

# CHAPTER 3

## Reaction Mechanism: Structure and Reactivity

### ❖ Types of Mechanisms

Although the number of mechanisms by which different organic reactions proceed is very large, certain patterns can still be used to profile them for more systematic and simplistic analysis. Now before we classify different types of organic reaction mechanisms in brief, it is better to recall the basic terminology involved first.

**1. Substrate and reagent:** A typical organic reaction is thought to proceed via the breaking or making of one or more covalent bonds, and it is very suitable to call one reactant “substrate” and the other as “reagent”. Generally, more reactive species is labeled as the reagent whereas the less reactive species is considered as the substrate.

**2. Molecularity:** The molecularity of a chemical reaction may simply be defined as the number of colliding molecular species involved in a single step. The most common types are unimolecular and bimolecular reactions that involve one and two molecular entities, respectively.

**3. Electrophiles and nucleophiles:** An electrophile is an electron-loving species or electron pair acceptor. Generally, the electrophiles are positively charged or neutral entities with vacant orbitals that are attracted to an electron-rich center. The electrophiles participate in the chemical reactions by accepting an electron pair to form a bond with the nucleophilic reactant. Now since the electrophiles accept electrons, they are seen as Lewis acids. A nucleophile is a nucleus (i.e. positive center) loving species or electron-pair donor. Normally, the nucleophiles are negatively charged or neutral electron-rich entities with lone pairs of electrons that are attracted to an electron-deficient center. The nucleophiles participate in the chemical reactions by donating an electron pair to form a bond with the electrophilic reactant. Now since the nucleophiles donate electrons, they are seen as Lewis bases.

**4. Leaving Group:** The part of the substrate molecule that gets detached is typically called as the leaving group. The leaving groups with electron-pair and without electron pairs are labeled as nucleofuges and electrofuges, respectively.

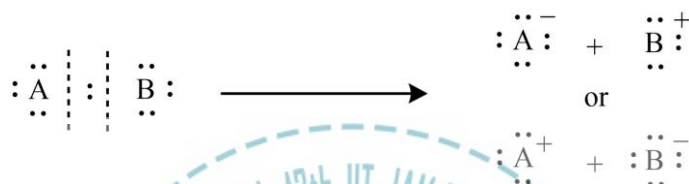
**5. Reaction intermediates:** The chemical species that are formed somewhere during the course of a chemical reaction are called as reaction intermediates. These are actual molecules that are short-lived and unstable. Sometimes they are called temporary reactants or products because they are neither present in actual reactants nor the actual products.

**6. Transition states:** The transition state of an organic reaction is a specific configuration along the reaction coordinate and corresponds to the highest potential energy along with this reaction coordinate. Unlike “reaction intermediate”, the transition state is not an actual molecule that can be isolated, and therefore it is often marked with the double dagger ‡ symbol to differentiate.

Now depending upon the bonds-breaking, the reaction mechanism of organic compounds can be divided basically into three basic types as given below.

➤ **1. Polar Mechanism (Bond Heterolysis)**

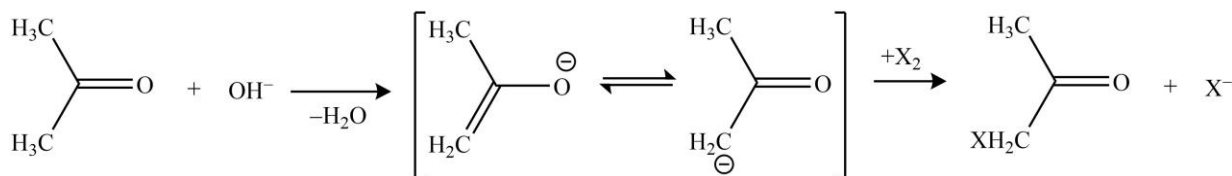
Polar or ionic or bond-heterolysis mechanisms have the characteristic feature of the electron-pair migrating from a well-defined source (such as lone pair or a nucleophilic bond) to a well-defined sink (some electrophilic center having low-lying antibonding molecular orbitals). This mechanism results from the heterolytic or unsymmetrical breaking of the covalent bond in which the bonding pair goes with one of the fragments.



The participating atoms in this type of mechanism undergo a change in their charges (formally as well as in reality). Most of the organic reactions fall into this category. For instance, the hydrolytic cleavage of tert-butyl bromide generates a carbocation and bromide ion.



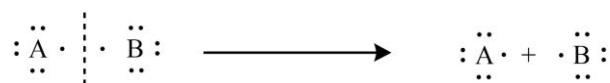
Similarly, the acetone's reaction with halogen in the presence of base occurs through the formation of carbonian.



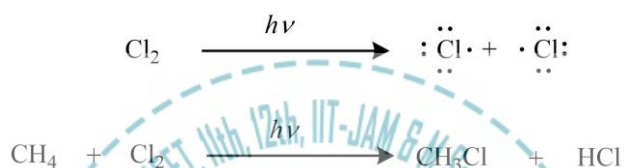
In an ionic mechanism, it's the electronegativity of the binding atom that primarily determines the fragment with bonding pair of electrons. The bond pair goes with the more electronegative atom and generates the anion. Now owing to the very small value of carbon's electronegativity, the heterolytic cleavage gives rise to carbocation most of the time; and therefore, carbocations are much more common than the carbanions.

➤ **2. Radical Mechanism (Bond Homolysis)**

Radical or bond-homolysis mechanisms have the characteristic feature of generating species with unpaired electrons (radicals) and the migration of single electrons. Furthermore, the radical reactions can also be divided into chain and nonchain processes. This mechanism results from the homolytic or symmetrical breaking of the covalent bond in which the bonding pair is distributed equally to the fragments.



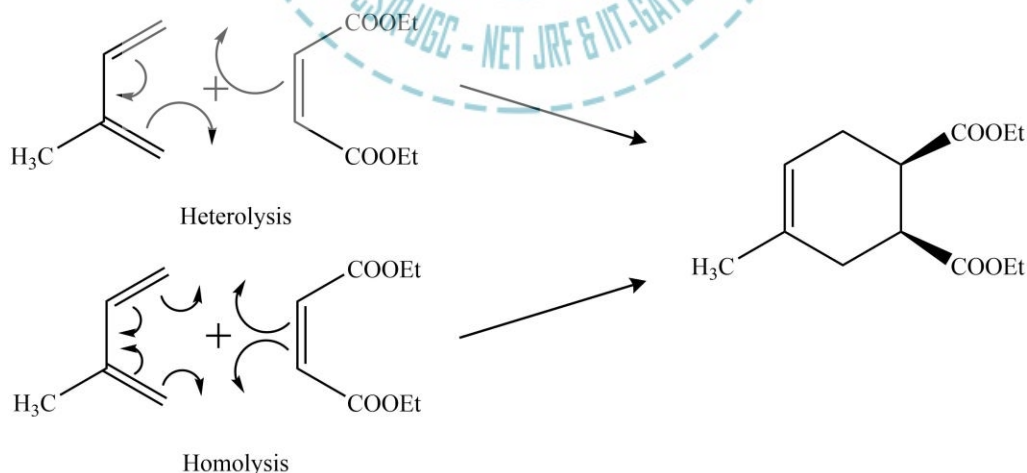
For instance, consider the photochlorination of methane in which the first step is the homolytic bond breaking of  $\text{Cl}_2$  i.e.



Both Cl atoms generated carry one unpaired electron each and are neutral. The chlorine atoms produced this way are called free radicals and are extremely reactive due to the availability of unpaired electrons.

➤ **3. Pericyclic Mechanism**

Pericyclic reactions involve a concerted cyclic shift of electrons to yield new chemical bonds via a ring transition state. Though the electron pairs are involved formally, no true source or sink can be assigned due to the cyclic movement. These reactions need a continuous overlap of participating orbitals and are dictated by orbital symmetry considerations; so, it is impossible to label them as homolytic or heterolytic cleavage.



In these reactions, bond breaking and bond making takes place simultaneously and these are said to occur via a concerted route.

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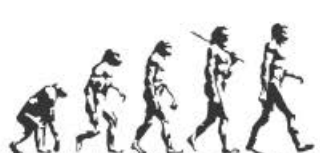
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**Volume I**

**MANDEEP DALAL**



*First Edition*

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