Bond type (*C – H*)	Bond length	Bond type (C – C)	Bond length
$sp^3 - s$ (alkanes)	1.112Å	$sp^3 - sp^3$ (alkanes)	1.54 Å
$sp^2 - s$ (alkenes)	1.103Å	$sp^2 - sp^2$ (alkenes)	1.34Å
$sp - s$ (alkynes)	1.08Å	$sp - sp$ (alkynes)	1.20Å

Note : ❑ *C–C* bond length in benzene lies between single and double bond due to resonance. (1.40Å).

(iv) ***Bond strength in hydrocarbons*** : *The shorter the bond, the greater the compression between atomic nuclei and hence greater the strength of that bond is*. Thus the bond formed by sp hybridised carbon is strongest (i.e., it has maximum bond energy) while that formed by sp^3 hybridised carbon is the weakest (i.e., it has minimum bond energy). This is evident by the bond energies of the various types of $C-H$ and $C-C$ bonds.

Bond type (*C – H*)	Bond energy (kcal/mole)	Bond type (C – C)	Bond energy (kcal/mole)
$sp^3 - s$ (in alkanes)	104	$sp^3 - sp^3$ (in alkanes)	80 – 90
$sp^2 - s$ (in alkenes)	106	$sp^2 - sp^2$ (in alkenes)	122 – 164
$sp - s$ (in alkynes)	121	$sp - sp$ (in alkynes)	123 – 199

(v) ***Acidity of hydrocarbons***

(a) Hydrogen present on electronegative carbon is acidic in character.

(b) Acidity of hydrogen is directly proportional to the electronegativity of atom on which hydrogen is present.

Thus

$$\underset{\text{Acidity of compounds in deceasing order}}{\underset{\text{Electroneg ativity of atom in decreasing order}}{H-O-H \qquad NH_3 \qquad CH\equiv CH}} \longrightarrow$$

(c) Acidity of hydrocarbon $\propto$ % *s-character*

	$CH \equiv CH$	$CH_2 = CH_2$	$CH_3 - CH_3$
% *s*-character	50	33.33	25
pKa	25	44	50

$\longrightarrow$ *s*- character in decreasing order and acidity in decreasing order

Note : ❑ Acidity $\propto Ka$ and Acidity $\propto \frac{1}{pKa} (pKa = -\log Ka)$

$$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$$

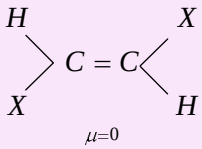
μ = 1.86 D 1.62 D 1.03 0

❑ Alkynes has larger dipole moment because the electronegativity of $sp - C$ is more than that of $sp^2 - C$.

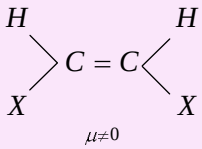
(4) μ cis $> \mu$ trans in geometrical isomers.

(5) Dipole moment of the trans derivative of the compound $(a)(b)C = C(a)(b)$ will only be zero if both a and b will be in the form of atoms.

Example :



$\mu = 0$



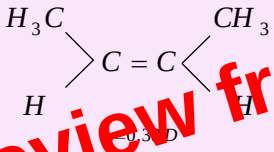
$\mu \neq 0$

($X = Cr, Br, I$ or F)

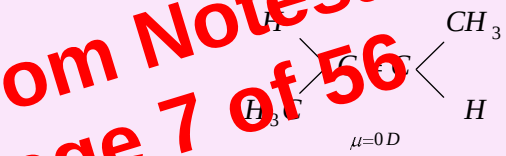
If both will not be atoms then μ trans may or may not be zero.

If group have non-linear moments, then the dipole moment of the trans isomer will not be zero. If group have linear moments, then the dipole moment of the trans isomer will be zero.

Example:



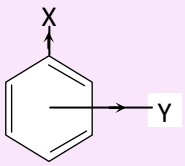
$\mu = 0.3$ D



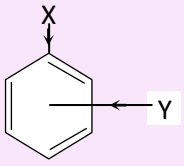
$\mu = 0$ D

(6) **Dipole moment of disubstituted benzene**

(i) When both groups X and Y are electron donating or both groups are electron with drawing



or



Then, $\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$

Where, $\mu_1 =$ dipole moment of bond $C - X$, $\mu_2 =$ dipole moment of bond $C - Y$, $\theta =$ angle between X and Y.

If value of θ will be more, then $\cos\theta$ will be less. Hence, dipole moment will be as,

$$\underset{\mu \text{ in decreasing order}}{o-\text{derivative} > m\text{-derivative} > p\text{-derivative}} \longrightarrow$$

The relative order of these intermolecular forces is,

Hydrogen bonding > dipole-dipole forces > Vander waal's forces.

Mechanism of organic reactions

When a chemical reaction takes place between two or more chemical species, new products are formed. This change is represented by a chemical equation. In a chemical equation, reactants are written on the left hand side while the products are written on the right hand side. The two are separated by an arrow (→). The reactants normally consists of two species,

(1) **Substrate :** The species, which is attacked by some other chemical species, is called a substrate.

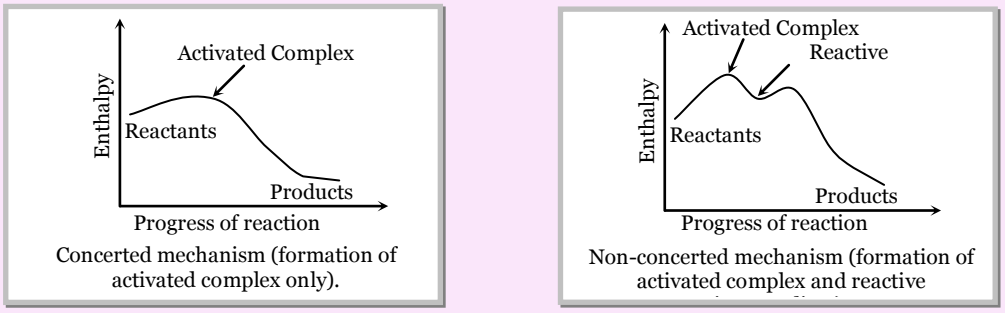
(2) **Reagent :** The species, which attacks the substrate in order to get the major product, is called a reagent. Thus, Substrate + Reagent → Products.

Normally, a substance and a chemical reagent form a highly energetic species, called **activated complex**, before it changes into the product. In certain cases, a relatively energetically more stable species than the activated complex may also be formed. It is called **reaction intermediate**. Thus, a chemical reaction, in general, may follow either of the following two paths,

Path I : Substrate + Reagent → Activated complex → Products

Path II : Substrate + Reagent → Activated complex → Intermediate → Products.

The detailed step by step description of a chemical reaction is called *mechanism of a reaction* which is only a hypothesis. If the reaction mechanism involves the breaking and making of bonds simultaneously without the formation of any intermediate, it is called **concerted mechanism**. On the other hand, if the reaction mechanism involve the formation of intermediates before the formation of products, it is called **non-concerted mechanism**.



Enthalpy curves for concerted and Non-concerted mechanisms

To understand clearly the mechanism of various organic reactions, it is essential to have knowledge about the following concepts;

- Electronic displacements in covalent bonds,
- Cleavage (fission or breaking) of covalent bonds,
- Nature of attacking reagents.

(a) An acid may be defined as a species that has the tendency to loose proton. Furthermore, the strength of an acid depends on the tendency to release proton when the acid is dissolved in water.

$$R-\overset{\overset{O}{\|}}{C}-OH \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O^{\ominus}+H^{\oplus}$$

(b) The relative strength of acids are measured in their ionisation constants (K_a or pK_a values).

$$\underset{Acid}{HA} \rightleftharpoons H^{\oplus}+A^{\ominus};\quad K_a=\frac{[H^{\oplus}][A^{\ominus}]}{[HA]};\quad pK_a=-\log K_a$$

Greater the value of K_a or lower the value of pK_a stronger will be the acid.

(c) Any group or atom showing +I effect decreases the acid strength as it increases the negative charge on the carboxylate ion which holds the hydrogen firmly. Alkyl groups have + I effect.

Thus, acidic nature is, $HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH > C_4H_9COOH$

(+ Inductive effect increases, so acid strength decreases)

Formic acid, having no alkyl group, is the most acidic among these acids.

(d) The group or atom having – I effect increases the strength as it decreases the negative charge on the carboxylate ion. Greater is the number of such atoms or groups (having – I effect), greater is the acid strength.

Thus, acidic nature is $\underset{\text{Trichloro acetic acid}}{CCl_3COOH} > \underset{\text{Dichloro acetic acid}}{CHCl_2COOH} > \underset{\text{Monochloro acetic acid}}{CH_2ClCOOH} > \underset{\text{Acetic acid}}{CH_3COOH}$

(– Inductive effect increases, so acid strength increases)

(e) Strength of aliphatic carboxylic acids and benzoic acid

$$\underset{+I\ group}{R}\rightarrow COOH \qquad \underset{-I\ group}{C_6H_5}\leftarrow COOH$$

Hence benzoic acid is stronger acid then aliphatic carboxylic acids but exception is formic acid. Thus,

$$HCOOH \qquad C_6H_5COOH \qquad RCOOH$$

Acid strength in decreasing order

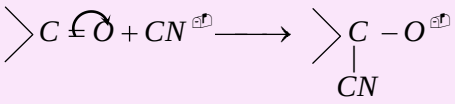
Note : ❑ Decreasing order of acids : $NO_2CH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH$.

$F_3C-COOH > Cl_3C-COOH > Br_3C-COOH > I_3C-COOH$.

(v) ***Acidity of alcohols*** **:** Acidity of alcohol depends on the stability of alkoxide ion (i.e., conjugate base of alcohol) which is obtained by the dissociation of alcohols.

$$R-O-H \rightleftharpoons \underset{\text{Alkoxide ion}}{R-\overset{\ominus}{O}}+\overset{\oplus}{H}$$

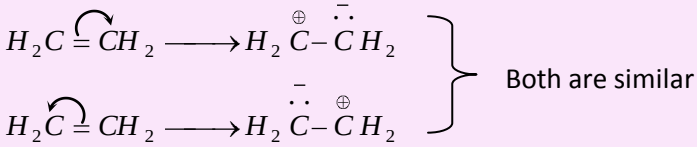
(b) When the transfer of electrons takes place away from the attacking reagent, the effect is called $-E$ effect. Example, The addition of cyanide ion to carbonyl compounds.



The attacking reagent does not attached to that atom on which electrons have been transferred.

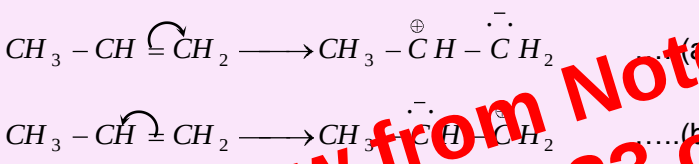
(3) **Direction of the shift of electron pair :** The direction of the shift of electron pair can be decided on the basis of following points.

(i) When the groups linked to a multiple bond are similar, the shift can occur to either direction. For example, in ethylene the shift can occur to any one of the carbon atoms.



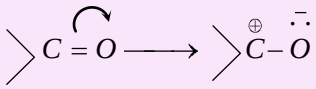
Both are similar

(ii) When the dissimilar groups are linked on the two ends of the double bond, the shift is decided by the direction of inductive effect. For example, in propylene the shift can be shown in the following ways,



Due to electron repelling nature of methyl group, the electronic shift occurs according to Eq. (a) way and not by Eq. (b) way.

In the case of carbonyl group, the shift is always towards oxygen, *i.e.,* more electronegative atom.



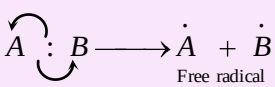
Note : ❑ In cases where inductive effect and electromeric effect simultaneously operate, usually electrometric effect predominates.

Cleavage (fission or breaking) of covalent bonds

Breaking of covalent bond of the compound is known as **bond fission**. A bond can be broken by two ways,

(1) **Homolytic bond fission or Homolysis**

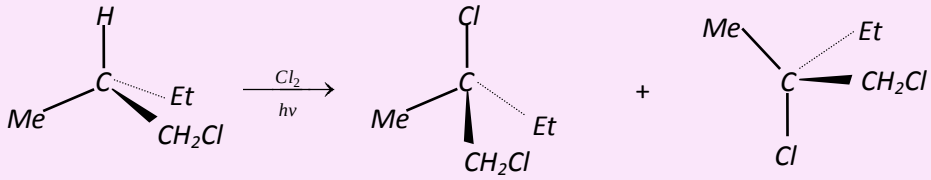
(i) In homolysis, the covalent bond is broken in such a way that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.



$\dot{C}H_3 < \dot{C}H_2F < \dot{C}HF_2 < \dot{C}F_3$.

So, CF_3 is essentially pyramidal in shape.

(4) **Stereochemistry of free radicals :** To learn about the stereochemistry of free radical reaction. We choose the reaction, chlorination of 1-chloro-2-methyl butane. The reaction products are,



If we review the insight of the reaction, it is clear that the reaction involves racemization at the reaction centre. The free radical should have the sp^2 hybridisation. Obviously a Cl_2 molecule could attack either the upper or lower lobe of the p -orbital with equal chances, leading to racemic mixture.

Intermediate $\xrightarrow{Cl_2} \underset{(50\%)}{d-\text{form}} + \underset{(50\%)}{l-\text{form}}$

(5) **Reactions involving free radicals,**

(i) Chlorination of alkanes (ii) Pyrolysis of alkanes (iii) Wurtz reaction

(iv) Anti-markownikoff rule (v) Kolbe electrolytic synthesis (vi) Polymerisation initiated by free radical.

Carbonium ions (carbocations)

Carbocation is defined as a group of atoms which contain positively charged carbon having only six electrons. It is obtained by heterolytic fission of a covalent bond involving carbon atom. It is denoted by putting a positive charge (+) against the symbol of group of atoms.

$CH_3^{\oplus}$	$C_2H_5^{\oplus}$	$(CH_3)_2CH^{\oplus}$	$(CH_3)_3C^{\oplus}$
Methyl carbonium ion	Ethyl carbonium ion	Isopropyl carbonium ion	Tert. Butyl carbonium ion
Primary		Secondary	Tertiary

(1) **Characteristics of carbocations**

(i) The formation of carbocations can be done,

(a) By heterolysis of halogen compounds : $(CH_3)_3 - \overset{\curvearrowright}{C} - Cl \longrightarrow (CH_3)_3 \overset{\oplus}{C} + \overset{\ominus}{Cl}$

(b) *By protonation of alkenes or alcohols* : $CH_2 = CH_2 \xrightarrow{H^{\oplus}} \overset{\oplus}{C}H_2 - CH_3$

(ii) ***By decomposition of azides in presence of heat or light.***

$$\underset{\text{Alkylazide}}{R-\ddot{N}=\overset{+}{N}=\ddot{N}:^{-}} \xrightarrow{\Delta \text{ or } h\nu} \underset{\text{Alkylnitrene}}{R-\ddot{N}:} + N \equiv N$$

(iii) Unsubstituted nitrene ($H-\ddot{N}:$) can be obtained by photolysis of (or by passing electric discharge through) NH_3, N_2H_4 or N_3H .

Attacking reagents

Most of the attacking reagents carry either a positive or a negative charge. The positively charged reagents attack the regions of high electron density in the substrate molecule while the negatively charged reagents will attack the regions of low electron density in the substrate molecule. The fission of the substrate molecule to create centres of high or low electron density is influenced by attacking reagents. Most of the attacking reagents can be classified into two main groups.

(1) Electrophiles or electrophilic reagents. (2) Nucleophiles or nucleophilic reagents.

(1) **Electrophiles :** Electron deficient species or electron acceptor is electrophile.

It can be classified into two categories :

(i) Charged electrophiles ($E^{\oplus}$), (ii) Neutral electrophiles (E)

(i) ***Charged electrophiles*** : Positively charged species in which central atom has incomplete octet is charged electrophile.

$$H^{\oplus}, X^{\oplus}, B^{\oplus}, N\begin{matrix}O\\ \diagdown\\ \diagup\\ O\end{matrix}^{\oplus}, N=O, S^{\oplus}O_3H^{\ominus}$$

Note : ❒ All cations are charged electrophiles except cations of IA, IIA group elements, Al^{+++} and $\overset{\oplus}{N}H_4$

(ii) ***Neutral electrophiles*** : It can be classified into three categories,

(a) Neutral covalent compound in which central atom has incomplete octet is neutral electrophile,

$$BeCl_2, BH_3, ZnCl_2, AlX_3, FeX_3, \dot{C}H_3, \ddot{C}H_2, \ddot{C}X_2$$

(b) Neutral covalent compound in which central atom has complete or expended octet and central atom has unfilled –*d*-sub-shell is neutral electrophile,

$$SnCl_4, SiCl_4, PCl_5, SF_6, IF_7$$

(c) Neutral covalent compound in which central atom is bonded only with two or more than two electronegative atoms is neutral electrophile.

$$BeCl_2, BX_3, AlX_3, FeX_3, SnCl_4, PCl_3; \quad PCl_5, \quad NF_3, \quad \ddot{C}X_2, \quad CO_2, SO_3, \quad CS_2,$$

Note : ❒ Cl_2, Br_2 and I_2 also behave as neutral electrophiles.

❒ Electrophiles are Lewis acids.

(2) **Nucleophiles :** Electron rich species or electron donor is nucleophiles. Nucleophiles can be classified into three categories :

(i) ***Charged nucleophiles*** : Negatively charged species are charged nucleophiles.

$$\overset{\ominus}{H}, O\overset{\ominus}{H}, R-\overset{\ominus}{O}, C\overset{\ominus}{H}_3, \overset{\ominus}{X}, S\overset{\ominus}{H}, R-\overset{\ominus}{S}$$

(ii) ***Neutral nucleophiles*** **:** It can be classified into two categories :

(a) Neutral covalent compound, in which central atom has complete octet, has at least one lone pair of electrons and all atoms present on central atom should not be electronegative, is neutral nucleophile.

$$\overset{..}{N}H_3, R-\overset{..}{N}H_2, R_2\overset{..}{N}H, R_3\overset{..}{N}, \overset{..}{N}H_2-\overset{..}{N}H_2$$ (Nitrogen nucleophile)

$$H-\overset{..}{\underset{..}{O}}-H, R-\overset{..}{\underset{..}{O}}-H, R-\overset{..}{\underset{..}{O}}-R$$ (Oxygen nucleophiles)

$$H-\overset{..}{\underset{..}{S}}-H, R-\overset{..}{\underset{..}{S}}-H, R-\overset{..}{\underset{..}{S}}-R$$ (Sulphur nucleophiles)

$$\overset{..}{P}H_3, R\overset{..}{P}H_2, R_2\overset{..}{P}H, R_3\overset{..}{P}$$ (Phosphorus nucleophiles)

(b) Organic compound containing carbon, carbon multiple bond/ bonds behaves as nucleophile.

Alkenes, Alkynes, Benzene $CH_2=CH-CH=CH_2, CH_2=CH-C\equiv CH$

(iii) ***Ambident nucleophiles*** **:** Species having two nucleophilic centres, one is neutral (complete octet and has at least one lone pair of electrons) and other is charged (negative charge) behaves as ambident nucleophile

$$\overset{\ominus}{C}\equiv\overset{..}{N}, \overset{\ominus}{O}-\overset{..}{N}=O, \overset{\ominus}{O}-\underset{\downarrow}{\overset{\uparrow}{\underset{O}{\overset{O}{S}}}}-OH$$

Note : ❒ Organometallic compounds are nucleophiles.

❒ Nucleophiles are Lewis bases.

Organic compounds which behave as electrophile as well as nucleophile : Organic compound in which carbon is bonded with electronegative atom (*O, N,S*) by multiple bond/bonds behaves as electrophile as well as nucleophile :

$$R-\overset{O}{\overset{||}{C}}-H, R-\overset{O}{\overset{||}{C}}-R, R-\overset{O}{\overset{||}{C}}-OH, R-\overset{O}{\overset{||}{C}}-Cl, R-\overset{O}{\overset{||}{C}}-OR, R-\overset{O}{\overset{||}{C}}-NH_2, R-C\equiv N, R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$$

Note : ❒ During the course of chemical reaction electrophile reacts with nucleophile.

❒ Strong Lewis acids stronger is electron phile $CO_2 < \overset{\oplus}{N}O_2 < \overset{\oplus}{S}O_3H$. Stonger is an acid weaker is its conjugated base or weaker is nucleophile.

Examples : $HF > H_2O > NH_3 > CH_4$

TS of slow step	$:\overset{\delta^-}{Nu}---C---:\overset{\delta^-}{L}$	$:Nu---\overset{\delta^+}{C}---\overset{\delta^-}{L}---Nu:$
Reacting nucleophile	The nucleophile attacks the carbon of the substrate exclusively from the back side.	The nucleophile can attack the carbon of the substrate both on the back and front sides although the back side attack predominates.
Stereochemistry	Complete inversion of configuration takes place.	Inversion and retention takes place.
Reactivity order of alkyl halides	Methyl>1°>2°>3°halides. $(I > Br > Cl > F)$	3°>2°>1° > methyl halides. $(I > Br > Cl > F)$
Rearrangement	No rearrange product is form (except for allylic).	Rearrange products can be formed.
Nature of nucleophiles	Favoured by strong and high concentration of nucleophiles.	Favoured by mild and low concentration of nucleosides.
Polarity	Favoured by solvents of low polarity.	Favoured by solvents of high polarity.
Reaction rate determining factor	By steric hindrance.	By electronic factor (stability of $\overset{\oplus}{R}$).
Catalysis	Not catalysed by any catalyst (phase tarnsfer).	Catalysed by Lewis and Bronsted acids, *e.g.*, $\overset{\oplus}{Ag}, AlCl_3, ZnCl_2$ and strong *HA*.

(2) **Electrophilic substitutions reactions :** Electrophilic substitution involves the attack by an electrophile. It is represented as S_E (*S* stands for substitution and *E* stands for elctrophile). If the order of reaction is 1, it is written as S_{E^1} (unimolecular)and if the order is 2, it is S_{E^2} (Bimolecular).

S_E^1 Reaction mechanism : Electrophilic substitution in aliphatic compounds (S_E^1) are very rare; some of the important examples are:

(i) Replacement of the metal atom in an organometallic compound by hydrogen :

$$R-M+\overset{\oplus}{H}\rightarrow R-H+\overset{\oplus}{M}$$

e.g., $CH_3-CH_2-MgBr\xrightarrow{-MgBr}CH_3-\overset{\ominus}{C}H_2\xrightarrow{\overset{\oplus}{H}}CH_3-CH_3$

$$CH_3-CH_2-MgBr+H-Br\rightarrow CH_3-\overset{\ominus}{C}H_2\xrightarrow{\overset{\oplus}{H}}CH_3-CH_3+MgBr_2$$
$$CH_3-CH_2Na+C_6H_6\rightarrow CH_3-CH_3+C_6H_5Na$$

(ii) Decarboxylation of silver salt of carboxylic acid by means of bromine:

$$R_3C-\underset{\underset{O}{||}}{C}-OAg+Br-Br\rightarrow R_3C-\underset{\underset{O}{||}}{C}-\overset{\ominus}{O}+\overset{\delta^+}{Br}-\overset{\delta^-}{Br}+\overset{\oplus}{Ag}$$
$$\rightarrow R_3C-Br+CO_2+AgBr$$

(iii) Isotopic exchange of hydrogen for deuterium or tritium:

$$R-H+\overset{\oplus}{D}\rightleftharpoons R-D+\overset{\oplus}{H}$$

$$R-H+\overset{\oplus}{T}\rightleftharpoons R-T+\overset{\oplus}{H}$$

S_E^2 Reaction mechanism : Electophilic substitution (S_E^2) is very common in benzene nucleus (aromatic compounds) in which π-electrons are highly delocalized and an electrophile can attack this region of high electron density.

In all electorphilic aromatic substitution reactions, it involves:

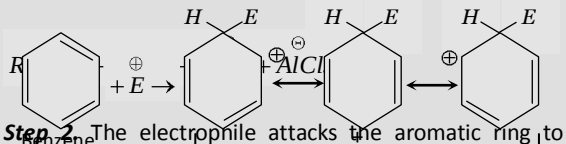
Step 1. The formation of an electrophile, $\overset{\oplus}{E}$, *i.e.,*

In halogenation; $Cl-Cl+FeCl_3\rightarrow\overset{\oplus}{Cl}+Fe\overset{\ominus}{Cl}_4$

In nitration; $HNO_3\,2H_2SO_4\rightarrow\overset{\oplus}{NO}_2+2\,\overset{\ominus}{HSO}_4+\overset{\oplus}{H_3O}$

In sulphonation; $2H_2SO_4\rightarrow SO_3+\overset{\ominus}{HSO}_4+\overset{\oplus}{H_3O}$

In Friedel-crafts reaction; $R-Cl+AlCl_3\rightarrow\overset{\oplus}{R}+\overset{\ominus}{AlCl_4}$



Benzene

Step 2. The electrophile attacks the aromatic ring to form carbonium ion (or arenium ion) which is stabilized by resonance.