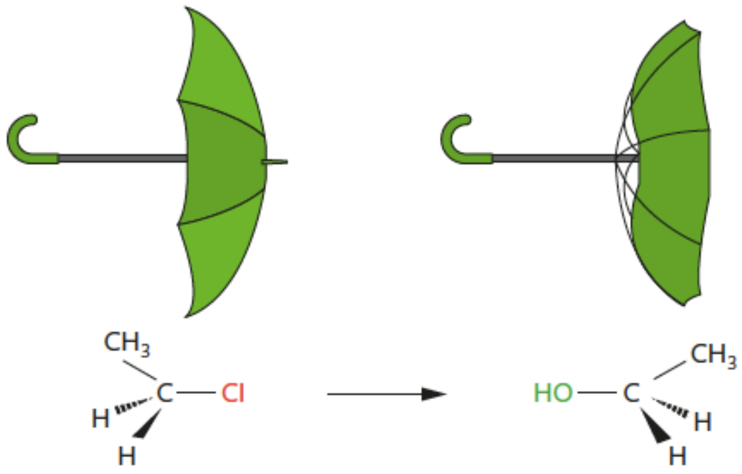
- Primary halogenoalkanes favour S_N2 mechanism.
- Rate = k[halogenoalkane][nucleophile]
- One step mechanism with an unstable transition state.
- The transition state is formed with partially broken C–Cl bond and partially formed C–OH bond.
- Bimolecular reaction because the mechanism is dependent on the concentration of both the halogenoalkane and the hydroxide ion.

$CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$



- **Inversion of configuration**
- The nucleophile attacks the electropositive carbon from the opposite side from the halogen atom due to the electron repulsion.

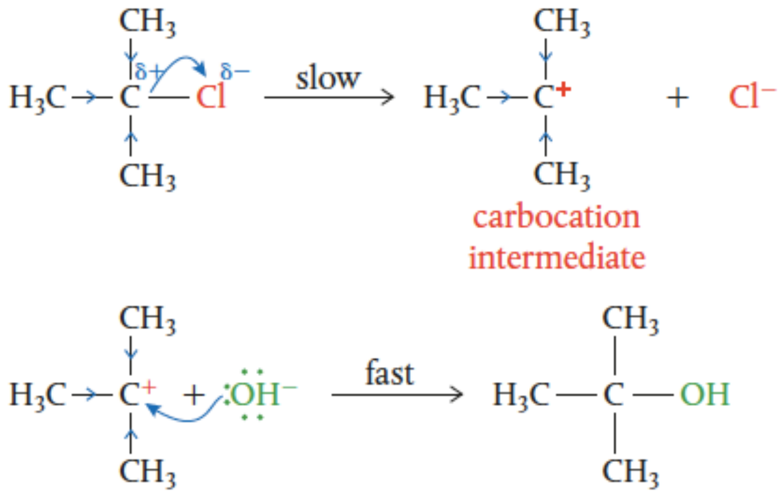
- S_N2 is favoured by **polar, aprotic** solvent such as propanone $(CH_2)_3CO$ or ethanenitrile CH_3CN.
- Polar, aprotic solvent doesn't contain O–H or N–H bond and can't form hydrogen bonds.
- They won't solvate the nucleophile (OH^-) so that is free to attack the electropositive carbon.


CH3
C
Cl
H
H
HO
C
CH3
H
H

2. Unimolecular nucleophilic substitution (S_N1)

- Tertiary halogenoalkanes favour S_N1 mechanism.
- Rate = k[halogenoalkane]
- Two steps mechanism
- The first step is the heterolytic fission of C – X bond in the halogenoalkane, forming a carbocation intermediate and halide ion.
- The first step is the slowest step, rate determining step, with high activation energy due to the bond broken process.
- The second step is the nucleophile attacks the carbocation intermediate forming the alcohol.
- Unimolecular reaction because the mechanism is dependent on the concentration of the halogenoalkane only.
- S_N1 is favoured by **polar, protic** solvent such as water, alcohols and carboxylic acids.
- Polar, protic solvent contains O–H or N–H bond and can form hydrogen bonds.
- They can stabilize the carbocation by solvation involving ion–dipole interactions.

$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$



- Secondary halogenoalkanes can undergo both **S_N1 and S_N2.**

Factors that affect the rate of nucleophilic substitution reactions

1. Mechanism

S_N1 mechanism is faster than S_N2 mechanism. So tertiary halogenoalkanes have faster nucleophilic substitution reactions than primary halogenoalkanes.

Secondary halogenoalkanes show an intermediate rate of reaction using a mixture of both mechanisms.

Reaction rate: Tertiary > Secondary > Primary

2. The halogen atoms

C – X bond length

Atomic size: F < Cl < Br < I

C – X bond length: C – F < C – Cl < C – Br < C – I

C – X bond strength: C – F > C – Cl > C – Br > C – I

Longer C – X bond length, Stronger C – X bond, harder to break

Overall, the factor of C – X bond strength outweighs the electronegativity.

The relative rate of reaction: iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes

Tertiary halogenoalkanes favour S_N1 mechanism

The tertiary carbocation intermediate R_3C^+ is more stable than the secondary carbocation intermediate R_2HC^+.

Alkyl group is an electron donating group which stabilizes the carbocation through the positive inductive effect.

Since the tertiary carbocation intermediate R_3C^+ has three alkyl groups, there is more positive inductive effect, it is a more stable carbocation than the secondary carbocation intermediate R_2HC^+.

Primary halogenoalkanes favour S_N2 mechanism

For primary halogenoalkane, there is only one alkyl group bonded to the electropositive carbon, the nucleophile is much free to attack the electropositive carbon in the halogenoalkane.

While for secondary and tertiary, there are more alkyl groups bonded to the electropositive carbon, the steric hindrance makes the nucleophile harder to attack the electropositive carbon.

Question 1

Write the mechanism for the reaction of 1-chloroethane with sodium hydroxide with curly arrows to represent movement of electron pairs and write the rate expression for the reaction.

Question 2

Write the mechanism for the reaction of 2-bromo-2-methylbutane with sodium hydroxide with curly arrows to represent movement of electron pairs and the rate expression for the reaction.