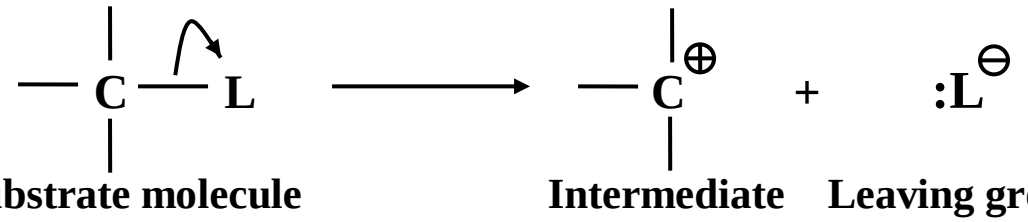
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Leaving Groups

An atom or a group which separates out from the substrate molecule as stable species during a reaction is called a **leaving group**. For example,



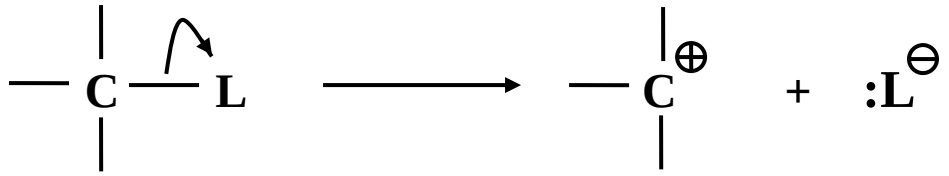
Leaving groups are usually anions (*e.g.* Cl^-, Br^-, I^- etc.) or neutral molecules (*e.g.* H_2O, NH_3 etc.). However, for some times, they may also be cations e.g. H^+ ion released during nitration of benzene.

Leaving group ability

The ease to which a leaving group departs from the substrate molecule is called its leaving group ability.

Such leaving groups which depart more easily are considered to be the good leaving groups, while those who depart with difficulty are considered to be the bad leaving groups . In fact, leaving group ability of a group or ion depends upon its stability. The greater the stability of a leaving group more easier is its departure and therefore, more is its leaving group ability i.e. better is the leaving group.

Let us consider, loss of leaving group in SN^1 reactions-



Here, the greater the stability of a leaving group LG^-, more easier is its leaving and therefore, better is its leaving group ability. Thus, the factors stabilizing a group, increase the leaving group ability of respective group.

Furthermore, in this reaction, leaving group separates as anion by taking away the bonded pair of electrons i.e. as a Lewis base. Here, if the Lewis base is weak, its tendency to take electron pair is more and therefore, it is a better leaving group.

In general, a better leaving group is the conjugated base of a strong acid i.e. it is a weak Bronsted base.

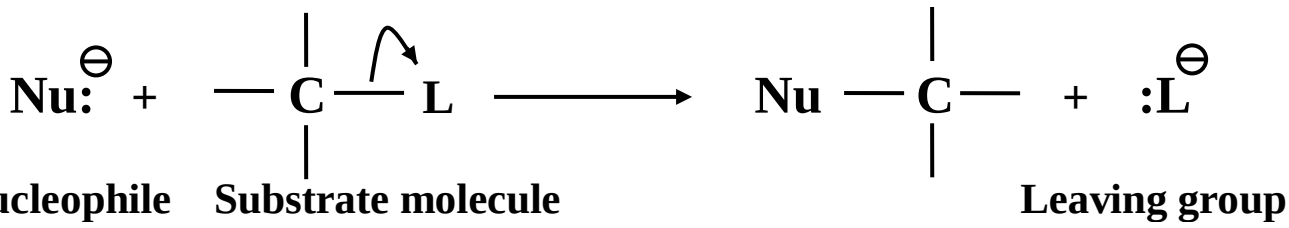
Some common leaving groups along with their category are listed here-

Category	Examples
Excellent	TsO^-, NH_3
Very Good	I^-, H_2O
Good	Br^-
Fair	Cl^-
Poor	F^-
Very Poor	HO^-, NH_2^-, RO^-

Here, HO^- is a poor leaving group because it is the conjugate base of water (H_2O) which is a weak Bronsted acid. On the other hand, H_2O is a better leaving group, because it is the conjugate base of H_3O^+, which is a strong Bronsted acid.

Let us consider, loss of leaving group in SN^2 reactions-

Here, the reactions are more likely to occur when a better leaving group is displaced.



Here, the greater the stability of leaving group, more is the reactivity of substrate molecule.

Leaving group ability of a leaving group is decided by its basic strength. Weak bases are good leaving groups. The stronger the acid, weaker is its conjugate base and therefore, more is its leaving group ability.

The ability of the leaving groups to leave increases with the increase of electronegativity of directly bonded atom. On moving left to right in a period of the periodic table, electronegativity of atoms increases, so that, basicity of respective atom or group decreases. Thus, the ability of the leaving group to leave increases. In fact, an increase in electronegativity of a species increases its tendency to hold the electrons rather than to donate them. Thus, the relative order of leaving group ability of $-CH_3$, $-NH_2$, -OH and -F will be as under-

$-CH_3$ < $-NH_2$ < -OH < -F

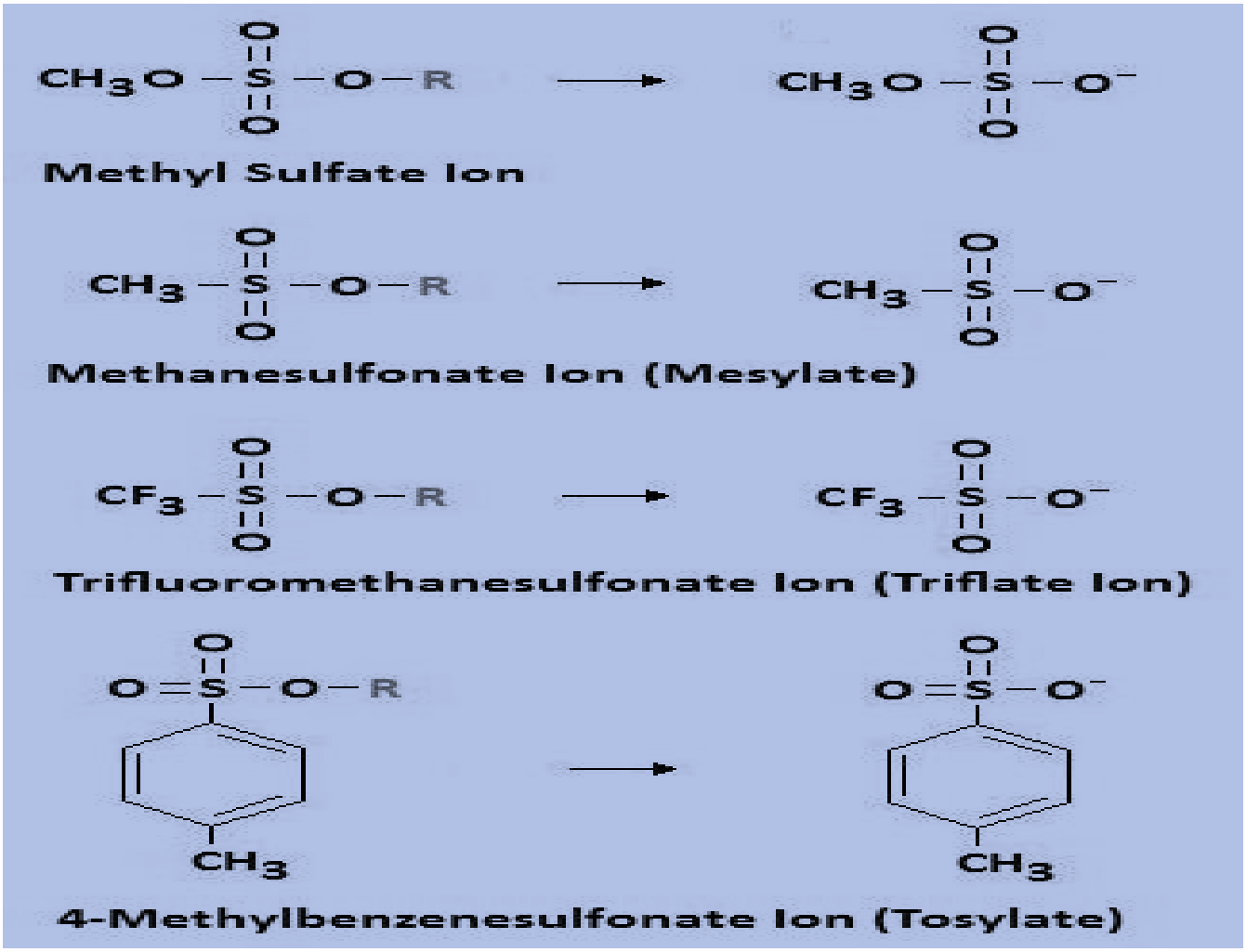
Worst **Best**

Here, CH_3^- should be the worst leaving group and F^- should be the best leaving group. However, in practice all these groups are not good leaving groups at all. For example, fluoride is such a poor leaving group that S_N2 reactions of fluoroalkanes are rarely observed.

The ability of the leaving groups to leave increases with the increase of atmic size. On moving down the group in periodic table, atomic size increases and therefore, basicity decreases and the ability of the leaving group to leave increases. Thus, the relative order of leaving group ability of halogens will be as under-

F	<	**Cl**	<	**Br**	<	**I**
Worst		**Fair**		**Good**		**Excellent**

Resonance stabilization Increases the Ability of the Leaving Groups to Leave. In fact, resonance stabilized structures are weak bases and therefore, they are considered to be the excellent leaving groups. For example, sulphur derivatives of the type $ROSO_3^-$ and RSO_3^- are the excellent leaving groups due to their resonance stabilization.



K_a or pKa values of different acids is a useful tool for deciding the relative leaving group ability of their conjugate base.

If pKa value of an acid is lesser, then it is stronger acid and its respective conjugate base is weaker base i.e. better leaving group. This correlation is very good but not perfect because of some exceptions.