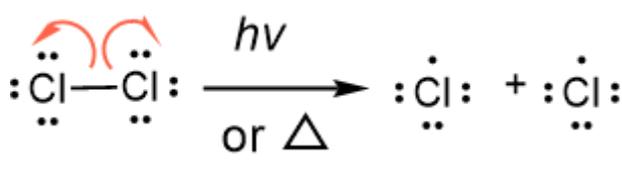


UNIT - I FREE RADICAL REACTIONS MECHANISM AND HUNSDIECKER REACTION**Free radical reaction mechanism**

Homolytic bond breaking requires energy equal to the bond dissociation energy, and homolytic bond making releases energy equal to the bond dissociation energy. When a molecule absorbs energy in the form of heat or a photon of UV light, some of the weak bonds, like

bond (239 kJ/mol) or

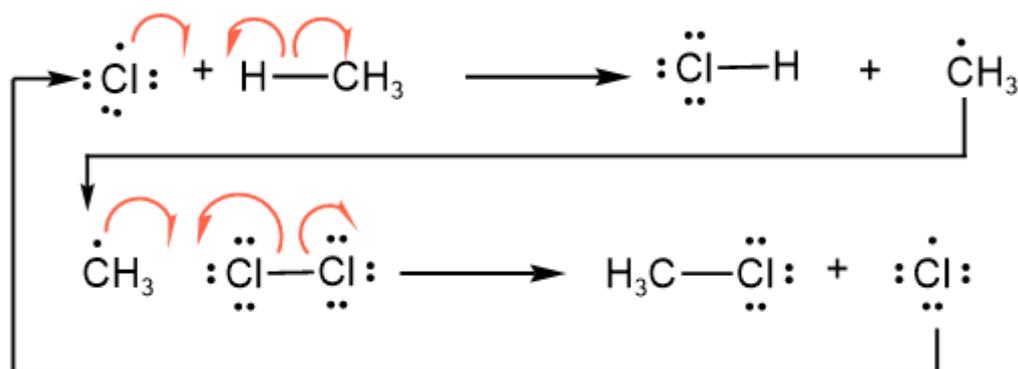
bond (146 kJ/mol) breaks initiating free radicals, e.g.:



where $h\nu$ represents a photon of UV light and Δ represent heat energy

. The reaction in which free radicals are created from neutral species, as in the above example, is called the **free radical initiation** step in a free radical reaction mechanism.

Free radicals are very reactive species. They usually abstract an atom, e.g., an H atom, from a hydrocarbon molecule, e.g.:

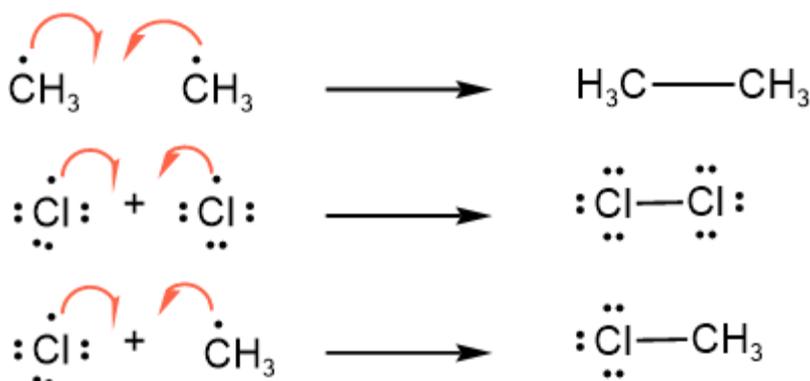


This reaction happens easily because the energy needed to break an bond (413 kJ/mol) is compensated by the energy released by making bond (427 kJ/mol). The repeats similar process when it collides with a molecules shown in the second reaction above. Again, the energy released by making bond (339 kJ/mol) compensates for the energy needed in breaking bond (239 kJ/mol). Reactions in which one radical converts into a neutral specie and create another free radical that repeats the process, as in the above two reactions, are called **propagation reactions**. The propagation reactions often

happen easily as the energy released in the bond-making compensates fully or partially for the energy needed in bond-making. The propagation reactions shown above happen in a cycle as the free radical produced in one is the reactant in the other and vice versa. The two propagation steps add up to the following overall reaction:

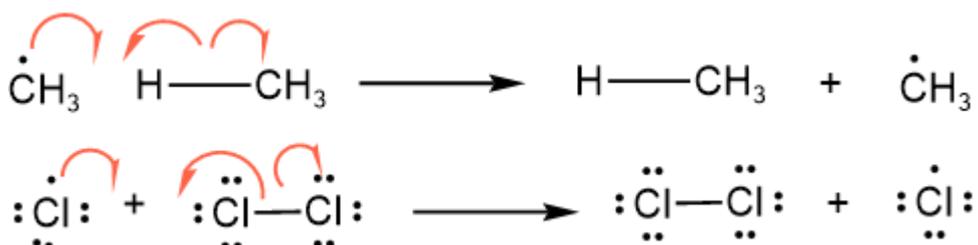
Overall reaction:

This cycle of propagation reaction may repeat hundreds of times until one of the reactant exhaust or a free radical may collide with another free radical and terminate each other, as in the following reactions.



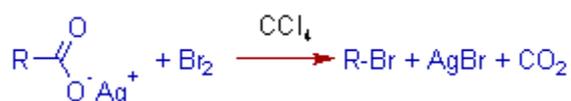
The homolytic bond-making between two free radicals that terminate the two radicals is called the **termination reaction**. The initiation, propagation, and termination are typical elementary reactions in a free radical reaction mechanism.

A CH_3 collide with molecule and abstract a Cl atom and a CH_3 may collide with a Cl_2 molecule and abstract a Cl atom, but there is no net chemical change in these elementary steps as shown below.



The decarboxylation of silver salts of carboxylic acids to alkyl bromides by treating with bromine is known as **Hunsdiecker reaction**. The alkyl bromide contains one carbon less than those in carboxylic acid.

This reaction is also known as Borodin-Hunsdiecker reaction.



* Very good yields are obtained with alkyl groups containing 2 to 18 carbons. This reaction works with linear as well as branched chains. However the reaction seldom works with alkyl groups containing unsaturation.

* This reaction is usually carried out in carbon tetrachloride solvent.

* Although bromine is used often, the reaction is also possible with chlorine and iodine.

* When iodine is used, the ratio between the silver carboxylate and iodine is very important and determines the products.

A 1:1 ratio of silver salt and iodine gives the alkyl halide.

However, an ester, RCOOR is formed when the reaction is carried out with a 2:1 ratio of silver carboxylate and iodine. This is called as **Simonini reaction**.

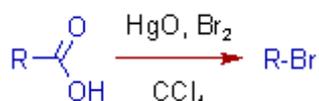
* In case of aromatic carboxylates, the Hunsdiecker reaction is possible when the aromatic ring contains electron-withdrawing groups.

Otherwise, if the aromatic system contains electron-donating groups, the bromine will substitute one of the hydrogen on the aromatic ring rather than promoting the Hunsdiecker reaction.

However the use of NBS instead of bromine will give the desired Hunsdiecker product. This reagent is especially useful since it produces bromine free radicals slowly.

* The silver carboxylate used as the starting material must be sufficiently pure and dry. It can be prepared from the corresponding carboxylic acid by treating it with silver oxide, Ag₂O.

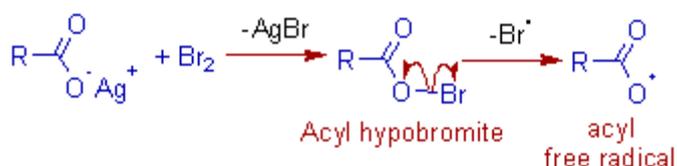
Christol-Firth Modification: It is possible to perform the Hunsdiecker reaction conveniently on the free carboxylic acid instead of the silver salt, which otherwise requires purification. In this modification the free carboxylic acid is treated with a mixture of mercuric oxide, HgO and bromine in CCl₄. There is no need to isolate an intermediate salt.



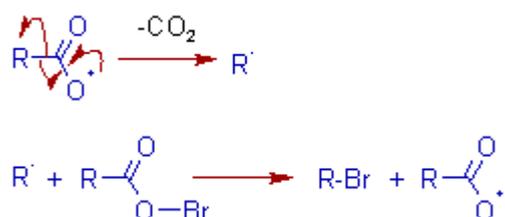
Mechanism of Hunsdiecker reaction

Initiation: Initially the bromine reacts with the silver carboxylate to give an unstable acyl hypobromite. The driving force of this step is the precipitation of the extremely poorly soluble and stable AgBr.

The acyl hypobromite decomposes by homolytic cleavage of relatively weak O-Br bond to furnish an acyl free radical.



Propagation: The acyl free radical undergoes decarboxylation to furnish an alkyl free radical, which reacts with acyl hypobromite to give the final product alkyl bromide along with the formation of a new acyl free radical.

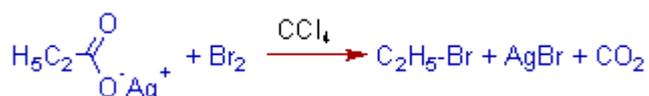


The following facts support the above proposed free radical mechanism for Hunsdiecker reaction.

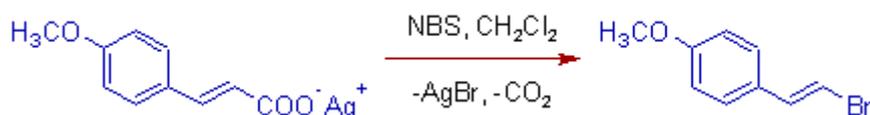
- i) No rearrangement of alkyl groups
- ii) The formation of side products like R-R.
- iii) If the alkyl group, R is chiral, it loses its optical activity during this reaction.

ILLUSTRATION

1) The silver salt of propionic acid is converted to ethyl bromide when treated with bromine in tetrachloromethane.



2) In the following reaction, the use of NBS (N-Bromosuccinimide) reduces the chances of electrophilic substitution on benzene ring.



3) The Christol-Firth Modification is used in the preparation of [1.1.1]propellane (tricyclo[1.1.1.0^{1,3}]pentane). The conversion of Bicyclo[1.1.1]pentane-1,3-dicarboxylic acid to the corresponding dibromide is achieved by using mercuric oxide and bromine in carbon tetrachloride as shown below.

