

## PROPERTIES OF ALKYL HALIDES

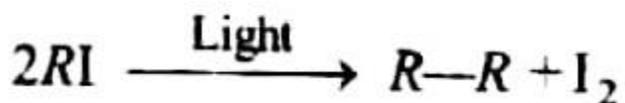
**Physical properties :** (i)  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{C}_2\text{H}_5\text{Cl}$  are gases at room temperature, while  $\text{CH}_3\text{I}$  is a liquid at temperature. The alkyl halides upto  $\text{C}_{18}$  are colourless liquids while higher members are colourless solids.

(ii) Alkyl halides are insoluble in water but soluble in organic solvents.

(iii) They burn on copper wire with green edged flame (Beilstein test for halogens).

(iv) Alkyl bromides and iodides are heavier than water. Alkyl chlorides and fluorides are lighter than water.

(v) Alkyl iodides become violet or brown in colour on exposure as they decompose in light.



(vi) For a given alkyl group, the boiling points of alkyl halides are in the order  $\text{RI} > \text{RBr} > \text{RCi} > \text{RF}$  and for a given halogen, the boiling points of alkyl halides increase with the

increase of the size of the alkyl group. In a group of isomeric alkyl halides, the order of boiling point is:

**Primary > Secondary > Tertiary**

(vii) Alkyl halides are in general toxic compounds and bring unconsciousness when inhaled in large amounts.

**Chemical properties :** The alkyl halides are highly reactive, the order of reactivity is:

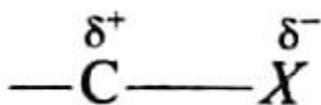
Iodide > Bromide > Chloride (nature of the halogen atom)

Tertiary > Secondary > Primary (type of halogen atom)

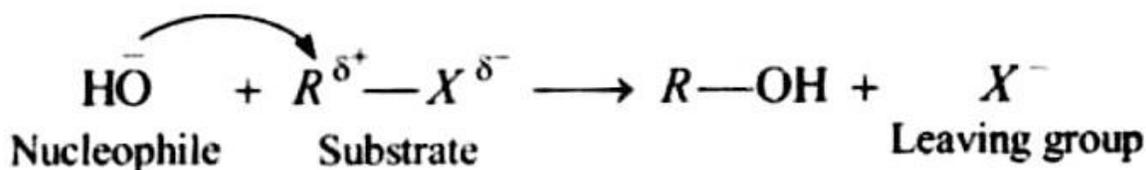
Amongst the primary alkyl halides the order of reactivity is:



The high reactivity of alkyl halides can be explained in terms of the nature of C-X bond which is highly polarized covalent bond due to large difference in the electronegativities of carbon and halogen atoms. The halogen is far more electronegative than carbon and tends to pull the electrons away from carbon, i. e., halogen acquires a small negative charge and carbon a small positive charge.



**Nucleophilic substitution** : Many substitution Reactions, especially at the saturated carbon atom in aliphatic compounds such as alkyl halides, are brought about by nucleophilic reagents or nucleophiles



Such substitution reactions are called nucleophilic substitution reactions, i. e., S<sub>N</sub> reactions (S stands for substitution and N for nucleophile). The nucleophilic substitution reactions are divided into two classes:

**(a) S<sub>N</sub>2 Reactions** : These are **bimolecular reactions**.

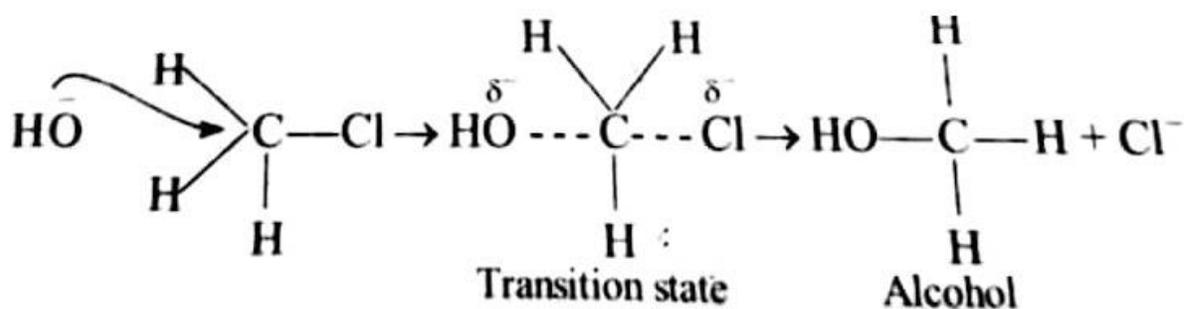
When the rate of reaction depends on the concentration of both Substrate and the nucleophile, the reaction is said to be

$S_N2$ , i. e. , 2nd order change.

$$\text{Rate} \propto [\text{Substrate}] [\text{Nucleophile}]$$

Hydrolysis of methyl chloride is an example of  $S_N2$  reaction and high concentration of the nucleophile ( $\text{OH}^-$ ) favours  $S_N2$  reaction. The chlorine atom present in methyl chloride is more electronegative than the carbon atom. Therefore, C-Cl bond is partially polarized.

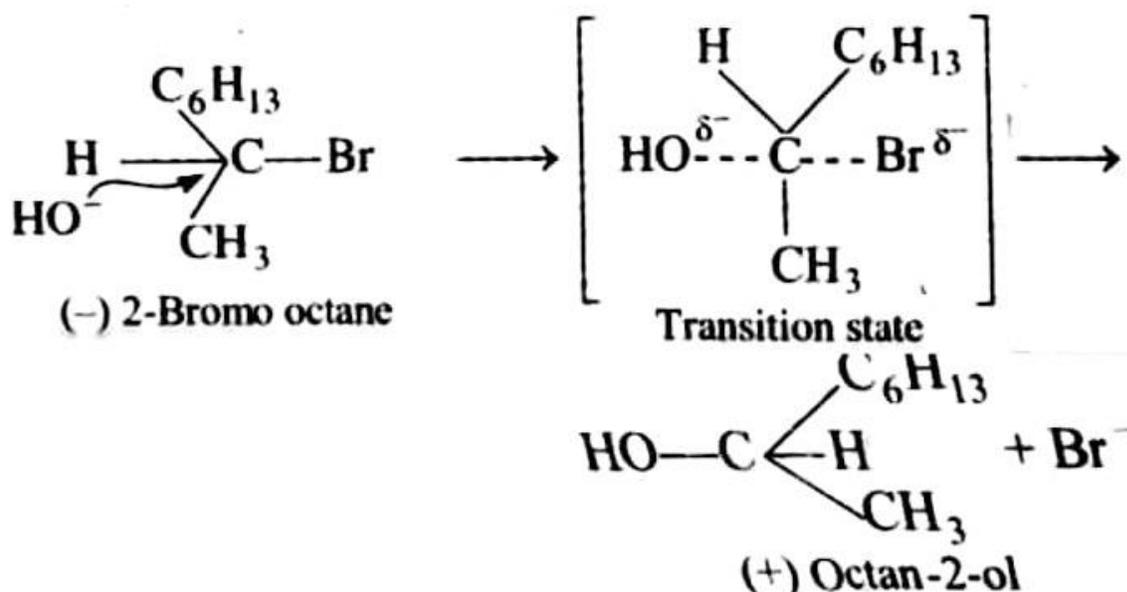
When the methyl chloride is attacked by  $\text{OH}^-$  strong nucleophile from the opposite side of the chlorine atom, an intermediate, transition state (TS) results in which both  $\text{OH}^-$  and  $\text{Cl}^-$  are partially bonded to carbon atom.



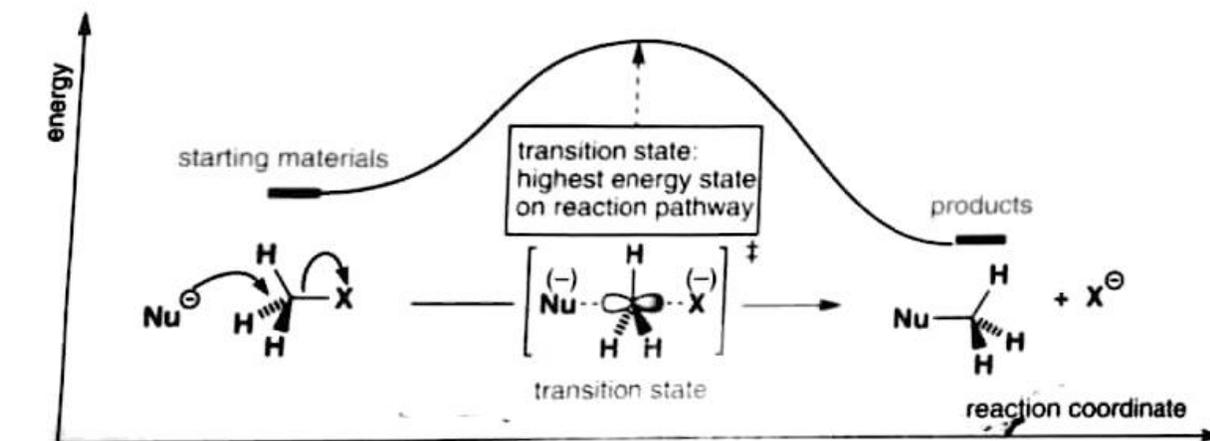
In transition state, chlorine starts taking hold of the electron pair through which it is bonded to carbon and the  $\text{OH}^-$  ion offers a pair of electrons for the formation of bond with carbon. Such a transition state is characterised by maximum potential energy and hence minimum stability. Finally, chlorine leaves the molecule as a chloride ion and  $\text{OH}^-$  ion forms a covalent bond with the carbon giving alcohol as a reaction product. According to this, hydrolysis is assumed to be a one stage process, where in two molecules simultaneously undergo covalency change and the older bond is broken and a new bond is formed

simultaneously. In this reaction the nucleophile attacks only from the opposite side of the leaving group causing a change in the configuration of carbon, i. e., complete inversion takes place.

When (-) 2-bromo octane is allowed to react with sodium hydroxide under conditions where second order kinetics are followed, there is obtained (+) 2-octanol.

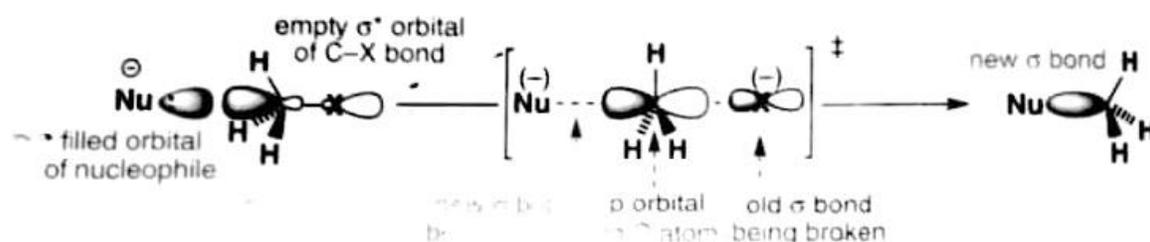


Another way to put this would be to say that the nucleophile, the methyl group, and the leaving group are all present in the transition state for the reaction. The transition state is the high energy point on the reaction pathway. In the case of an SN<sub>2</sub> reaction it will be the point where the new bond from the nucleophile is partly formed while the old bond to the leaving group is not yet completely broken. It will look something like this:



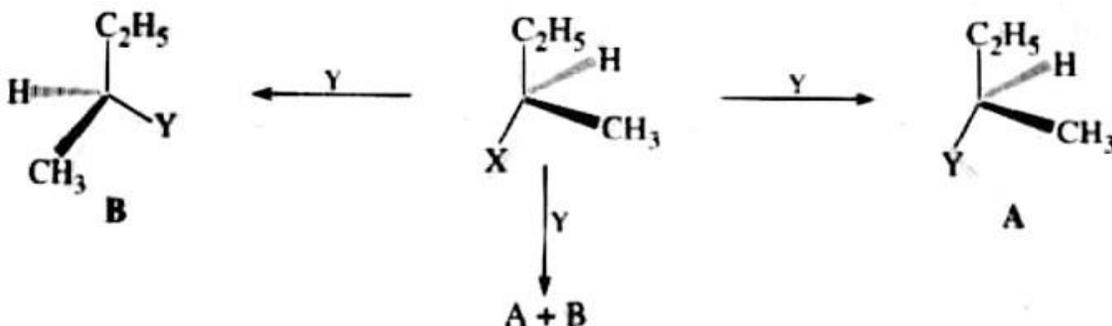
The dashed bonds in the transition state indicate partial bonds (the C- u bond is partly formed and the C-X bond partly broken) and the charges in brackets indicate substantial partial charges (about half a minus charge each in this case). Transition states are often shown in square brackets and marked with the symbol

Another way to look at this situation is to consider the orbitals. The nucleophile must have lone-pair electrons, which will interact with the  $\sigma^*$  orbital of the C-X bond



In the transition state the carbon atom in the middle has a p orbital that shares one pair of electrons between the old and the new bonds. Both these pictures suggest that the transition state for an  $S_N2$  reaction has a more or less planar carbon atom at the centre with the nucleophile and the leaving group arranged at  $180^\circ$  to each other. This picture can help us explain two important observations concerning the  $S_N2$  reaction—firstly the types of structures that react efficiently, and secondly the stereochemistry of the reaction

**(P) Inversion** : If the relative configuration of atoms/groups around a stereo centre in the product is opposite to that in reactant, the reaction is said to proceed with inversion of configuration. There are three outcomes for a reaction at an asymmetric carbon atom. Consider the replacement of a group X by Y in the following reaction:

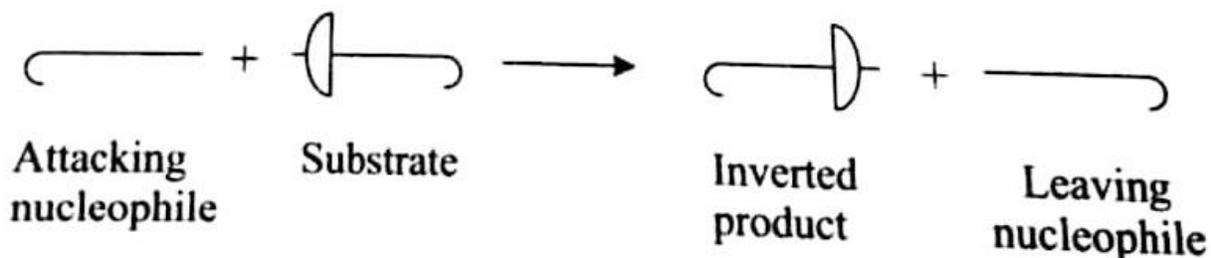


If (A) is the only compound obtained, the process is called retention of configuration.

If (B) is the only compound obtained, the process is called inversion of configuration.

**Walden inversion** is also based on umbrella inversion of  $S_N2$  reaction. So, the alcohol obtained has a configuration opposite to that of the bromide and is said to proceed with inversion of **configuration**. Hence, an  $S_N2$  reaction proceeds with

complete stereo-chemical inversion called umbrella inversion which can be diagrammatically represented as,



**S<sub>N</sub>2. mechanism** is followed in the case of primary and secondary alkyl halides, i.e. S<sub>N</sub>2 reaction is favoured by small groups on the carbon atom attached to halogens, so the order of reactivity is:



Primary is more reactive than secondary and tertiary alkyl halides, and nature of carbocation in substrate is:

S<sub>N</sub>2 order

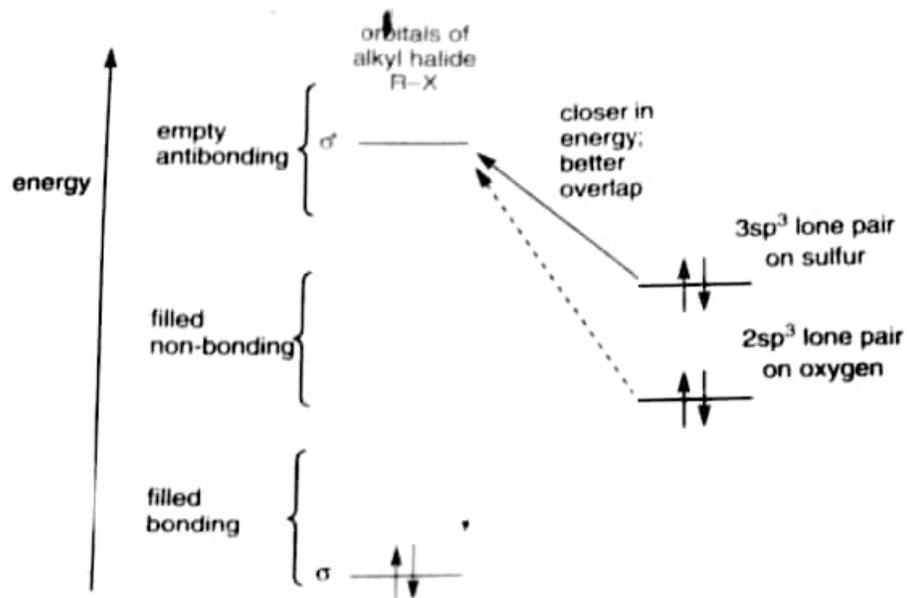
**Methyl > 1° > 2° > 3° > alkyl > benzyl halides**

## Effect of nucleophilicity of nucleophile on

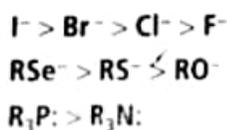
### S<sub>N</sub>2 reaction

What does matter is the strength of the HOMO-LUMO interaction. In a nucleophilic attack on the carbonyl group, the nucleophile adds in to the low-energy  $\pi^*$  orbital. In a nucleophilic attack on a saturated carbon atom, the nucleophile must donate its electrons to the  $\sigma^*$  orbital of the C-X bond, as illustrated in the margin for an alkyl bromide reacting with the non-bonding lone pair of a nucleophile.

$\sigma^*$  antibonding orbitals are, of course, higher in energy than non-bonding lone pairs, but the higher the energy of the nucleophile's lone pair, the better the overlap. The  $3sp^*$  lone-pair electrons of sulfur overlap better with the high-energy  $\sigma^*$  orbital of the C-X bond than do the lower energy  $2sp^3$  lone-pair electrons on oxygen because the higher energy of the sulfur electrons brings them closer in energy to the C-X  $\sigma^*$  orbital. The conclusion is that nucleophiles from lower down the periodic table are more effective in S<sub>N</sub>2 reactions than those from the top rows.



● Typically, nucleophilic power towards saturated carbon goes like this:



## Hard and soft nucleophiles

The fact that some nucleophiles, like  $\text{R}_3\text{P}$  and  $\text{RS}^-$  react very fast at saturated C atoms (they have high-energy lone pairs), but very poorly at  $\text{C}=\text{O}$  groups (they are either uncharged or have charge spread diffusely over large orbitals) gives them a different type of character from strongly basic nucleophiles like  $\text{HO}^-$  that attack  $\text{C}=\text{O}$  groups rapidly. We call nucleophiles that react well at saturated carbon soft nucleophiles; those that are more basic and react well with carbonyl groups are referred to as hard nucleophiles. These are useful and vocative terms because the soft nucleophiles are indeed rather large and flabby with diffuse high-energy electrons while the hard nucleophiles are small and spiky with closely held electrons and high charge density.

When we say 'hard' (nucleophile or electrophile) we refer to species whose reactions are

dominated by electrostatic attraction and when we say 'soft' (nucleophile or electrophile) we

refer to species whose reactions are dominated by HOMO-LUMO interactions.

**Solvent effects in S<sub>N</sub>2 Reaction:** The rates of many S<sub>N</sub>2 reactions are affected by the solvent. Protic solvents those that contain - OH or - NH group are generally the worst solvents for S<sub>N</sub>2 reactions. Polar protic solvents, (like water, alcohols and carboxylic acids), which have strong dipoles but don't have - OH or - NH groups are the best. In contrast to protic solvents, which decrease the rates of S<sub>N</sub>2 reactions by lowering the ground state energy of nucleophile, polar aprotic solvents increase the rates of S<sub>N</sub>2 reactions by raising the ground state energy of nucleophile. Particularly valuable solvents are acetonitrile (CH<sub>3</sub> CN); dimethyl formamide [(CH<sub>3</sub>)<sub>2</sub> NOCH, abbreviated DMF]; dimethyl sulphoxide [(CH<sub>3</sub>)<sub>2</sub> SO abbreviated DMSO] and hexamethylphosphoramide [{ (CH<sub>3</sub>)<sub>2</sub> N}<sub>3</sub> PO, abbreviated HMPA]. For instance a rate increase of 2,00,000 has been observed on changing from methanol to HMPA for the reaction of azide ion with 1-bromobutane.

	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br + 1-Bromobutane	N <sub>3</sub> <sup>-</sup> Azide ion	→	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N <sub>3</sub> + 1-Azidobutane	Br <sup>-</sup> Bromide ion	
Solvent	CH <sub>3</sub> OH	H <sub>2</sub> O		DMSO	DMF	CH <sub>3</sub> CN
Type of Solvent (Polar)	Protic	Protic		Aprotic	Aprotic	Aprotic
Relative reactivity (Increasing)	1	7		1300	2800	5000
Dielectric constant (ε)	32.6	78.5		48.9	36.7	37.5