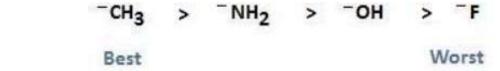
☐ Effect of Nucleophile on the Reaction Rate

The strength of the nucleophile does not effect the reaction rate of S_N1 as the RDS does not involved the nucleophile. However in S_N2 the transition state involves the nucleophile. Greater the nucleophilicity or concentration of a nucleophile more rapid is the rate of S_N2 reaction.

Nucleophilicity depends on the following factors

Anions are usually more reactive than neutrals

When moving across a row nucleophilicity decrease from left to right.

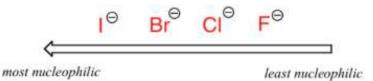


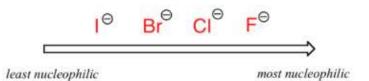
Due to increase of electronegativity

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Solvents and Nucleophilicity

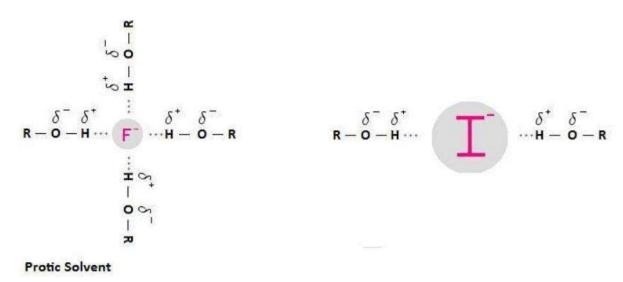
Along the column





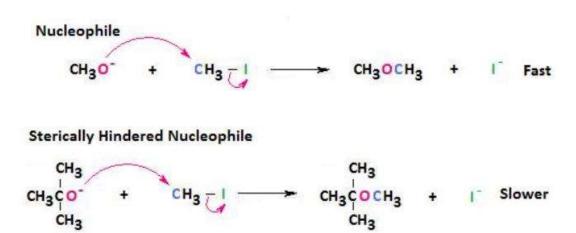
Relative nucleophilicity in a protic solvent

Relative nucleophilicity in a polar aprotic solvent



Smaller anions are heavily solvated than the larger anions making its electrons less avaliable

Sterically Hindered Nucleophiles React More Slowly



Difference between S_N2 and S_N1

	S _N 2	S _N 1
Molecularity	Bimolecular	Unimolecular
Order	Second Order	First Order
Alkyl halide	CH ₃ X> 1°>2°>3°	CH ₃ X< 1°<2°<3°
Nucleophile	Strong	Not Important (usually weak)
Leaving Group	Good One	
Stereochemistry	Inversion	Inversion + Retention
Rearrangements	No	Yes

S_Ni Reactions (Substitution nucleophilic, internal)

 S_N i or Substitution Nucleophilic intramolecular stands for a specific but not often encountered nucleophilic aliphatic substitution reaction mechanism

$$\begin{array}{c} \mathsf{R} \\ \mathsf{H}^{\mathsf{MH}} \\ \mathsf{R}^{\mathsf{1}} \end{array} \qquad \qquad \begin{array}{c} \mathsf{R} \\ \mathsf{CI} \\ \mathsf{R}^{\mathsf{1}} \\ \mathsf{Retention} \end{array} \qquad \qquad \begin{array}{c} \mathsf{R} \\ \mathsf{HCI} \\ \mathsf{R}^{\mathsf{1}} \\ \mathsf{Retention} \end{array}$$

Mechanism

R
$$CI$$
 CI
 S_{Ni}
 R^{1}
 R^{1}

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Preparation of alkyl halide

☐ From alcohol

R-OH
$$\longrightarrow$$
 R-X

R-OH + Conc. HCl $\xrightarrow{\text{Anhydrous ZnCl}_2}$ R-Cl + H₂O

A mixture of ZnCl₂ and Conc HCl is known as Lucas reagent

Mechanism

ii)
$$H$$
— $CI + R$ \bigoplus R — $CI + H$ \bigoplus

iii)
$$H^{\oplus}$$
 + $HO \longrightarrow ZnCl_2$ \longrightarrow $H_2O + ZnCl_2$

- ☐ Reactivity order- 3°>2°>1°
- ☐ Lucas test is use to distinguish Primary, Secondary and Tertiary alcohols.

$$\begin{array}{c} \text{CH}_{3} & \text{anhydrous} & \text{CH}_{3} \\ \text{CH}_{3} - \text{C} - \text{OH} + \text{HCl} \xrightarrow{Zn\text{Cl}_{2}} & \text{CH}_{3} - \text{C} - \text{Cl} + \text{H}_{2}\text{O} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{2-methylpropan-2-ol (3°)} & \text{2-chloro-2-methylpropane} \\ & & & & & & & & \\ \text{(immediate appearance of turbidity)} \\ \text{CH}_{3} & & & & & & & & \\ \text{CH}_{3} - \text{CH} - \text{OH} + \text{HCl} \xrightarrow{Zn\text{Cl}_{2}} & \text{CH}_{3} - \text{CH} - \text{Cl} + \text{H}_{2}\text{O} \\ \text{propan-2-ol (2°)} & & & & & & \\ \text{2-chloropropane} \\ & & & & & & \\ \text{(slow appearance of turbidity)} \\ \text{CH}_{3} - \text{CH}_{2} - \text{OH} + \text{HCl} \xrightarrow{Zn\text{Cl}_{2}} & \text{No reaction at room temperature} \\ \text{ethanol (1°)} & & & & & \\ \text{(Turbidity appears only on heating)} \end{array}$$



Alkyl bromides can be obtained by heating alcohol with KBr in presence of excess of Conc. H_2SO_4 or by refluxing the alcohol with constant boiling HBr (40%) in presence of a little conc. sulphuric acid.

$$CH_3CH_2OH$$
 + HBr $KBr/Conc.H_2SO_4$ CH_3CH_2Br + $KHSO_4$ + H_2O

- \square The mixture of KBr and conc. H_2SO_4 is not used in case of secondary and tertiary alcohols to prevent their dehydration.
- ☐ Alkyl halides may be obtained by refluxing alcohol with excess of 57% HI. These can also be obtained by heating alcohol with KI in presence of phosphoric acid.

$$CH_3CH_2OH$$
 + HI \longrightarrow CH_3CH_2I + H_2O

Reaction of alcohol with thionyl chloride (Drazen's Process)

Mechanism

Already discussed

Reaction with Phosphorous trihalides

Reaction with phosphorous pentachloride

$$R \longrightarrow OH + PCl_5 \longrightarrow R \longrightarrow CI + POCl_3 + HCl$$
 $CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$

$$\begin{array}{c} \text{Mechanism} \\ \text{R} \stackrel{\circ}{\longrightarrow} \stackrel{\longrightarrow} \stackrel{\circ}{\longrightarrow} \stackrel{\circ}{\longrightarrow} \stackrel{\circ}{\longrightarrow} \stackrel{\circ}{\longrightarrow} \stackrel{\circ}{\longrightarrow} \stackrel{\circ}{\longrightarrow} \stackrel{\circ}{\longrightarrow} \stackrel{\circ}{\longrightarrow$$

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