

Organic Reaction Mechanisms – Review

1. Breaking a Covalent Bond

Consider the breaking of the covalent bond between the carbon atoms – it can be broken in two ways...

1) Homolytic fission

The bond is broken so that, of the two electrons in the bond, one goes to each of the carbon atom:

The resulting species are *free radicals* and they each contain a single unpaired electron. Free radicals are extremely short-lived and readily undergo further reaction. This type of bond breaking usually occurs in the gas phase and in non-polar solvents, especially in uv light.

2) Heterolytic fission

The bond is broken so that one carbon atom receives both electrons, while the other receives none:

The positively charged ion is called a carbocation (*carbonium ion*) and the positively charged carbon atom is liable to attack by a negatively charged species, which is called a *nucleophile*. (Remember nucleophile and negative both begin with the letter 'n').

The negatively charged ion is called the *carbanion* and this is liable to attack by a positively charged species called an *electrophile*. This kind of species is likely to exist in solution in polar solvents.

Although free radicals, carbocations, and carbanions may exist for the shortest possible period of time, they have a particular importance in controlling how a reaction takes place.

1. Stability of Carbocation Ions

There are four possible carbocations with a formula $C_4H_9^{+1}$. They are...

There are two primary carbocations, a secondary carbocation and a tertiary carbocation. In general $3^0 C^{+1}$ are more stable than $2^0 C^{+1}$, which are, in turn, more stable than $1^0 C^{+1}$. It is possible for rearrangement of C^{+1} to take place. Carbocation ions can eliminate a H^{+1} ion and produce an alkene...

2. Free Radical Chain Reactions

A most commonly quoted free radical chain reaction is the reaction between methane and chlorine, in the presence of uv light. The light energy breaks a few Cl – Cl bonds to produce chlorine free radicals – **Initiation**.

The following step then takes place – **Propagation**

The following reactions also take place, but they do not promote further reaction – **Termination**

The mechanism explains why, in practice, small amounts of ethane are detected in the products. The reactions between H_2 and Cl_2 and $C_6H_5CH_3$ (methylbenzene, toluene) and Cl_2 have similar mechanisms.

3. Addition Reactions

Addition reactions can take place between carbon-carbon double bonds in alkenes or in carbon-oxygen double bonds in alkanals and alkanones.

i) Addition to alkenes – electrophilic addition

The $C = C$ as in ethene can be represented as...

The double bond between the two C-atoms consists of a σ -bond and a π -bond formed by the overlap of p-orbitals on the two C-atoms. There is a concentration of negative charge between the two C-atoms making it susceptible to attack by electrophiles (positive species). Consider the addition of HBr to C_2H_4 ...

The reaction between Br_2 and C_2H_4 has a similar mechanism...

The addition reaction between propene and HBr can, in theory, lead to two products...

This can occur because the groups attached to the two C-atoms, joined by the double bond, are different. The alkene is not symmetrical. In practice, addition produces 2-bromopropane only according to **Markownikoff's rule**:

During addition reactions the more negative part of the molecule adds on to the alkene adds to the carbon atom attached to the lesser number of hydrogen atoms.

Markownikoff's rule can be explained in terms of the stability of carbocation ions. Depending upon which carbon atom the H^+ of the HBr attaches to, there are two possible carbocation ions, which can be formed...

The secondary carbocation ion is more stable than the primary carbocation ion. It is therefore formed in preference to the primary carbocation ion and leads to the formation of 2-bromopropane.

ii) addition to alkanals (aldehydes) and alkanones (ketones) – nucleophilic addition

The carbon - oxygen double bond has a permanent shift of electrons because oxygen is more electronegative than carbon. As a result, there is a slight positive charge on the carbon and a slight negative charge on the oxygen...

The carbon atom is then prone to attack by a nucleophile, e.g. CN^- ...

Protonation of the oxygen in the intermediate then occurs to form the product...

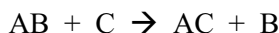
The slow reaction or lack of certain ketones with a nucleophile can be explained by the +ve inductive effect of the alkyls attached (\therefore less +ve charge on the C-atom), and by steric hindrance of the alkyl groups, there is insufficient space available for the large nucleophile to penetrate and attack the +vely charged C-atom!

Condensation reaction (addition followed by elimination) involve attack by a molecule containing a nitrogen atom, e.g. hydrazine (NH_2-NH_2), phenylhydrazine:

This nitrogen has a lone pair of electrons...

4. Substitution Reaction

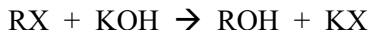
A substitution reaction is a reaction where an atom or group of atoms replaces an atom or group of atoms already in the molecule.



Both nucleophilic substitution and electrophilic substitution reaction may occur.

i) Nucleophilic substitution reactions

The hydrolysis of haloalkanes by refluxing with aqueous alkali is a nucleophilic substitution reaction.



The carbon atom attached to the halogen atom is attacked by the nucleophile, OH^{-1} ...

The rate of hydrolysis of iodoalkanes is greater than the rate of hydrolysis of bromoalkanes which in turn, is greater than the rate of hydrolysis of chloroalkanes. The rate of hydrolysis is related to the strength of the C-X bond. The stronger the bond between the C-X, the slower the reaction.

Nucleophilic substitution reactions occur more readily with tertiary haloalkanes than secondary, and more readily with secondary than with primary. This can be explained by the intermediate – carbocation ion formed.

The reaction of a haloalkane with aqueous OH^{-1} can occur in two ways...

$\text{S}_{\text{N}}1$ mechanism

This is a two-stage process that first involves the loss of X^{-1} ion and the formation of a carbocation (*slow – rate determining step, independent of the concentration of OH^{-1}*). The carbocation reacts rapidly (fast with the OH^{-1} ion...

The total order of the reaction is one: $\text{Rate} \propto [\text{R-X}]$

$\text{S}_{\text{N}}2$ mechanism

This is a one-stage process involving a simultaneous loss of X^{-1} and a gain of OH^{-1} ion. The rate of the reaction is dependent on both $[\text{R-X}]$ and $[\text{OH}^{-1}]$.

The total order of the reaction is two: $\text{Rate} \propto [\text{R-X}] [\text{OH}^{-1}]$

Elimination reactions are also possible when haloalkanes are refluxed with hot, conc. Alkali (OH^{-1}) dissolved in ethanol (the second stage of elimination involves the abstraction of a proton by the base of OH^{-1}).

There is always competition between substitution and elimination reactions, (dil. aq. Alkali \rightarrow substitution favored).

ii) Electrophilic substitution reaction

Common examples of electrophilic substitution are found with benzene and similar aromatic compounds. The common examples are nitration, sulphonation, halogenation and Friedel-Crafts reactions.

Benzene has a ring of negative charge above and below the ring. The following sequence takes place, using X^{+1} to represent an electrophile...

In the first stage a weak complex is formed between the negative ring on the benzene and the electrophile. This then breaks down with the loss of H^{+1} to form the product. By doing this the stability of the C_6H_6 nucleus is restored. Common electrophilic reactions of benzene are...

- A) nitration
- B) sulphonation
- C) halogenation
- D) Friedel – Crafts reaction

5. Introducing a Second Substituent into a Benzene ring

The rate at which a second substituent can be introduced into a C_6H_6 ring and the position of the second substituent, relative to the first, is determined by the substituent already present in the ring.

Common substituents in order of electron donating or withdrawing power

Electron donating	- OH		
decreasing	- NH ₂		
power	- OCH ₃	↓	Decreasing rate of reaction
↓	- CH ₃	↓	
Electron withdrawing	- Cl	↓	
↓	- CHO		
	- SO ₃ H	↓	
	- NO ₂		

Directive effects of some common substituents	
Meta directing	Ortho- para directing
- NO ₂	- CH ₃
- COOH	- OCH ₃
- CHO	- Cl
- CN	- NH ₂
- SO ₃ H	- OH

i) Rate of substitution

Since the substitution reactions in C_6H_6 are electrophilic, if the substituent already present donates electrons to the ring, the rate of reaction will be increased.

The common substituents in order of power of electron donating or withdrawing from a benzene ring are listed in the Table: Common Substituents in Order of Electron Donating or Withdrawing. Phenol undergoes electrophilic substitution reactions more easily than benzene, e.g. with Br_2 ...

ii) Position of substitution

The position of the second substituent is determined by the nature of the substituent already present. There are three possible isomers...

In practice, when carrying out electrophilic substitution with a monosubstituted benzene, either the meta (1, 3-) product is obtained or some mixture of the ortho (1, 2-) and para (1, 4-) is formed. See the Table: Directive Effects of Some Common Substituents.