

1) $SN^1 \rightarrow$ Unimolecular Nucleophilic Substitution

Here, Nucleophile = +ve charge seeking

Nucleus loving

\therefore Nucleophiles are -ve ly charged / has lone pairs

Uni molecular = reaction takes place 1 molecule

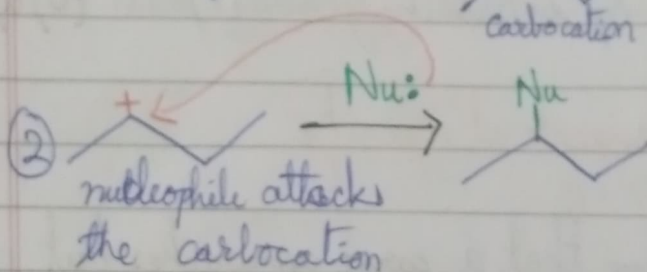
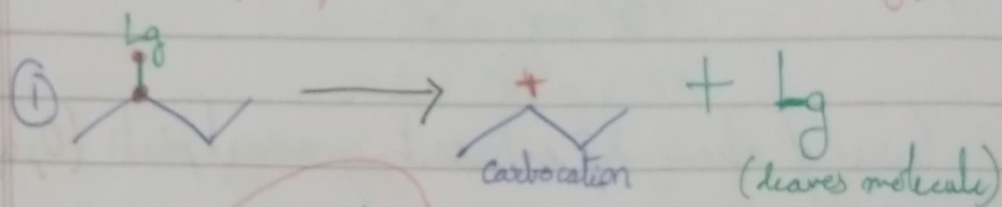
one

at a time or it's a 1st order reaction

(*) SN^1 is not a 1 step reaction. It can have 2 or 3 steps

Mechanism:- Let $Lg \rightarrow$ leaving group, $Nu:$ \rightarrow nucleophile

It is the group that leaves the molecule during reaction



Analyse:- Step ① \rightarrow It is a slow step because:-

① Bond dissociation is slow:-

The leaving group takes the bonding e^- with it.

Thus, the carbocation has +ve charge

② Carbocation formation:-

Carbocation is highly unstable due to lack of e^-

Hence, it is reluctant to form

For SN^1 reaction to proceed further, it must overcome this instability, which requires energy

Here, the Intermediate \rightarrow Temporary species, unstable molecules \rightarrow Carbocation

Intermediates are molecules formed during course of chemical reaction, but not present in the final products

Rate \therefore 1st step of S_N1 reaction is the rate determining step
2nd step of S_N1 reaction is a fast step [Nu: attacks C^+]

In terms of Kinetics,

Rate is dependent on the substrate concentration

Leaving group \therefore Lg is the substrate

$$\therefore \text{Rate} = k [\text{substrate}]$$

$k \rightarrow$ rate constant
 $[\text{substrate}] \rightarrow$ conc. of Lg

* Nucleophile does not influence the rate of the reaction

This is because it does not take part in Step 1 which is the rate determining step

Stability \therefore Carbocation stability \therefore

Tertiary > Secondary > Primary

\leftarrow Stability increases

Rate of reaction decreases \rightarrow

\therefore Tertiary carbocations \rightarrow most stable & faster S_N1 reaction

Secondary carbocation \rightarrow lesser stable & slower S_N1 reaction

Primary carbocation \rightarrow least stable & slowest S_N1 reaction

Leaving groups :-

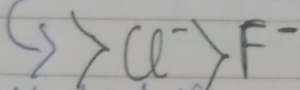
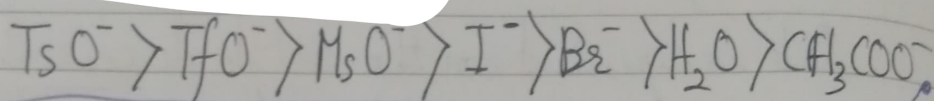
1) Good Leaving groups :- They can effectively stabilize the negative charge after departure.

(i) Halides ~~(Anions)~~ :- I^- , Br^- , Cl^-

(ii) Sulfonates :- TsO^- , MsO^- , TfO^-

(iii) Acetate (CH_3COO^-), Water (H_2O), Alcohol (ROH)
(Tertiary)

Order :-



2) Moderate Leaving groups :- They are somewhat effective

(i) Fluoride (F^-)

(ii) Hydroxide (OH^-)

(iii) Ammonia (NH_3)

(iv) Alcohol (ROH)
(Primary)

Order :- $F^- > ROH_{(primary)} > NH_3 > OH^-$

3) Poor Leaving groups :- They cannot stabilize negative charge

(i) Hydride (H^-)

(ii) Amine (NH_2^-)

(iii) Carbanion ($R-C^-$)

(iv) Phosphates (PO_4^{3-})

Order :- $NH_2^- > H^- > R-C^- > PO_4^{3-}$

⊗ Sulfonates > Halides > H_2O > Acetate > Fluoride

Solvent Stability:-

Solvent can affect the :-

- Stability of intermediates
- Reactivity of nucleophiles
- How easily leaving groups depart

Two main Types of Solvent :-

- 1) Polar Solvent

- Polar Protic
- Polar Aprotic

• Polar Protic Solvent :- Has high hydrogen-bonding capabilities due to presence of polar groups

Eg:- H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CH_3COOH , NH_3

2) Non polar Solvent

• Polar Aprotic Solvent :- Lack high hydrogen-bonding capabilities because they have ~~no~~ no hydrogen bond donors

Eg:- Acetone (CH_3COCH_3), Dimethylformaldehyde (DMF)

• Non polar Solvent :- They do not solvate ions effectively and do not take part in nucleophilic/elimination reaction

They do not have polarity and cannot stabilize nucleophile (leaving group)

Eg:- Hexane (C_6H_{14}), Toluene ($\text{C}_6\text{H}_5\text{CH}_3$), Cyclohexane

Here,

- Polar Protic Solvents favours SN^1 reactions [can stabilize carbocations]
But less effective for SN^2 reactions
- Polar Aprotic Solvents favours SN^2 reactions [cannot stabilize carbocations]
But less effective for SN^1 reactions
- Non polar Solvents does not take part in SN^1 & SN^2 as they cannot solvate ions/stabilize nucleophiles