

INORGANIC,
ORGANIC,
PHYSICAL
CHEMISTRY-III

UNIT-I

Acids and Bases

Arrhenius theory of acid

- Arrhenius was a Swedish chemist
- Put forward a theory of acids in the 1880's
- Stated that:

An acid is a substance that dissociates in water to form H^+ ions.



Arrhenius theory of acid

For example: when HCl is added to water:



In general:



Acids

- HCl and HNO₃ are monobasic acids as they donate one H⁺ ion.



- H₂SO₄ is a dibasic acid as it donates two H⁺ ions.



- H₃PO₄ is a tribasic acid as it donates three H⁺ ions.



- A strong acid is one which dissociates fully in water

Example: HCl, H₂SO₄, HNO₃



- A weak acid is one which does not fully dissociate in water

Example: CH₃COOH (ethanoic acid)



Common laboratory bases

- Sodium hydroxide - NaOH
- Calcium hydroxide - Ca(OH)_2
- Ammonia - NH_3
- Sodium carbonate - Na_2CO_3

Common laboratory bases

- Sodium hydroxide - NaOH
- Calcium hydroxide - Ca(OH)_2
- Ammonia - NH_3
- Sodium carbonate - Na_2CO_3

Arrhenius theory of bases

- Arrhenius defined a base as:
A substance that dissociates in water to produce OH^- ions.
- For example: when NaOH is added to water:



- In general:



- A strong base is one which dissociates fully in water

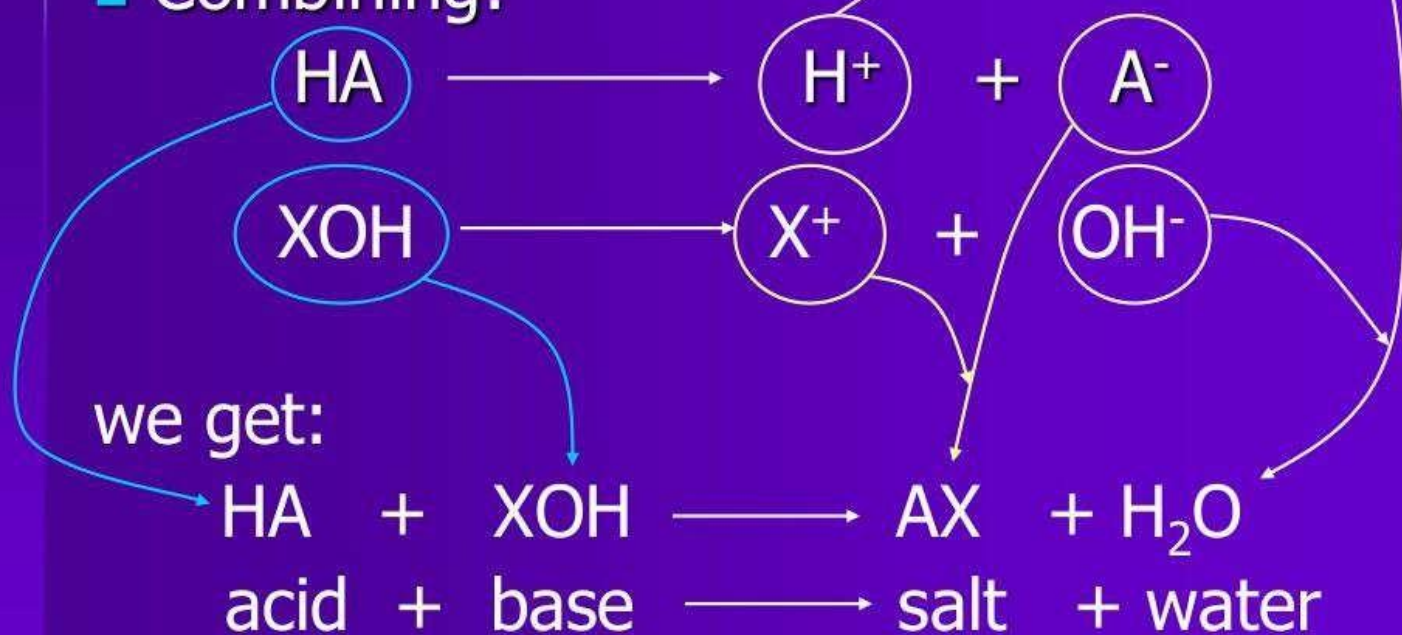
Example: NaOH

- A weak base is one which does not fully dissociate in water

Example: Mg(OH)₂

Arrhenius theory

■ Combining:



Limitations of Arrhenius theory

1. The acids and bases must be in aqueous solutions (i.e. water). This prevents the use of other solvents benzene.
2. Not all acid – base reactions are in solution, e.g. ammonia gas and hydrogen chloride gas produce ammonium chloride.
3. According to Arrhenius, the salt produced should not be acidic or basic. This is not always the case, for example in the above reaction ammonium chloride is slightly acidic

Hydronium Ion

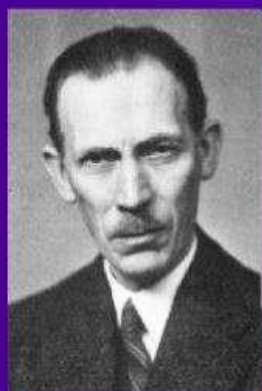
- Arrhenius thought that an acid gives off H^+ ions in solution.
- H^+ ions are protons and can not exist independently.
- When the acid dissociates, the H^+ ions react with water molecules:



- The H_3O^+ ion is called the hydronium ion.
- This is another limitation of the Arrhenius theory.

Brønsted-Lowry Theory

- In 1923, Johannes Brønsted (a Danish chemist) and Thomas Lowry (an English chemist) proposed new definitions of acids and bases.



Brønsted



Lowry

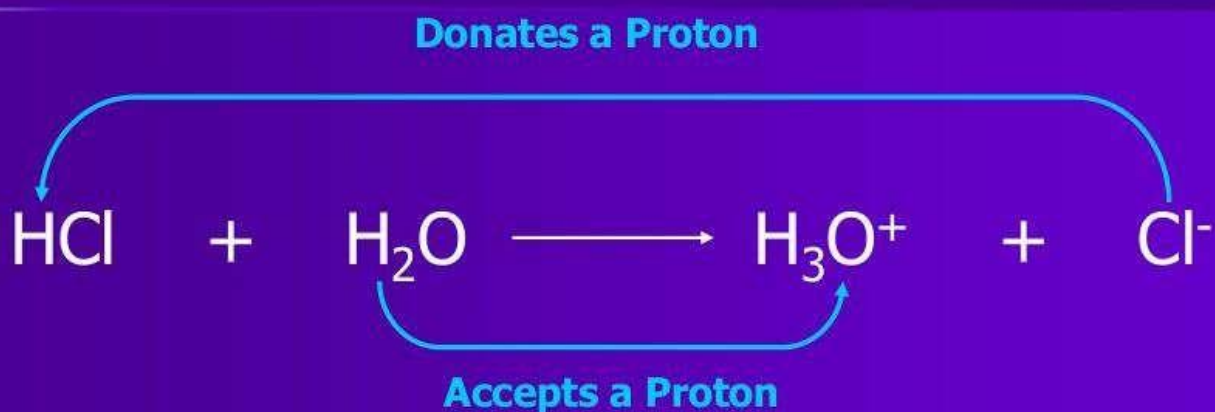
Brønsted-Lowry Theory

- Brønsted and Lowry had worked independently of each other but they both arrived at the same definitions:

An acid is a substance that donates protons (hydrogen ions).

A base is a substance that accepts protons.

Acid = Proton Donor



- The HCl donates a proton and so is an acid
- The H₂O, in this case, accepts a proton and so is a base

Remember: Proton = H⁺

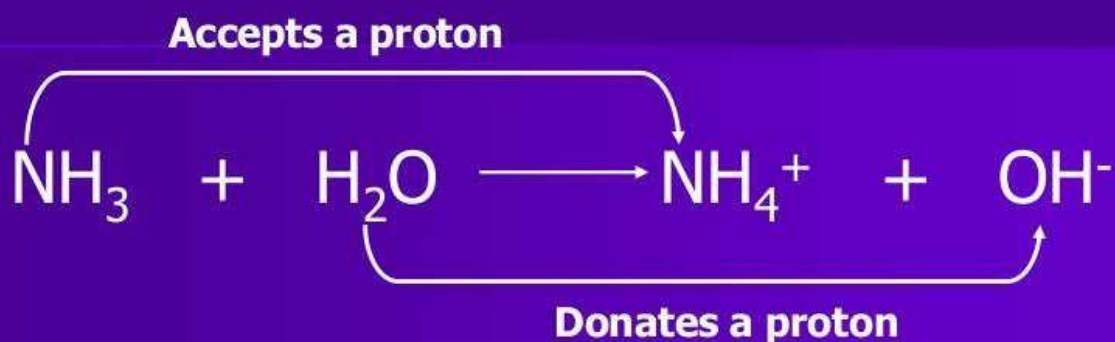
Likewise:



and



Base = Proton Acceptor

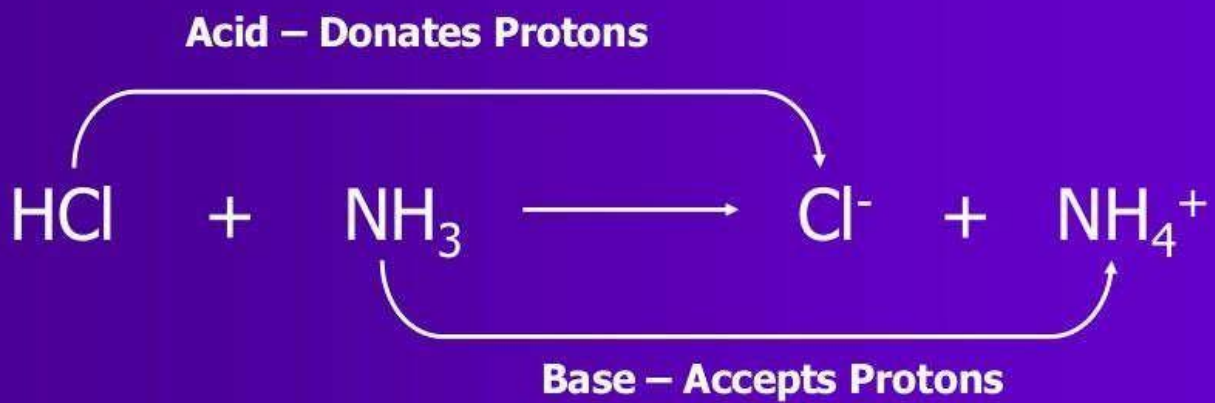


- The NH_3 accepts a proton and so is a base.
- The H_2O , in this case, donates a proton and so is an acid.

Amphoteric

- As can be seen from the previous two examples, water is capable of acting as both an acid and a base.
- Any substance that can act as both an acid and a base is said to be **amphoteric**.

Acid – Base Reaction



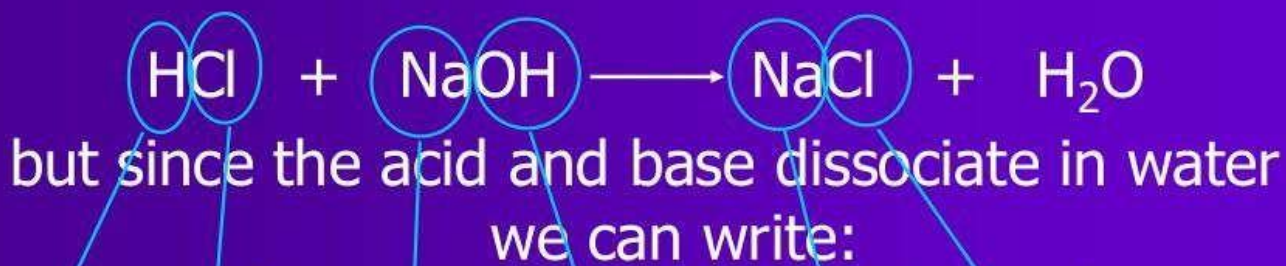
Neutralisation

The reaction between an acid and a base to produce a salt and water

A salt is formed when the hydrogen of an acid is replaced by a metal (or ammonium ion)

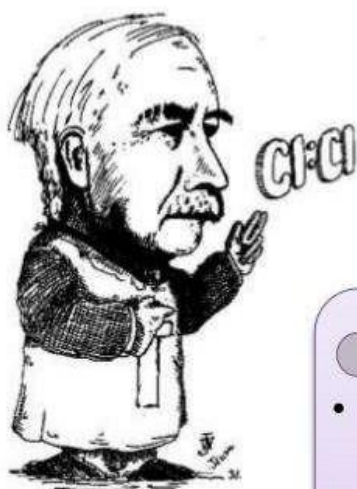
Neutralisation

Acid + Base \longrightarrow Salt + Water



we can cancel the Na^+ and Cl^- on both sides
leaving:

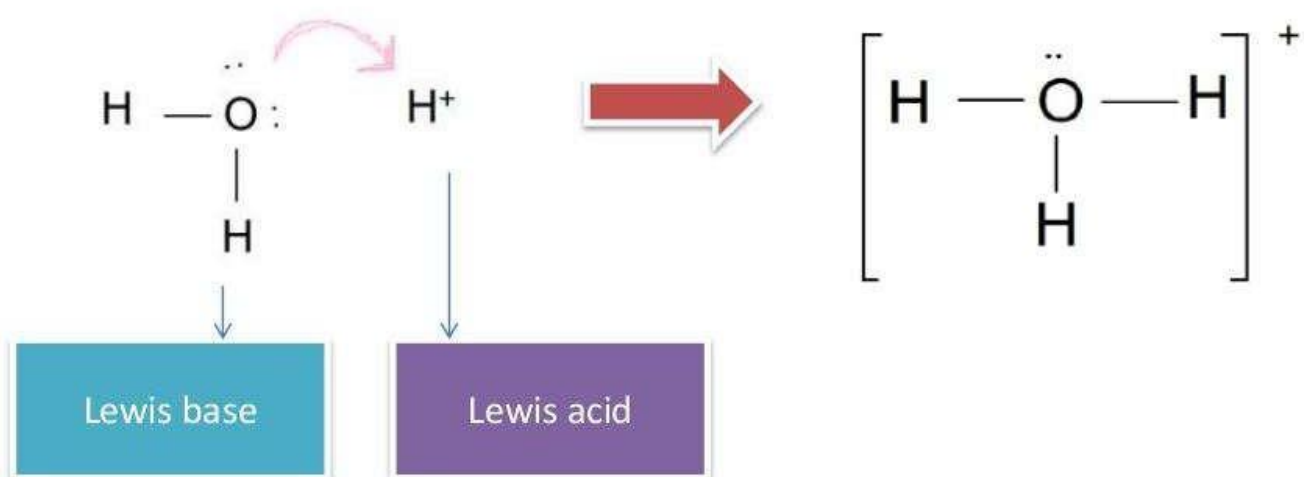




Lewis Theory

- Lewis acid is an atom, ion or molecule that accepts a pair of electrons to form a coordinate covalent bond.
- Lewis base is an atom, ion or molecule that donates a pair of electron to form a coordinate covalent bond.

Example ;



H^+ ACTING AS A LEWIS ACID WHEN H ACCEPTS A PAIR OF ELECTRON FROM H_2O TO FORM H_3O^+ .

CONVERSELY ;

H_2O IS A LEWIS BASE SINCE IT DONATES A PAIR OF ELECTRONS TO H^+ .

Definition of d-block elements

▶ d-block elements:

The elements of periodic table belonging to group 3 to 12 are known as d-Block elements. because in these elements last electron enters in d sub shell or d orbital .

- ▶ The d -block elements lie in between s- and p-block elements in the long form of periodic table



1st Series

Z	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd Series

Z	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3rd Series

Z	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

4th Series

Z	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

Transition Elements

A transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states. i.e.

A transition element should have partially filled $(n-1)$ *d* orbital.



Electronic Configuration

Electronic Arrangement

Element	Z		3d					4s
Sc	21	[Ar]	↑					↑↓
Ti	22	[Ar]	↑	↑				↑↓
V	23	[Ar]	↑	↑	↑			↑↓
Cr	24	[Ar]	↑	↑	↑	↑	↑	↑
Mn	25	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe	26	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co	27	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni	28	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	29	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	30	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓



Table 9.1 Outer electron configurations of the transition elements (ground state)

1st Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

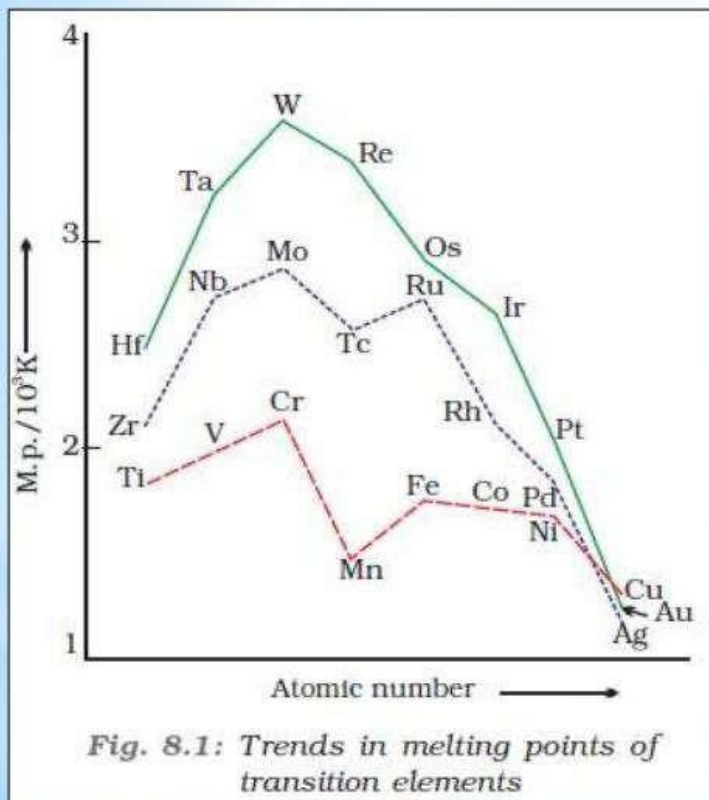
2nd Series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3rd Series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

MELTING AND BOILING POINTS (ENTHALPIES OF ATOMISATION) :



Melting and boiling points are high. A large number of unpaired electrons take part in bonding so they have very strong metallic bonds and hence high m.pt & b.pt

- Along the rows nuclear charge increases but the penultimate d-sub shell has poor shielding effect so atomic and ionic size remain almost same .
- The radii of the third (5d) *series are virtually the same* as those of the corresponding members of the second series.

- This phenomenon is associated with the intervention of the *4f orbital*, the filling of *4f* before *5d orbital* results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number.
- The net result of the lanthanoid contraction is that the second and the third *d series* exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm)

Oxidation States

- Transition elements have **variable oxidation states**, due to very small energy difference between $(n-1)d$ & ns sub-shell electrons from both the sub-shell take part in bonding

Table 8.3: Oxidation States of the first row Transition Metals
(the most common ones are in bold types)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
+3	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

- The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7.
- Low oxidation states are found when a complex compound has ligands capable of π -acceptor character in addition to the σ -bonding.
- * For example, in $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$, the oxidation state of nickel and iron is zero.

COLOURED IONS

Most of the transition metal compounds (ionic as well as covalent) are colored both in solid state & in aqueous state.

Generally the elements/ions having unpaired electrons produce colored compound.

VOLUMETRIC ANALYSIS

- ♥ It is a general term for a method in **quantitative chemical analysis** in which the amount of a substance is **determined by the measurement of the volume** that the substance occupies.
- ♥ It is commonly used to **determine the unknown concentration of a known reactant**.
- ♥ Volumetric analysis is often referred to as **titration**, a laboratory technique in which one substance of known concentration and volume is used to react with another substance of unknown concentration.

Definition of terms

Volumetric Analysis

- Involves the preparations, storage, and measurement of volume of chemicals for analysis

Volumetric Titrimetry

- Quantitative chemical analysis which determines volume of a solution of accurately known concentration required to react quantitatively with the analyte (whose concentration to be determined).
- The volume of titrant required to just completely react with the analyte is the **TITRE**.

Definition of terms

Titration

- A process in which a standard reagent is added to a solution of analyte until the reaction between the two is judged complete

Primary Standard

A reagent solution of accurately known concentration is called a **standard solution**.

Standardization

- A process to determine the concentration of a solution of known concentration by titrating with a primary standard

Definition of terms

End point

- The point at which the reaction is observed to be completed is the end point
- The end point in volumetric method of analysis is the signal that tells the analyst to stop adding reagent and make the final reading on the burette.
- Endpoint is observed with the help of indicator

Equivalent point

- The point at which an equivalent or stoichiometric amount of titrant is added to the analyte based on the stoichiometric equation

Definition of terms

- Concentration: is a general term expressing the amount of solute contained in a given material. Expressed by different ways
- Molarity(M): The number of moles of solute divided by the number of liters of solution containing the solute. (is gram molecular weight dissolved in one liter of solution)
- Molarity = moles of solute / volume in liters
- Milli moles of solute / volume in milliliters.
- Moles = weight (gms) / MW or
- Millimoles = weight(mg) / MW

Normality (N)

- Defined as no of equivalents of solute divided by the number of liters of solution containing the solute. (gm equivalent weight dissolved in one liter of solution)
- Normality = equivalents of solute / volume in liters
- Milli eq. of solute / volume in milliliters.
- Equivalents = weight (gms) / EW or
- Milliequivalent = weight(mg) / EW

Relation of Normality and Molarity

- Molarity = weight / MW x Volume
- MW = Weight / Molarity x volume similarly
- Normality = weight / EW x Volume
- EW = Weight / normality x volume
- EW = MW / h
 - Where h reacting unit.
 - For acid H⁺ is reacting unit and for base OH⁻
 - For Oxdⁿ redⁿ e⁻ is reacting unit
 - For Ionic species valences

Equivalent weight

- Is defined as part by wt of substance which is chemically equivalent to one part by wt of hydrogen or 8 part by wt of oxygen or 35.5 part by wt of chlorine.
- Thus in finding out equivalent wt we find out how many grams of that substance are directly or indirectly equivalent to one gram of hydrogen
- It depends on reaction in which it takes place

Percent (%)

- Weight percent (w/w) = $\frac{\text{weight of analyte} \times 100}{\text{weight of sample}}$
- Volume percent (v/v) = $\frac{\text{volume of analyte} \times 100}{\text{volume of sample}}$
- Weight percent (w/v) = $\frac{\text{weight of analyte} \times 100}{\text{volume of sample}}$

Parts per million (ppm)

- Ppm = $\frac{\text{weight analyte}}{\text{weight of sample}} \times 10^6$
- Or ie 1 gm / 10 liters
- Or 1mg / Liter
- Or microgram / ml
- Molal Solution: Gram molecular wt dissolved in 1000gm of solution
- Formal solution: gram formula wt dissolved in 1000ml of solution.

Standard solution

- A solution whose con is accurately known
- Prepared by dissolving an accurately wt quantity of highly pure material called primary std. and diluted to an accurately volume in volumetric flask.
- Otherwise a solution of approximately desired con is titrated against the primary standard solution and concentration is determine, this is called standardization

Primary Standards

- Measurements are made with reference to standards
- The accuracy of a result is only as good as the quality and accuracy of the standards used
- A standard is a reference material whose purity and composition are well known and well defined
- Primary Standards – Used as titrants or used to standardize titrants
 - Eg. Acid base titration Na_2CO_3 , KHP, Succinic acid, Benzoic acid, Oxalic acid.
 - Eg for redox titration: $\text{K}_2\text{Cr}_2\text{O}_7$, Potassium bromate, KIO_3 , Sodium Oxilate, arsionus trioxide
 - Eg for PPT titrations: NaCl , KCl , KBr , Silver nitrate
 - Eg for Complometric titration: Pure matels like Zn , Mg , Mn and its salts

Strong Acids

- an acid that **dissociates completely** into ions in water

Ex. All molecules of $\text{HCl}_{(\text{aq})}$ dissociate into H^+ and Cl^- ions

- H^+ ions that are formed bond with H_2O to form H_3O^+



- Some examples of strong acids:
 - HBr , HI , HNO_3 , H_2SO_4 , HClO_4

Weak Acids

- an acid that **dissociates** very slightly into ions in water

Ex. Not all molecules of $\text{CH}_3\text{COOH}_{(\text{aq})}$ break apart, some remain intact

- only about 1% of acetic acid molecules dissociate



Strong Base

- a base that **dissociates completely** into ions in water

Ex. All molecules of $\text{NaOH}_{(\text{aq})}$ dissociate into Na^+ and OH^- ions



- Some other strong bases are:
- **KOH, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$**

Weak Base

- Most bases are weak
- Weak bases **dissociates** *very slightly* into ions in water
 - Ex. Ammonia \rightarrow $[\text{OH}^-]$



[H⁺] in Strong Acids

- If you have a dilute amount of a strong acid:

$$[\text{H}^+] = [\text{Strong Acid}]$$

- Ex. If a bottle of $\text{HCl}_{(\text{aq})}$ has a concentration of 1.0 mol/L, then:

$$[\text{Strong Acid}] = [\text{H}^+] = 1.0 \text{ mol/L}$$

This is because of 100% dissociation.

[H⁺] in Weak Acids

- If you have a dilute amount of a weak acid:

$$[\text{H}^+] \llll [\text{Weak Acid}]$$

- Ex. If a bottle of $\text{CH}_3\text{COOH}_{(\text{aq})}$ has a concentration of 1.0 mol/L, then:

$$\begin{aligned} [\text{Weak Acid}] &= 1.0 \text{ mol/L} \\ [\text{H}_+] &= \sim 1\% \text{ of original} \end{aligned}$$

This is because of poor dissociation.

Aliphatic Nucleophilic Substitution Reaction

Unit-II

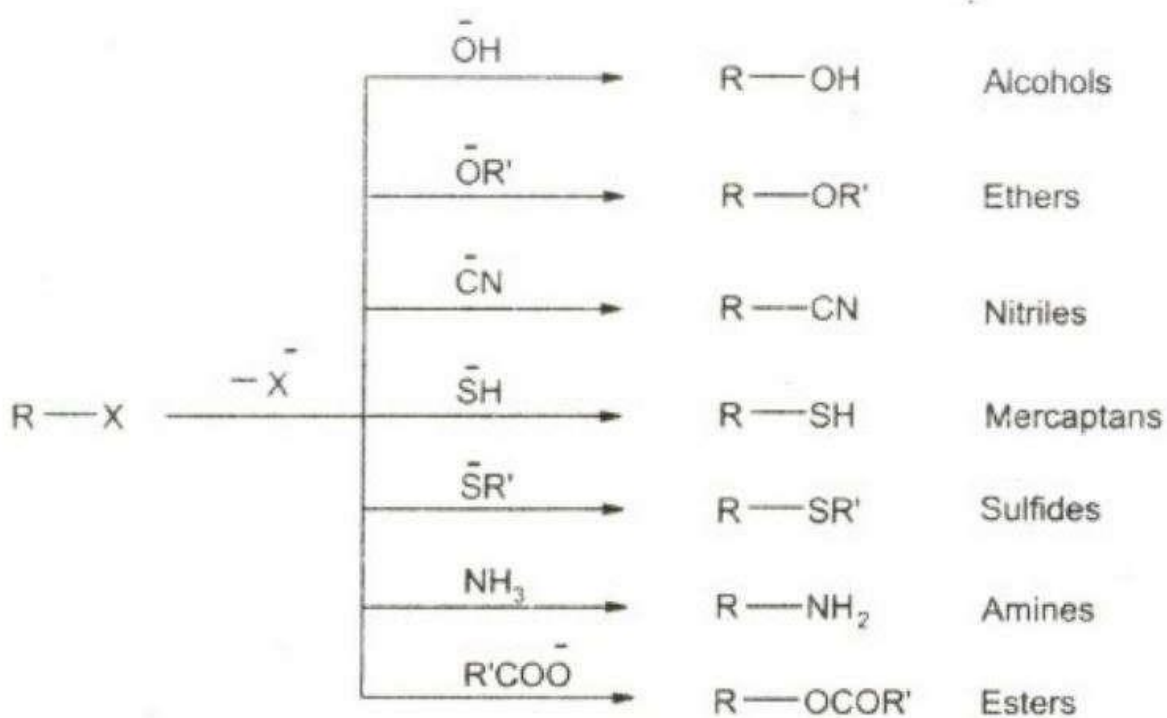
Nucleophilic substitution at saturated carbon atom

The replacement of one group by another is called substitution reaction. There are three main types of these reactions: radical, electrophilic and nucleophilic substitution. In this section we will deal with nucleophilic substitution at saturated carbon atom.

Attack of a nucleophile at a saturated carbon atom bearing a substituent, known as leaving group, results in substitution reaction. The group that is displaced (leaving group) carries its bonding electrons. The new bond is formed between nucleophile and the carbon using the electrons supplied by the nucleophilic reagent.



This is exemplified by the displacement of halogen atom with a hydroxide ion in the conversion of alkyl halide into an alcohol. Alkyl halides undergo substitution reactions with a variety of different nucleophilic reagents and are extremely important synthetically, as can be seen by the wide variety of compounds which can be prepared by its applications. The halogen is lost as a halide ion.



The compound on which substitution takes place is called the **substrate** and the group that becomes displaced from carbon, taking the electron pair with it, is called **leaving group**. The leaving group often leaves as an anion but may also be a neutral molecule. The substrate consists of two parts, alkyl group and leaving group. For example, reaction of methyl bromide with sodium hydroxide affords methanol and sodium bromide. In this reaction methyl bromide is substrate, bromide is leaving group and hydroxide ion is the nucleophile.



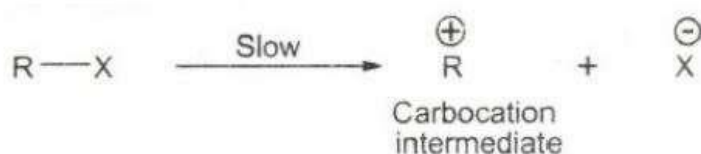
Nucleophilic substitution reactions have been studied extensively from a mechanistic viewpoint. Many factors influence the course of nucleophilic substitution reactions, including the nature of the nucleophile, its strength and concentration, the solvent, the nature of substrate, and the nature of leaving group.

Substitution reactions at saturated carbon can be mechanistically categorized as unimolecular (S_N1) or bimolecular (S_N2).

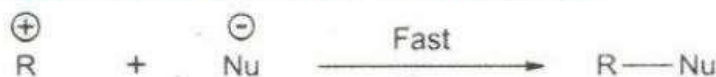
S_N1 (Substitution Nucleophilic Unimolecular)

An S_N1 reaction proceeds in two steps. The first step (slow step) is the rate determining step and involves the ionization of the reactant to form a carbocation intermediate. The breaking of C-X bond in RX takes place in a heterolytic fashion, in which both the bonding electrons go to the leaving group. In the second step (fast step), the intermediate carbocation is attacked by the nucleophile to give the final product.

Step 1. Formation of carbocation



Step 2. Capture of the carbocation by the nucleophile



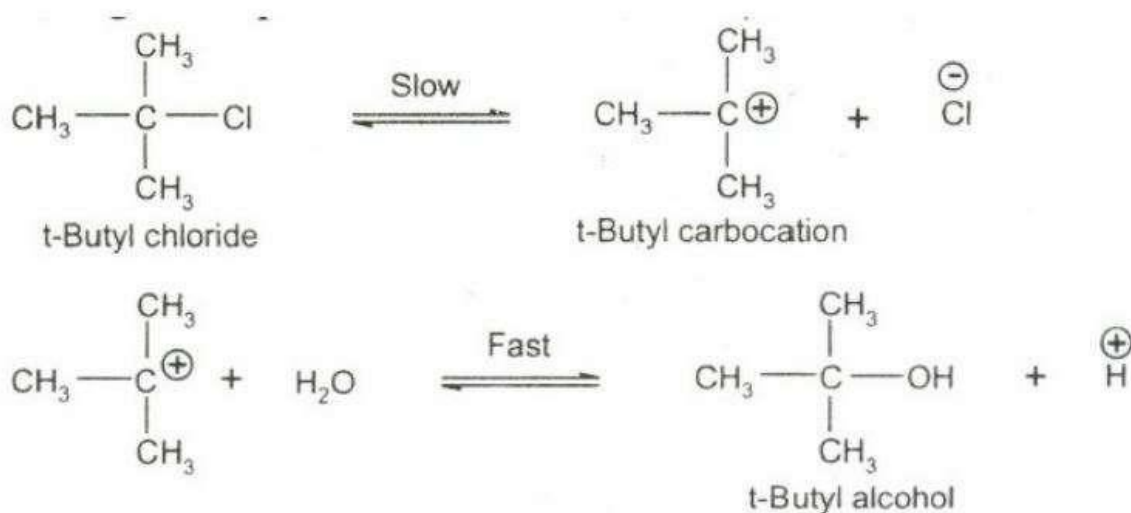
The S_N1 reaction shows first-order kinetics as rate of the reaction depends only on the concentration of the substrate (RX) and does not depend on the concentration of the nucleophile reacting with it. The rate expression is therefore:

$$\text{Rate} = k[\text{RX}]$$

where k is rate constant and quantity in square brackets represents concentration.

In several reactions, nucleophile is a solvent molecule such as water, ammonia or alcohol such substitution reactions are called solvolysis.

For example, hydrolysis of tert-butyl chloride to tert-butyl alcohol follows S_N1 process. In the first step, tert-butyl chloride ionizes to a tert-butyl carbocation, which is captured in a second step by the nucleophilic solvent, water, to give the protonated alcohol first and then alcohol itself.



Effect of solvent

The solvent plays an important role in S_N1 reactions as the energy required to effect the initial ionization is largely recovered from the energy evolved through solvation of the resulting ion pair. The S_N1 process requires the ionization of a covalent bond which is encouraged by solvents with high dielectric constants. There is a greater charge on the intermediate ions than that on starting substrate as majority of the substrates are neutral. Polar protic solvent (such as water or alcohol) will thus solvate and stabilize the intermediate ions more than it does the reactant. Since ions are usually formed in the rate determining step (slow step) of the reaction, therefore the S_N1 reaction will usually be favoured by a polar protic solvent. Good solvents for S_N1 displacements almost always contain hydroxyl groups (as in water, alcohols, or carboxylic acids) because the electronegative oxygen atom interacts with the incipient positive charge, and the electropositive hydrogen atom (through hydrogen bonding) interacts with the incipient negative charge. Thus, in addition to dielectric constant, the ability to form hydrogen bond with X^- makes a protic solvent the better solvent than aprotic solvent which cannot form hydrogen bond. The S_N1 process occurs mainly when water is present as a solvent or as a co-solvent.

Effect of nucleophile on rate

The rate of S_N1 reaction is independent of the nucleophile. A better nucleophile will not accelerate the S_N1 reaction, and yet it may determine which product is formed. For example, t-butyl bromide in water containing small amount of cyanide ions gives t-butyl cyanide. This is because the cyanide is many times more reactive towards carbocations than the water. Weak nucleophiles with low concentrations favor the S_N1 mechanism.

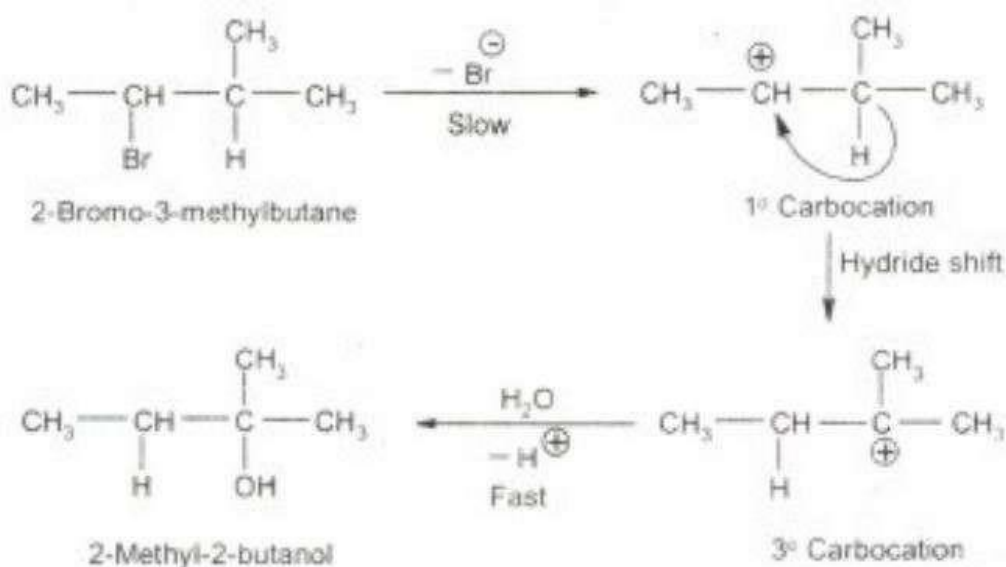
Effect of leaving group on rate

The rate of S_N1 reaction is largely influenced by the nature of the leaving group. The rate of ionization is affected by the stability of the leaving group, X^- . The more stable the leaving group, the more easily it will be lost. S_N1 reactions therefore are favored by the presence of good leaving group such as sulfonates (tosylate or mesylate).

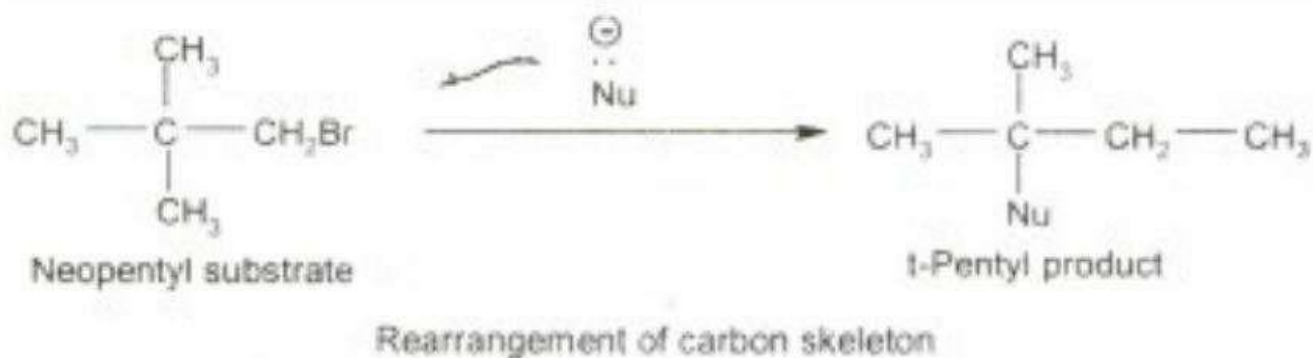
The weaker the Bronsted basicity of X^- , the better leaving group is X. In case of halides the order of basicity is : $I^- < Br^- < Cl^- \ll F^-$, therefore, iodide is a better leaving group than bromide and bromide is a better leaving group than chloride. Presence of acid catalysts or metal ions sometimes favour the departure of the leaving group, e.g., silver ions aid the departure of halide ion from alkyl halides.

Rearrangement in S_N1 reactions

The evidence for the formation of carbocations is that they undergo reactions other than simple addition to nucleophiles. For example, carbocations may rearrange before combining with nucleophiles. Since S_N1 mechanism involves carbocation intermediate, therefore, unexpected products are also formed. For example, hydrolysis of 2-bromo-3-methylbutane yields 2-methyl-2-butanol.



We see that in S_N1 reactions, a carbocation is formed by loss of the leaving group from the substrate. If a 1,2-shift of hydrogen can form a more stable carbocation, then such a rearrangement takes place. The rearranged carbocation can react with nucleophile to afford the substitution product or it may lose a proton to yield an alkene. If the intermediate carbocation can rearrange to a more stable carbocation *via* 1,2-alkyl shift, the reaction often proceeds with rearrangement of the carbon skeleton of the organic substrate.



Effect of the nature of substrate on the rate

The rate determining step is the formation of planar carbocation in S_N1 process. Therefore, the order of reactivity among organic substrates will depend upon the stability of carbocation formed after ionization of substrate. Hence tertiary alkyl halides, which give rise to tertiary carbocations, react faster than secondary ones, which react faster than primary halides.

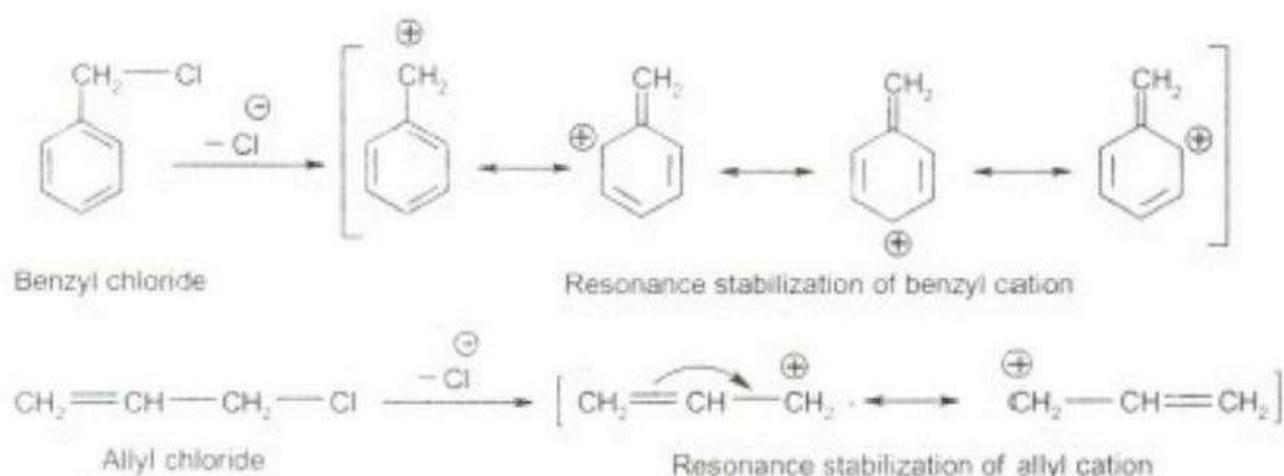
The introduction of a methyl group in place of a hydrogen atom attached to the positive carbon of a carbocation appears to stabilize the ion by 15 to 30 kcal / mol (through inductive and hyperconjugation effects). In most of the cases, the substituents which have +I and or +M effects, stabilize the carbocations. Allylic, benzylic, and tert-carbocations are relatively stable carbocations, therefore, allylic, benzylic and tert-halides can react by an S_N1 mechanism.

Stability of carbocations

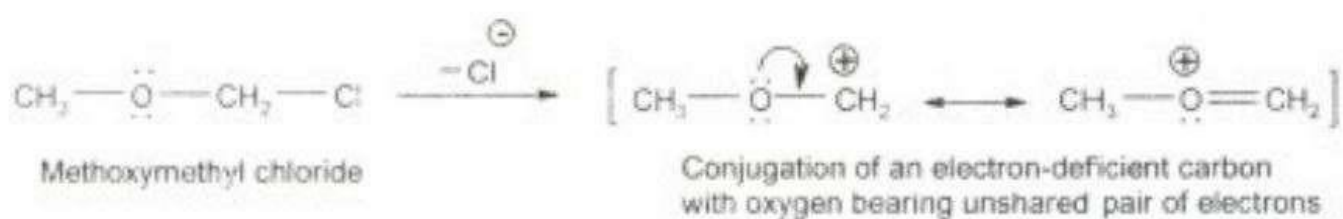


Both benzyl and allyl carbocations disperse the charge by resonance and are more stable than primary alkyl or secondary alkyl carbocations. The primary alkyl and methyl halides, which would form extremely unstable carbocations, do not generally react by the S_N1 process. The order of reactivity among organic halides is as follows:

t-alkyl halides > allyl halides ~ benzyl halides > s-alkyl halides > 1°-alkyl halides

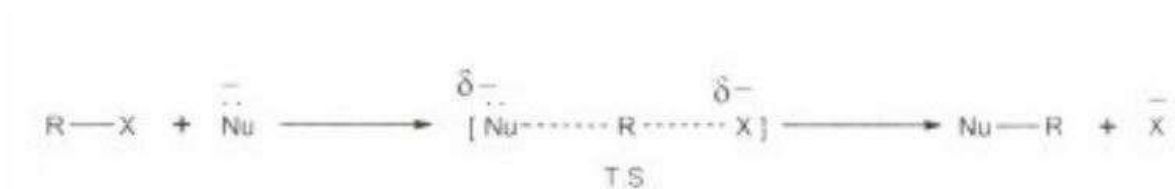


Methoxymethyl chloride undergoes hydrolysis more than 10^4 times faster than methyl chloride. This is because, the carbocation formed after ionization of methoxymethyl chloride is resonance stabilized. The CH_3O - group has unshared pairs of electrons that it tends to share, thus acquiring a positive charge.



S_N2 (Substitution Nucleophilic Bimolecular)

S_N2 process proceeds in one step *via* a transition state. The nucleophile attacks the substrate carbon simultaneously pushing out the leaving group in a concerted fashion.



The reaction between methyl iodide and hydroxide ion is an example of the S_N2 mechanism. Kinetic evidence shows that the rate of this reaction is proportional to both the concentrations of substrate and nucleophile. Thus, S_N2 reactions follow second-order kinetics and is described by the rate expression:

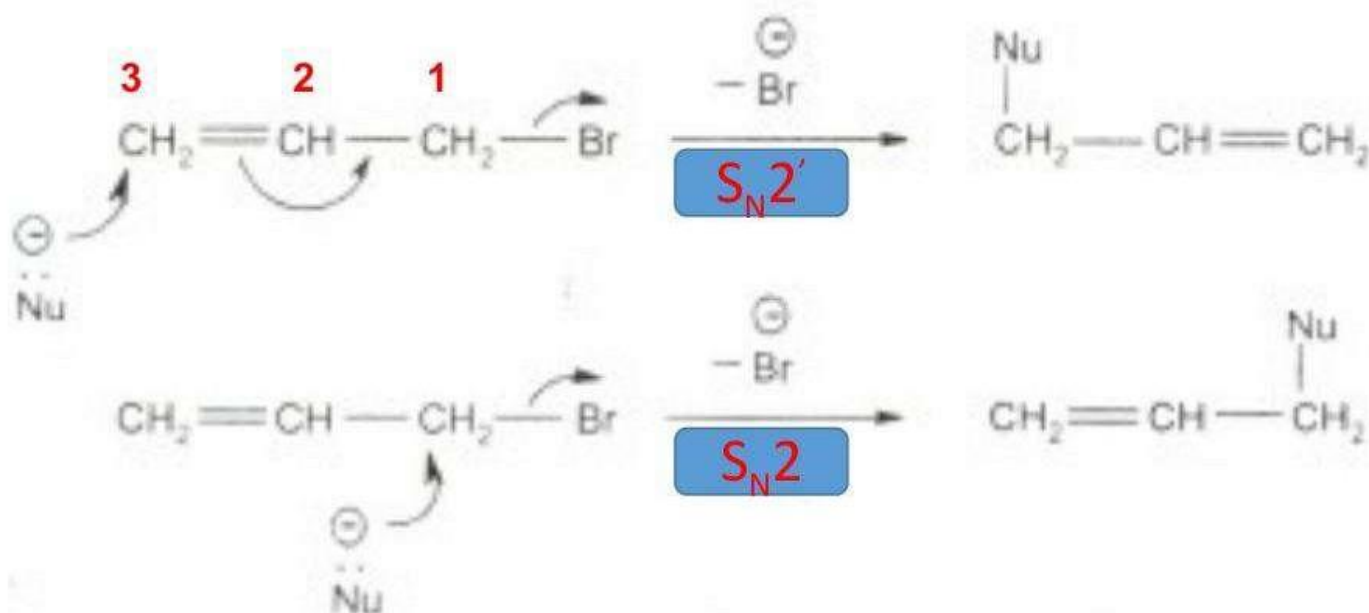
$$\text{rate} = k [\text{RX}] [\text{Nu}]^{\ominus}$$

where k is rate constant and quantities in square brackets represent concentrations.

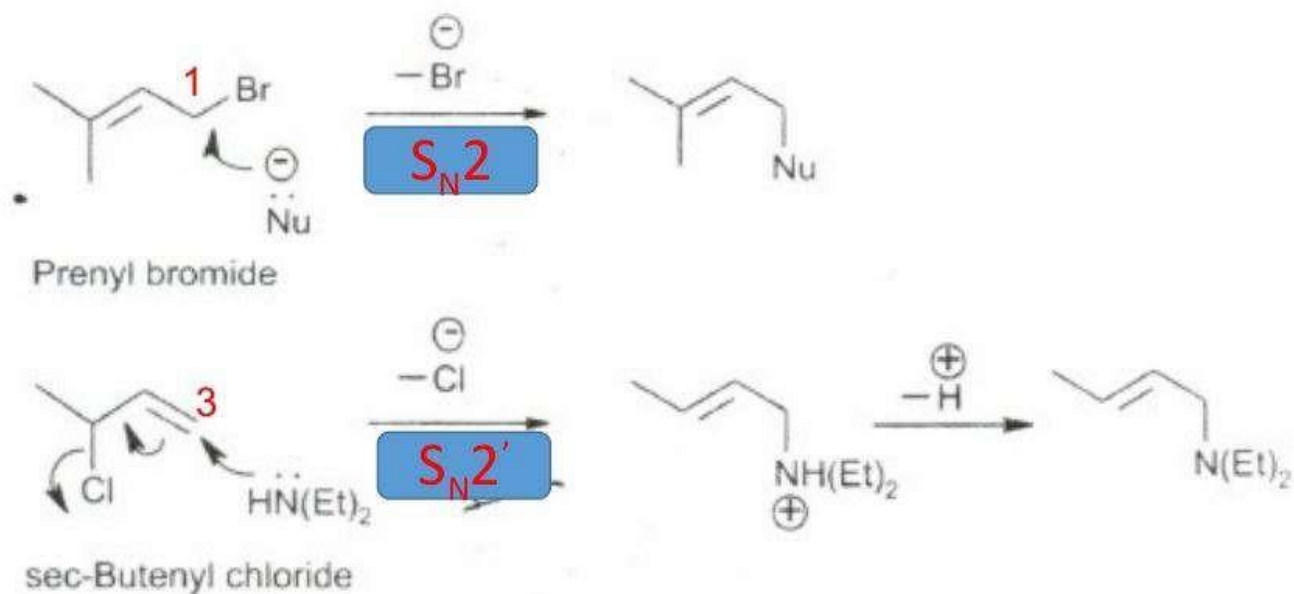
In S_N2 process there is synchronous attack by the nucleophile from the opposite side of the carbon atom of substrate bearing the leaving group, such that C-X bond of the substrate breaks only as the new C-Nu bond of the product is forming. Therefore, in transition state, the nucleophile-carbon bond is partially formed and the C-X bond is partially broken. The approach of the nucleophile from the side of the molecule bearing the leaving group is **unfavorable** due to electrostatic repulsion and also due to steric factors. In the transition state for this reaction, the three non reacting substituents on carbon lie in a plane with the carbon undergoing reaction. This plane is between the incoming and outgoing groups.

Rearrangement in S_N2

Since no free carbocation is generated, therefore, S_N2 displacement afford unrearranged products. However, **some times S_N2 reaction, leads to allylic rearrangement.** The attack of nucleophile takes place at the end of the π -system i.e. on C-3 of the allylic-system, with simultaneous expulsion of a leaving group. Such reactions are **referred to as S_N2'** , to distinguish them from the normal S_N2 process.

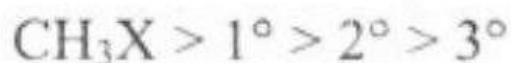


S_N2' mechanism leads to the same product as S_N2 , **however, if the allylic halide is unsymmetrically substituted**, we can tell which mechanism operates and the product formed will be from the nucleophilic attack at the less hindered end of the allylic system. Prenyl bromide, for example, reacts entirely *via* S_N2 process. If we react the secondary butenyl chloride with an amine we get the product from S_N2' mechanism.



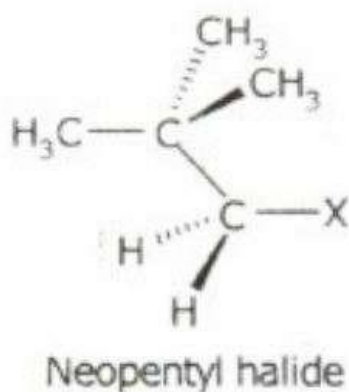
Effect of the nature of substrate on rate

The steric hindrance around the carbon site makes a huge difference in the rate of the S_N2 reaction. The central carbon atom in reactant and product is tetrahedral, whereas carbon in the transition state is bonded to five atoms or groups therefore, there will be an increase in crowding on going from the starting substrate to the transition state. A transition state with five groups crowded around the central carbon atom is a high-energy transition state. The more crowded the transition state relative to substrate, the higher its energy will be, and the slower it will be formed. As hydrogen atoms are replaced by the larger methyl groups, there is increased crowding about the carbon. Therefore, the methyl compounds react faster than primary substrates and primary substrates react faster than the secondary substrates. Tertiary substrates have three bulky alkyl groups attached to reaction center which hinder the approach of the entering nucleophile. Thus, tertiary alkyl halides such as t-butyl bromide normally do not undergo substitution *via* this mechanism. The reactivity of substrates in S_N2 reactions is:



This order is the reverse of that in S_N1 reactions.

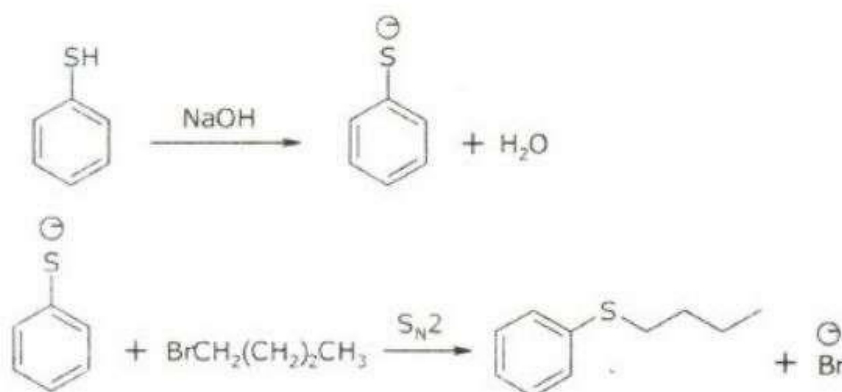
Even though the site of reaction in neopentyl derivatives is primary, the t-butyl group is large enough to slow down the bimolecular (S_N2) displacement.



In allyl and benzyl halides, the π -bond assists in expelling the leaving group, and both halides react faster than the alkyl halides.

Effect of the nucleophile

The rate of S_N2 reaction is strongly dependent on the nature of nucleophilic reagent used, it increases with the nucleophilic strength of the incoming nucleophile. Thus, with the change of nucleophile a shift in mechanistic type may occur, for example, the mechanism which is S_N1 with water may become S_N2 with hydroxide ion. Sulfur nucleophiles are better than oxygen nucleophiles in S_N2 reactions. For example, thiolate anions (excellent nucleophiles in S_N2 reactions) react with alkyl halides to give good yield of the sulfide as illustrated by the following reaction.



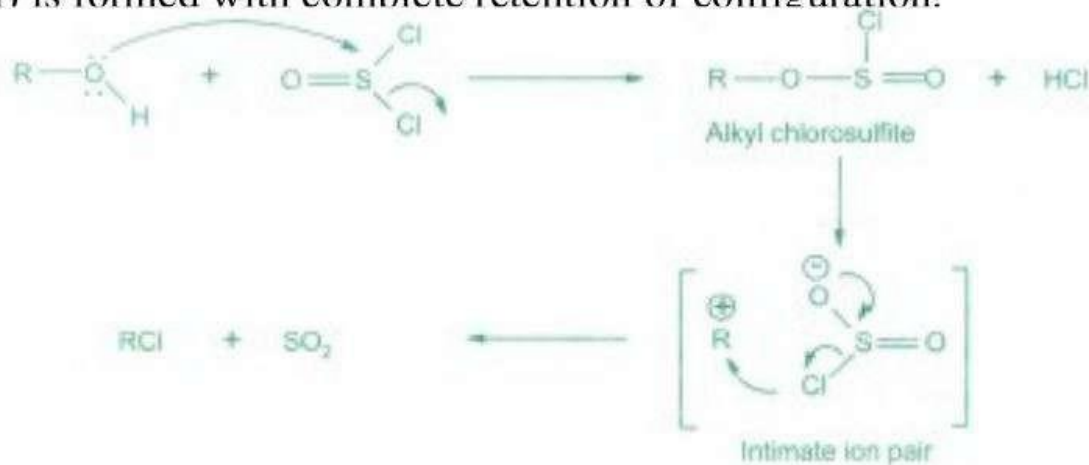
Effect of the leaving group

Weak base of strong acid is best leaving group, thus, the rate of S_N2 reaction (same as for S_N1) is higher if the leaving group is a stable ion and a weak base. In case of alkyl halides the order of reactivity is:



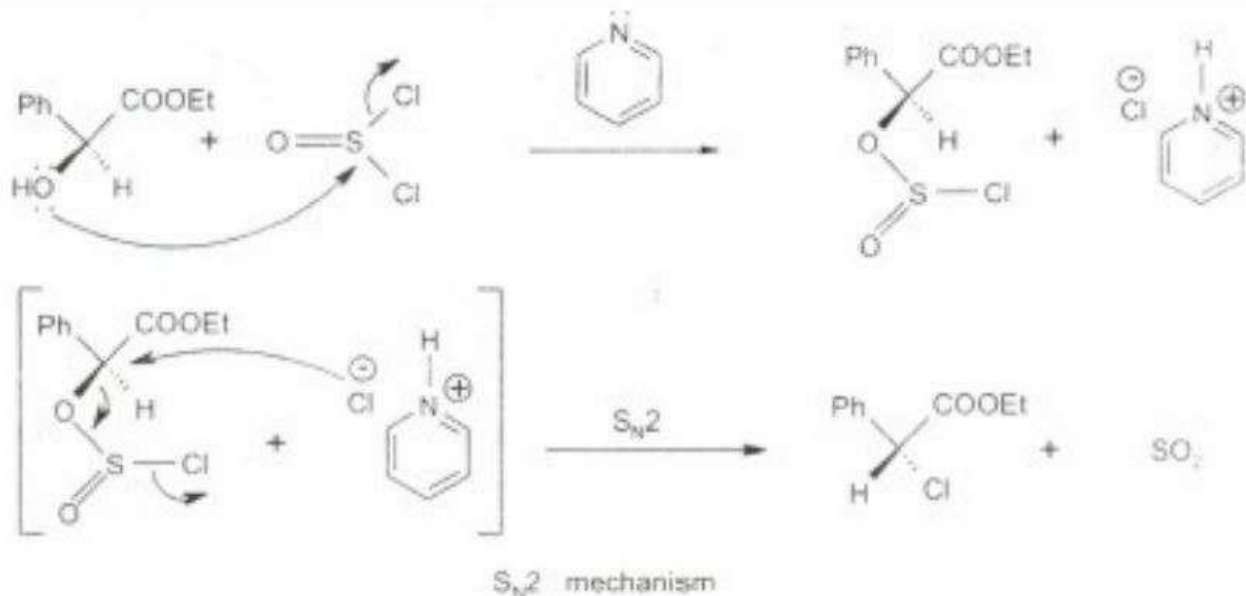
S_N^i (Substitution Nucleophilic internal)

In this process part of leaving group which attacks the substrate detaches itself from the rest of the leaving group. This is exemplified by the conversion of (R)-2-butanol to (R)-2-chlorobutane with SOCl_2 in nonpolar solvent and absence of base. The product formed is with complete retention of configuration, i.e., in which the starting material and product have the same configuration. The mechanism appears to involve the formation of intermediate chlorosulfite ester, ROSOCl (R = sec-butyl group), which dissociates into an intimate ion pair, $\text{R}^+ \cdot \text{OSOCl}^-$ as in S_N1 mechanism. The Cl, with pair of electrons, of the anion attacks the R^+ from the same side of the carbocation from which OSOCl^- departed and the product (RCl) is formed with complete retention of configuration.



S_N^i mechanism

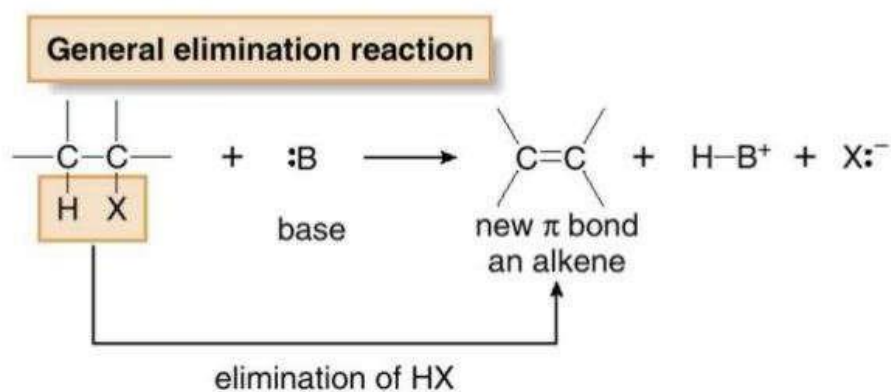
It is interesting to note that if a tertiary amine such as pyridine is added to the reaction mixture, the product RCl is found now to have undergone inversion of configuration. The pyridine co-ordinates with the HCl, produced during the formation of intermediate chlorosulfite from ROH and SOCl₂, to form pyridine hydrochloride and the Cl⁻ is an effective nucleophile. The displacement of the chlorosulfite ester by Cl⁻ via S_N2 mechanism gives product with complete inversion of configuration. The reaction of alcohols with thionyl chloride in presence of pyridine is known as **Darzen's procedure**.



Elimination Reaction

Elimination reactions involve the loss of elements from the starting material to form a new π bond in the product.

Alkyl halides (RX) undergo elimination with bronsted bases. The elements of HX are lost and alkene are formed.



Leaving groups

X, OH, OR, N_2^+ , N_3 , H_2O^+ , NR_3^+ and SR_2^+

Classification

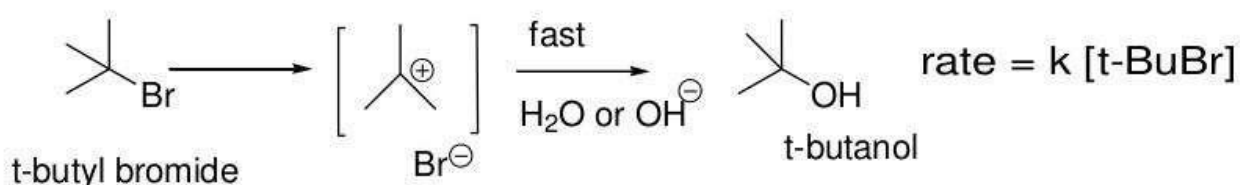
- α -elimination (1,1)
- β -elimination (1,2)
- γ -elimination (1,3)

β -elimination

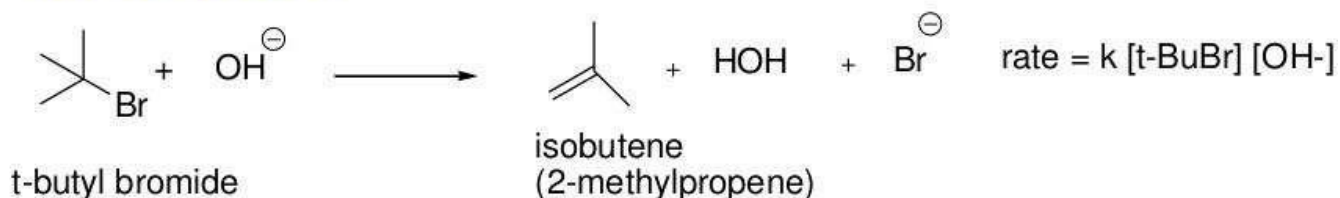
E1
E2
E1CB

Substitution and Elimination in alkyl halides

- Substitution on t-butyl bromide invariably follow SN1 mechanism. The following reaction can not be speeded up by 1) changing the nucleophile from H₂O to OH⁻, 2) increasing the concentration of OH⁻.



With conc. NaOH

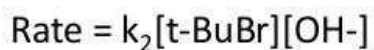


Elimination occurs when the nucleophile attacks H instead of carbon

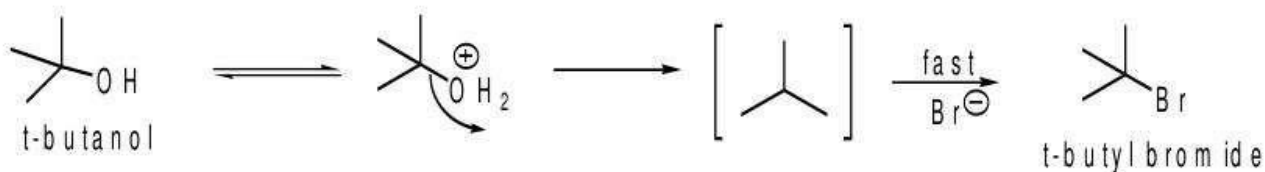


E2 (elimination bimolecular)

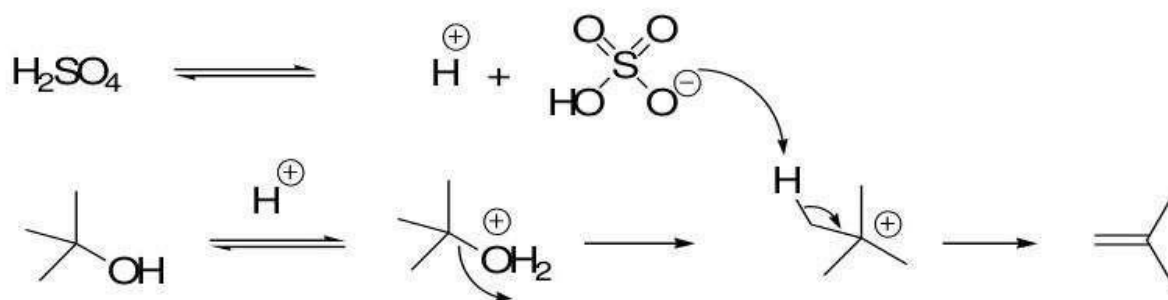
Elimination of t-butyl happens because here the Nu- (OH) is basic. Hydrogen is not acidic but proton removal occurs because Br⁻ is a good leaving group.



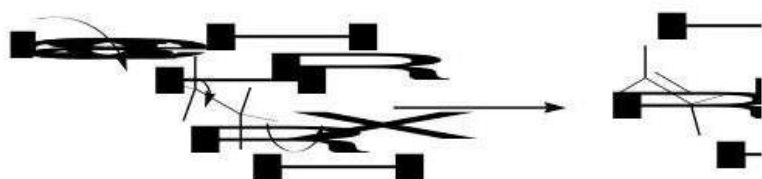
Nucleophilic substitution of t-BuOH with HBr



t-butanol in H₂SO₄ does not undergo substitution but elimination. HSO₄⁻ is a weak nucleophile.



E2 elimination



$$\text{Rate} = k[\text{Base}] [\text{alkyl halide}]$$

E2 describes an elimination that has a bimolecular (2) rate determining step that must involve the base. Loss of leaving group is simultaneous with removal of the proton by the base.

Factors that affect the nature of elimination

Base

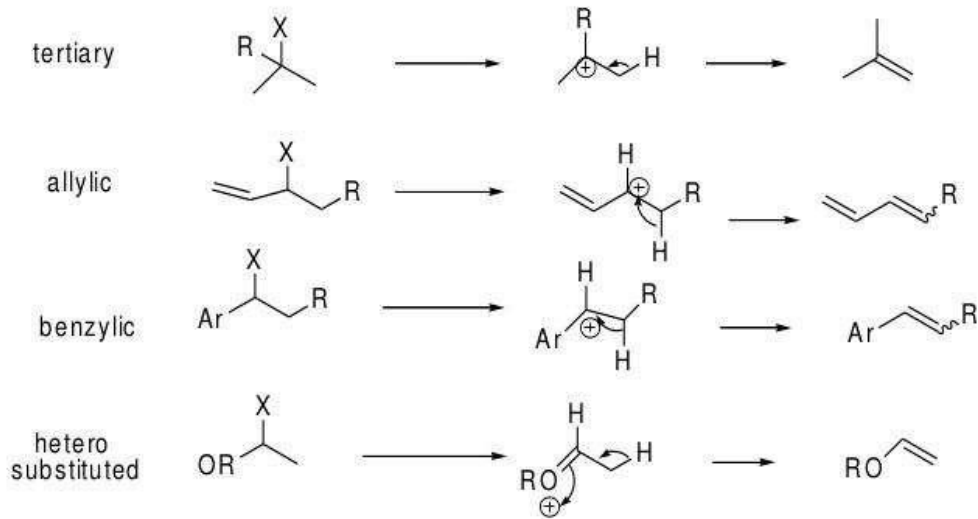
- High conc. of base favours E2
- Strong base favours E2 over E1

Substrate structure for E1

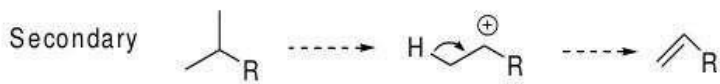
If the starting material is tertiary alkyl halide it would substitute only by SN1. But it eliminate either by E1 (with weak base) or E2 (with strong bases).

E1 occurs with substrates which ionise to give stable carbocations. Ex: tertiary, benzylic alkyl halides, allylic etc .

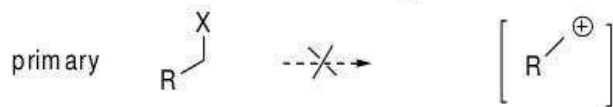
Substrates that eliminate by E1



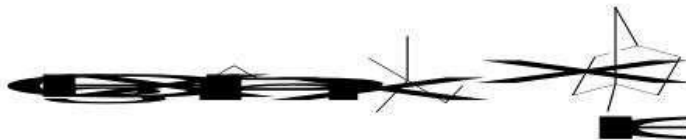
Substrates that may eliminate by E1



Substrate that never eliminate by E1



Substrates that can not eliminate by either mechanism



} May also eliminate by E2

} Can not eliminate by E2