



B: Organic Chemistry

Paper II - Physical and organic Chemistry

B.Sc. Part I (Honours)

By

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Reaction Mechanism: Substitution

Secondary Isotope Effect

When H is replaced with D

In S_N1 increases rate of reaction

Reason: D has more +I effect than H thus stabilises the intermediate

In S_N2 it slows down the rate

Reason: D increases activation energy

Effect of carbonyl

Leaving group is on α position to carbonyl ($>CX-CO-$)

S_N1 slows due to resonance

S_N2 becomes faster due to +ve charge on α carbon

Reaction Mechanism: Substitution

Effect of carboxyl ($>\text{CX}-\text{COO}^-$)

$\text{S}_{\text{N}}1$ faster

Reason: +I effect

$\text{S}_{\text{N}}2$ slower

Reason: negative charge on α -carbon

Effect of heavy metal (Ag^+)

$\text{S}_{\text{N}}1$ faster

Reason: coordination between Ag^+ and the intermediate

Reaction Mechanism: Substitution

Effect of halide

On rate

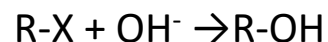


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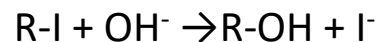
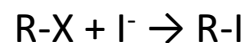
- Steric strain due to volume
- Polarizability of C-X bond

Catalysis by I^- in case of Br^- and Cl^- leaving group

High activation energy



Low activation energy



Reaction Mechanism: Substitution

Effect of nucleophile

Nucleophilicity: ability to form bond with carbon

Strong nucleophile favour S_N2

Weak nucleophile favour S_N1

Strength of nucleophile : $\text{PhS}^- > \text{CN}^- > \text{I}^- > \text{EtO}^- > \text{OH}^- > \text{Br}^- > \text{PhO}^- > \text{Cl}^- > \text{R}_3\text{N}:$

Nucleophilicity Vs Basicity

Nucleophilicity is kinetic property

Basicity is thermodynamic property

Rate with $\text{PhS}^- > \text{EtO}^-$ due to Higher polarizability and Solvation

Reaction Mechanism: Substitution

Effect of -R

Size of R

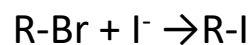
Larger the group S_N1 is favour over S_N2

Reason:

Increased steric crowding in 5 coordinated transition state decreases rate of S_N2

Decreased steric crowding in 3 coordinated intermediate increases rate of S_N1

Example:



in acetone solvent, mechanism; S_N2

Methyl	>	Ethyl	>	isopropyl	>	t-butyl
10000	>	65	>	0.5	>	0.0039

Reaction Mechanism: Substitution

Number of R

n-butyl	>	isobutyl	>	t-butyl
1	>	0.04	>	10^{-5}

When leaving group is on bridgehead (1-chloro apacamphene)

Non viability of planarity of intermediate slows S_N1

Non viability of attack slow S_N2

If the number of carbons in bridge increases there is relaxation in bridge strain S_N1 becomes faster.

Reaction Mechanism: Substitution

Effect of solvent

Two properties have effect; dielectric constant and solvation

Dielectric constant: it increases ionization

Solvation: solute-solvent interaction based on polarity

Solvent	Dielectric constant	Polarity (Debye, D)
Water	81.1	2-3
Formic acid	48.0	1.5
Nitrobenzene	37.7	4.0
Ethanol	25.8	1.7
Acetone	21.3	3
AcOH	7.1	1.5
Chloroform	4.6	1.1
Diethyl ether	4.3	1.25
Benzene	2.3	0
Carbon tetra chloride	2.2	0

Reaction Mechanism: Substitution

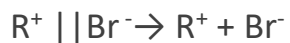
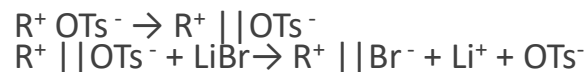
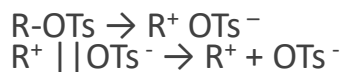
Detailed process of ionization



Evidence of salt effect



Rate of this reaction increases in presence of LiBr.



This shifts the equilibrium towards intermediate.