CHAPTER

4

Reactive Intermediates

Reactive intermediates are believed to be transient intermediates in majority of reactions. The main types of reactive intermediates of interest to organic chemists are carbocations, carbanions, radicals, radical ions, carbenes, nitrenes, arynes etc.

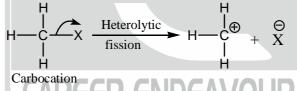
Reactive intermediates are usually short lived, very reactive and very seldom isolated under normal reaction conditions. However, their structures are established either by means of chemical trapping or spectroscopically or sometimes by isolating them at very low temperature.

4.1 Carbocation:

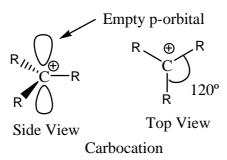
Carbocation has a positively-charged carbon atom which has only six electrons in its outer valence shell.

(A) Structure and stability of carbocations:

The heterolytic fission of a C-X bond in an organic molecule (X is more electronegative than carbon atom) generates the negatively charged anions (X^{-}) and positively charged species known as carbocations



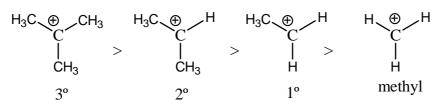
The carbon atom in a typical carbocation is sp^2 hybridized. The p_z , orbital is empty and is perpendicular to the plane of the other three bonds. Thus carbocation adopts a *trigonal planar* shape.



Planar structure of carbocation is more stable than pyramidal structure.

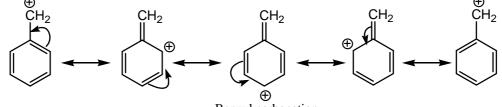
The stability of the carbocation increases when electron donating groups are present. The reason for the order of alkyl carbocation stability was simply as inductive stabilization of the positively charged carbon by its attached electron-releasing alkyl substituents and by hyperconjugation ("no-bond resonance"). This explains why a tertiary carbocation is more stable than a secondary carbocation which in turn is more stable than a primary carbocation.





However, the presence of electron attracting groups (like nitro, carbonyl etc.) adjacent to the carbon atom bearing positive charge makes the carbocation less stable.

Resonance effects can further stabilize carbocations. By resonance the positive charge on the central carbon atom gets dispersed over other carbon atoms and this renders stability to the carbocation. The more the canonical structures for a carbocation, the more stability will be.



Benzyl carbocation

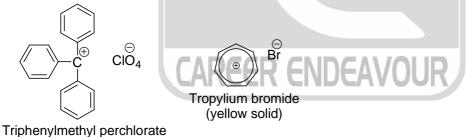
An allylic carbocation has two resonance structure.

$$H_2C \xrightarrow{\oplus} CH \xrightarrow{\oplus} CH_2 \xrightarrow{\oplus} H_2C \xrightarrow{\oplus} CH_2$$

The order of stability of the benzyl, allyl and iso-propyl carbocations is:

$$C_6H_5 \xrightarrow{\oplus} CH_2 > H_2C = CH \xrightarrow{\oplus} CH_2 > H_3C \xrightarrow{H_3} H_3C \xrightarrow{H_3}$$

In certain cases, the carbocations are so stable that their solid salts have been isolated. For example the tropylium bromide is stabilized by aromatization. The tropylium cation is planar and has 6 p electrons like benzene.



(real crystalline solid)

The order of stability of tropylium, triphenylmethyl, benzyl and allyl carbocations is:

Tropylium cation	>	(C ₆ H ₅) ₃ C	>	$C_6H_5CH_2$	>	$ H_2C=CH-CH_2 $
		Triphenyl methyl carbocation		Benzyl carbocation		Allyl carbocation

The carbocation stability order of alkyl $(1^{\circ}, 2^{\circ} \& 3^{\circ})$, allyl and benzyl carbocations.

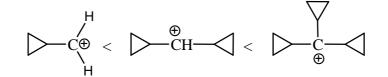
$$\mathsf{CH}_{3}^{\oplus} < \mathsf{CH}_{3}\mathsf{CH}_{2}^{\oplus} < (\mathsf{CH}_{3})_{2}\mathsf{CH}^{\oplus} = \mathsf{H}_{2}\mathsf{C} = \mathsf{CH} - \mathsf{CH}_{2} < \mathsf{C}_{6}\mathsf{H}_{5}\mathsf{CH}_{2}^{\oplus} < (\mathsf{CH}_{3})_{3}\mathsf{C}^{\oplus}$$

The carbocation stability is also increased due to the presence of heteroatom having an unshared pair of electrons, e.g. oxygen, nitrogen or halogen, adjacent to the cationic center. Such carbocations are stabilized by resonance. The methoxymethyl cation is obtained as a stable solid, $MeOCH_2^+SbF_4^-$.



$$R \xrightarrow{R}_{C} \xrightarrow{i}_{O} \xrightarrow{Me} \xrightarrow{R}_{R} \xrightarrow{R}_{C} \xrightarrow{i}_{O} \xrightarrow{Me}$$

The stability of the cyclopropyl carbocation increases with each additional cyclopropyl group.



(B) Generation of carbocation:

(1) From alcohols :

Alcohols on treatment with concentrated acids get protonated and then may lose a molecule of water to form carbocations.

$$\mathsf{R} \longrightarrow \mathsf{OH} + \mathsf{H} \stackrel{\textcircled{\oplus}}{\longrightarrow} \mathsf{R} \xrightarrow{\textcircled{\oplus}} \mathsf{OH}_2 \xrightarrow{-\mathsf{H}_2\mathsf{O}} \mathsf{R} \stackrel{\textcircled{\oplus}}{\longrightarrow} \mathsf{R} \stackrel{\textcircled{\oplus}}{\longrightarrow} \mathsf{R}$$

(2) From alkyl halides :

Ionization of alkyl halides give carbocations.

$$R \xrightarrow{X} \xrightarrow{\text{Solvent}} R^{\oplus} + X^{\ominus} \quad (X=I, Br, CI)$$

$$R-X + \text{AlCl}_3 \xrightarrow{} \left[\begin{matrix} \delta^+ & \delta^- \\ R^-X - \text{AlCl}_3 \end{matrix} \right] \xrightarrow{\oplus} R + \left[\begin{matrix} X-\text{AlCl}_3 \end{matrix} \right]^{\ominus}$$

(3) From alkenes:

Addition of proton to alkenes or other unsaturated species give carbocations.

$$(CH_3)_2C = CH_2 + H \longrightarrow (CH_3)_2C - CH_2H \xrightarrow{\bigcirc} (CH_3)_3CBr$$

$$3^{\circ} Carbocation t-butyl bromide$$
m diazonium ions:

(4) From diazonium ions:

The alkyl diazonium ions are unstable and decompose at room temperature to give carbocations.

$$R \xrightarrow{\bigoplus} N \xrightarrow{\bigoplus} R^{\bigoplus} + N_2$$

(5) From acyl halides: The acyl halides on treatment with anhydrous aluminium chloride gives a complex, which decomposes to give acyl carbocations. In most Friedel-Crafts acylation, the electrophile appears to be an acylium ion.

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$$R - COCI + AICI_{3} \rightleftharpoons \left[R COCH - AICI_{3} \right] \rightleftharpoons \left[R - C = \stackrel{\oplus}{\underset{i}{\bigcirc}} \longrightarrow R - C = \stackrel{\oplus}{\underset{i}{\bigcirc}} \right] + AICI_{4}^{\ominus}$$

An acylium ion

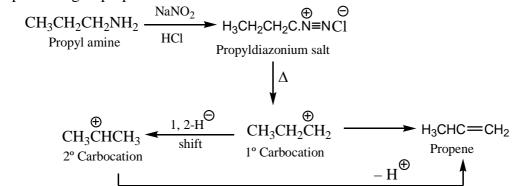
(C) Reactions of carbocation:

Carbocation usually undergoes elimination reactions, addition reactions, reactions with nucleophiles and rearrangements.

1. Elimination of a proton: A carbocation may loose a proton to form an alkene. For example, 1-propyl carbocation generated from diazonium salt may eliminate a hydrogen ion to form an alkene (propene).



Alternatively, 1-propyl carbocation may rearrange to more stable secondary carbocation, which may also loose a proton to give propene.



2. Reaction with nucleophile:

A carbocation may combine with a nucleophile to form a new bond.

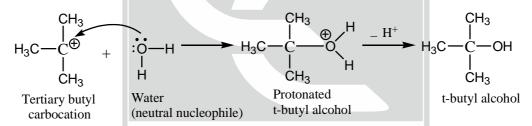
$$CH_{3}-CH=CH_{2} + HCI \xrightarrow{slow} H_{3}C-CH-CH_{3} + CI$$

$$H_{3}C-CH-CH_{3} + CI \xrightarrow{c_{1}} H_{3}C-CH-CH_{3} + CI$$

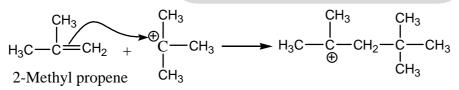
$$H_{3}C-CH-CH_{3} + CI \xrightarrow{c_{1}} H_{3}C-CH-CH_{3}$$

$$Isopropyl carbocation$$

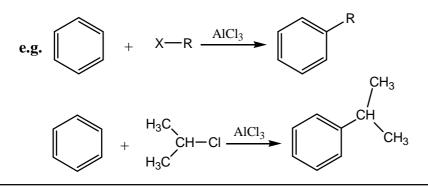
The reaction of a carbocation with a neutral nucleophile such as water gives a protonated alcohol. For example, Tertiary butyl carbocation reacts with water (neutral nucleophile) to give protonated *t*-butyl alcohol, which eliminates a proton to give *t*-butyl alcohol.



3. Reaction with alkenes and aromatic systems: A carbocation may react with an alkene to produce another carbocation.

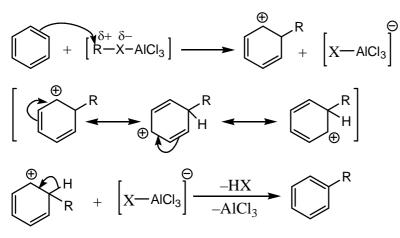


The alkyl carbocation formed from alkene, alcohols or alkyl halides and act as an electrophile in an Friedel-Crafts alkylation reaction.

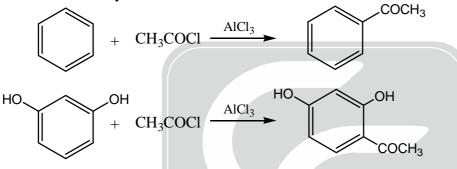




Mechanism:

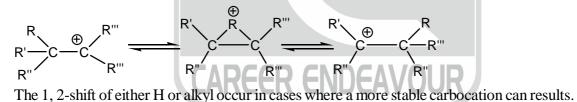


In a similar manner $(R-C \equiv \overset{\oplus}{O})$ acyl carbocations formed from acyl halides or acid anhydrides act as electrophile in Friedel Crafts acylation.



4. Rearrangement of carbocation:

Molecular rearrangements involving carbocations as reactive intermediates are very common in organic chemistry. The 1, 2-shift of a migrants, to an electron-deficient carbon atom is the most widespread.

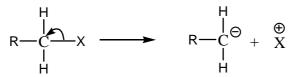


4.2 Carbanion:

A carbanion can be considered as a species containing a trivalent negatively charged carbon.

(A) Structure and stability of carbanion:

Carbanion are considered to be derived by the heterolytic fission of the C-X bond in an organic molecule, in which carbon is more electronegative than X.



(C is more electronegative than X) Carbanion

The shape of simple carbanions is determined on the basis of a number of experiments is found to be pyramidal, similar to that of amines. These species invert rapidly at room temperature, passing through a higher energy planar form in which the electron pair occupies a *p*-orbital.

