B: Organic Chemistry

Paper II - Physical and organic Chemistry

B.Sc. Part I (Honours)

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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 αcarbon

Reaction Mechanism: Substitution

Effect of carboxyl (>CX-COO^-)

S_N1 faster

Reason: +I effect

S_N2 slower

Reason: negative charge on α-carbon

Effect of heavy metal (Ag^+)

S_N1 faster

Reason: coordination between Ag^+ and the intermediate

Reaction Mechanism: Substitution

Effect of halide

On rate

-I > -Br > -Cl

Reason:

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

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

High activation energy

$R\text{-}X + OH^- \rightarrow R\text{-}OH$

Low activation energy

$R\text{-}X + I^- \rightarrow R\text{-}I$

$R\text{-}I + OH^- \rightarrow R\text{-}OH + I^-$

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 : $PhS^- > CN^- > I^- > EtO^- > OH^- > Br^- > PhO^- > Cl^- > R_3N$:

Nucleophilicity Vs Basicity

- Nucleophilicity is kinetic property
- Basicity is thermodynamic property

Rate with $PhS^- > EtO^-$ 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 cordinated transition state decreases rate of S_N2

Decreased steric crowding in 3 cordinated intermediate increases rate of S_N1

Example:

$R\text{-}Br + I^- \rightarrow R\text{-}I$ 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

$R\text{-}X \rightarrow R^{+}X^{-}$ (intimate ion pair)

$R^{+}X^{-} \rightarrow R^{+}||X^{-}$ (Extended ion pair) (favoured in low polar solvents)

$R^{+}||X^{-} \rightarrow R^{+} + X^{-}$ (dissociated ions) affected by common ion (salt effect)

Evidence of salt effect

$R\text{-}OTs + AcOH \rightarrow R\text{-}Oac$

Rate of this reaction increases in presence of LiBr.

$R\text{-}OTs \rightarrow R^{+}\ OTs^{-}$

$R^{+}\ OTs^{-} \rightarrow R^{+}\ ||OTs^{-}$

$R^{+}\ ||OTs^{-} \rightarrow R^{+} + OTs^{-}$

$R^{+}\ ||OTs^{-} + LiBr \rightarrow R^{+}\ ||Br^{-} + Li^{+} + OTs^{-}$

$R^{+}\ ||Br^{-} \rightarrow R^{+} + Br^{-}$

This shifts the equilibrium towards intermediate.