Topic 10: Organic chemistry

Reactions in organic chemistry

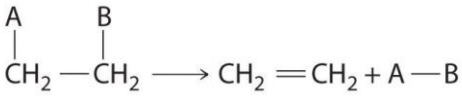
Substitution reaction

A substitution reaction is that which involves the direct replacement of an atom or a group of atoms in an organic molecule by another atom or group of atoms without any change in the remaining part of the molecule.

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

Elimination Reactions

Some reactions involve the removal, or "elimination," of adjacent atoms from a molecule. This results in the formation of a multiple bond and the release of a small molecule, so they are called elimination reactions.



Addition Reactions

A reaction in which the components of a species A–B are added to adjacent atoms across a carbon–carbon multiple bond is called an addition reaction.

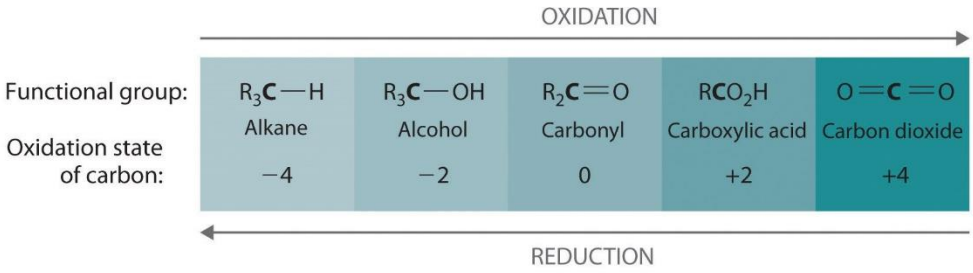
$$HCl + CH_2{=}CH_2 \rightarrow CH_3CH_2Cl$$

Oxidation–Reduction Reactions

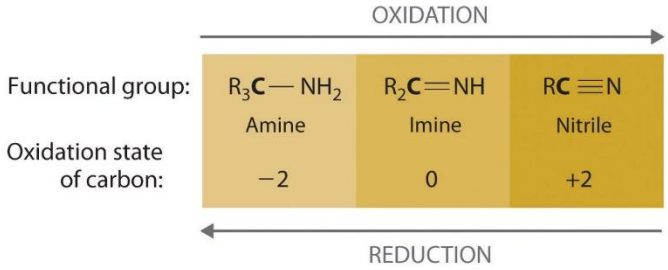
Oxidation–reduction reactions, which are common in organic chemistry, can often be identified by changes in the number of oxygen atoms at a particular position in the hydrocarbon skeleton or in the number of bonds between carbon and oxygen at that position. An increase in either corresponds to an oxidation, whereas a decrease corresponds to a reduction.

$$C_2H_5OH + 2[O] \rightarrow CH_3COOH + H_2O$$

$$CH_3COCH_3 + 2[H] \rightarrow CH_3CHOHCH_3$$



(a) Oxygen-containing organic compounds



(b) Nitrogen-containing organic compounds

Hydrolysis reactions

Hydrolysis is a chemical reaction in which water is used to break down the bonds of a particular substance. In this reaction OH group of water replaces an atom or group in the organic compound.

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

$$RCO—OR' + H_2O \rightarrow RCO—OH + R'—OH$$

Polymerization

Polymerization, any process in which relatively small molecules, called monomers, combine chemically to produce a very large chainlike or network molecule, called a polymer.

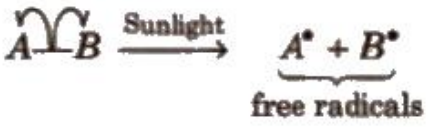
$$_nCH_2 = CH_2 \rightarrow -[-CH_2 --- CH_2-]-_n$$

Reaction mechanism

Fission of a Covalent Bond

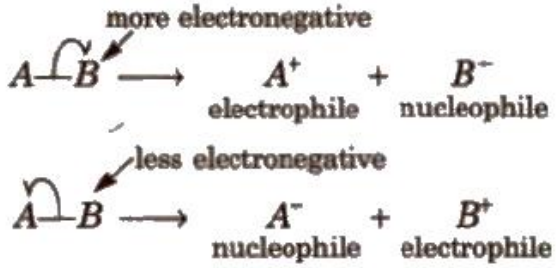
Homolytic Fission

In this, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. The neutral chemical species thus formed, is called free radical. Generally, homolytic fission takes place in non-polar, covalent molecules in the presence of sunlight or high temperature.



Heterolytic Fission

In this, the bond breaks in such a fashion that the shared pair of electrons goes with one of the fragments.



Electrophile:

An electron deficient atom, ion or molecule that has an affinity for an electron pair, and will bond to a base or nucleophile.

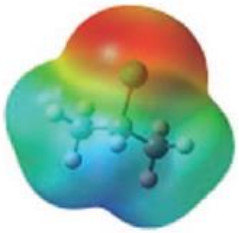
Nucleophile:

An atom, ion or molecule that has an electron pair that may be donated in forming a covalent bond to an electrophile (or Lewis acid).

Halogenoalkanes ($C_nH_{2n+1}X$)

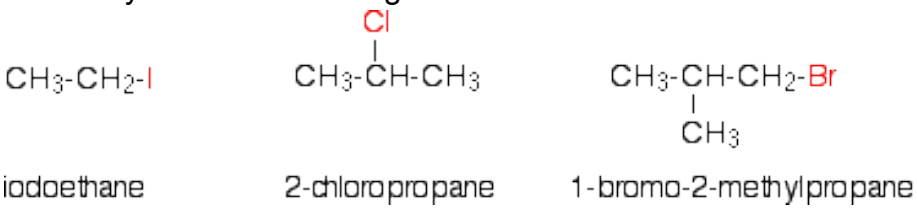
Halogenoalkanes (also known as alkyl halides) are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms. The generic formula for an alkyl halide is

where X _ fluorine, chlorine, bromine, or iodine.



2-Chloropropane

The IUPAC system uses the name of the parent alkane with a prefix indicating the halogen substituents, preceded by number indicating the substituent's location.



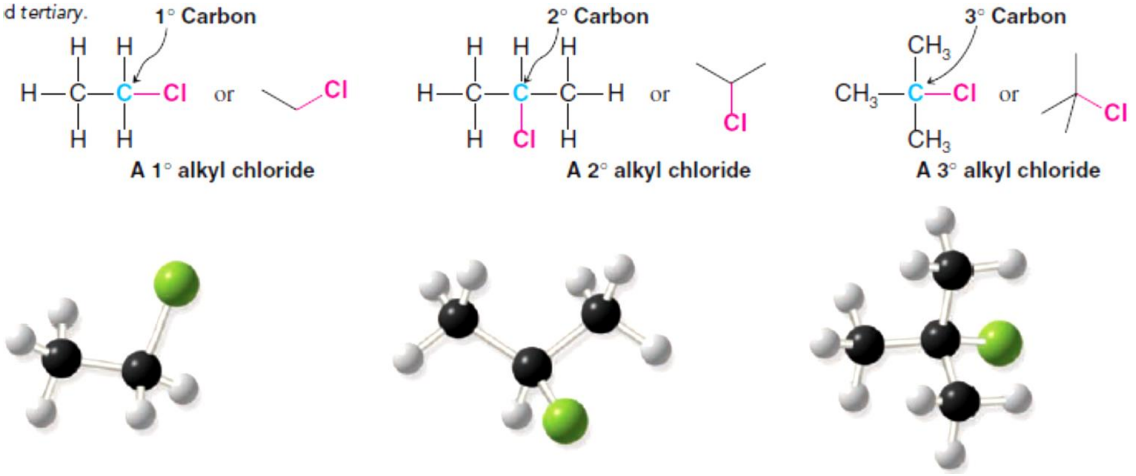
Haloalkanes in Nature

A large number of halogen-containing compounds have been found in nature and many of these are utilized in medicine and technology, for example:

- Ethyl chloride (chloroethane), used as a skin coolant in tropical areas
- Halothan (2-bromo-2-chloro-1,1,1-trifluoroethane), applied today as an anaesthetic - similarly to chloroform which was used previously
- Bromotrifluoromethane is a favorite fire-extinguishing agent which is used in airplanes and for electrical components

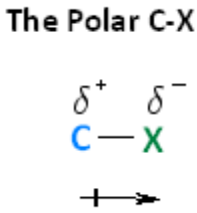
Classification of halogenoalkanes

Depending on the degree of substitution at the carbon atom carrying the halogen, alkyl halides are classified into primary, secondary and tertiary alkyl halides.

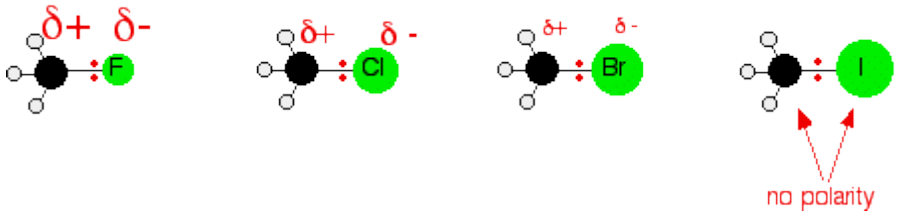


Reactivity of halogenoalkanes

Halogens (F, Cl and Br) are more electronegative than carbon. Consequently, carbon atoms that carry halogens are charged partially positive while the halogen is charged partially negative. The polarity of the C-X bond causes a measureable dipole moment. As a result of the partial positive charge, the carbon atom displays an electrophilic character. The chemical behavior of alkyl halides is determined mainly by the electrophilicity of the carbon.



The following image shows the relationship between the halogens and electronegativity, as we move up the periodic table from iodine to fluorine, electronegativity increases.



The image shows the relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result,

we also see an increase in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.

Bond length	C-F	<	C-Cl	<	C-Br	< C-I
Bond strength	C-I	<	C-Br	<	C-Cl	< C-F
Molecular size	F	<	Cl	<	Br	< I

One of the important set of reactions of halogenoalkanes involves replacing the halogen by something else - ***substitution reactions***. These reactions involve either:

- The carbon-halogen bond breaking to give positive and negative ions. The ion with the positively charged carbon atom then reacts with something either fully or slightly negatively charged.
- Something either fully or negatively charged attracted to the slightly positive carbon atom and pushing off the halogen atom.

Nucleophilic substitution of reactions

1. Hydrolysis reaction of halogenoalkane

When halogenoalkane react with water, alcohol and acid are the products the reaction is carried out under reflux. Oxygen of water contains partial negative charge which attracts to the partially positive charge of carbon atom in the halogenoalkane.

$$RX + H_2O \rightarrow ROH + HX$$

Similar reactions occur with other halogenoalkanes, but the reaction rates differ. The rate of hydrolysis can be investigated by using aqueous silver nitrate solution. The water in the silver nitrate solution acts as the nucleophile, and again an alcohol is formed.

Various precipitates may be formed from the reaction between the silver and halide ions:

$$Ag^+_{(aq)} + Hal^-_{(aq)} \longrightarrow AgHal_{(s)}$$

Fluoroalkanes	least reactive
Chloroalkanes	↓
Bromoalkanes	↓
Iodoalkanes	most reactive

The C– I bond is the weakest, so it is broken most easily

2. Substitution with ammonia, NH_3

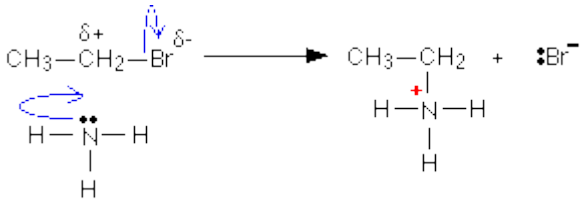
The halogenoalkane is heated with a concentrated solution of ammonia in ethanol. The reaction is carried out in a sealed tube.

$$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$$

Bromoethane ethylamine

If the ammonia is not in excess, we get a mixture of amine products. This is because the primary amine product will act as a nucleophile itself and will attack halogenoalkane molecules, forming secondary amines, and so on.

The reaction happens in two stages. In the first stage, a salt is formed



In the second step of the reaction an ammonia molecule may remove one of the hydrogens on the -NH3+. An ammonium ion is formed, together with a primary amine

3. Substitution with cyanide ions

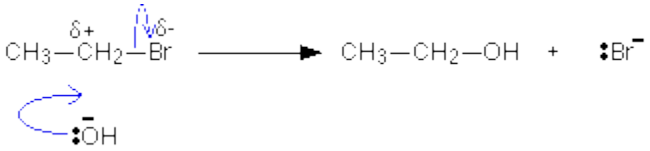
If a halogenoalkane is heated under reflux with a solution of sodium or potassium cyanide in ethanol, the halogen is replaced by a -CN group and a nitrile is produced.

$$CH_3CH_2CH_2Br + KCN \rightarrow CH_3CH_2CH_2CN + KBr$$

The solvent is important. If water is present you tend to get substitution by -OH instead of -CN. in the reaction with the cyanide ion, an extra carbon atom is added to the original halogenoalkane chain.

4. The reaction of primary halogenoalkanes with hydroxide ions

If a halogenoalkane is heated under reflux with a solution of sodium or potassium hydroxide, the halogen is replaced by -OH and an alcohol is produced



Elimination reactions

The reagent used in these elimination reactions is ethanolic sodium hydroxide:

$$CH_3CHBrCH_3 + NaOH(ethanol) \rightarrow CH_2CH{=}CH_2 + H_2O + NaBr$$

The ethanolic OH^- ion acts as a base, accepting an H^+ from the halogenoalkane to form water. The C--Br bond breaks heterolytically, forming a Br^- ion and leaving an alkene as the organic product.

Importance of the conditions:

If we use NaOH(aq), a nucleophilic substitution reaction occurs and an alcohol is produced. If we use NaOH(ethanol), an elimination reaction occurs and an alkene is produced.