

Organic Reactions and Mechanisms



Free Radical Substitution Reactions - Lecture Notes

Free radical substitution reactions are characteristic of alkanes and other saturated hydrocarbons. The process involves the substitution of a hydrogen atom by a halogen atom through a mechanism that generates free radicals. This reaction occurs in the presence of light or heat, which initiates the process by breaking bonds to form radicals.

General Mechanism

The free radical substitution reaction can be described in three main steps:

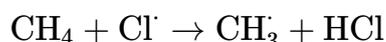
1. Initiation:

- This step involves the homolytic cleavage (symmetrical bond breaking) of a halogen molecule (X_2) under UV light or heat to form two halogen free radicals.

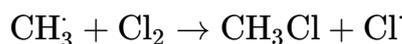


2. Propagation:

- The halogen radical reacts with the alkane (such as methane) to abstract a hydrogen atom, forming a new free radical (methyl radical) and a hydrogen halide.



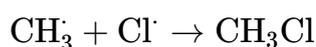
- The methyl radical then reacts with another halogen molecule to form the desired halogenated product and regenerate a halogen radical.



- The cycle of propagation continues as long as both radicals and reactants are available.

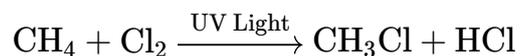
3. Termination:

- The reaction terminates when two radicals combine to form a stable product, removing radicals from the reaction mixture.

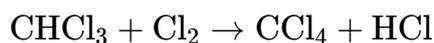
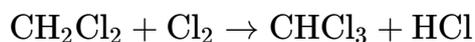
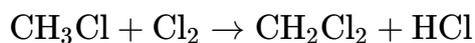


Example: Chlorination of Methane

The reaction of methane with chlorine is a classic example of free radical substitution:



The reaction can continue with the chlorination of methyl chloride to form dichloromethane, chloroform, and eventually carbon tetrachloride:



Key Features of Free Radical Substitution:

- **Homolytic Bond Cleavage:** The reaction is initiated by the homolytic cleavage of the halogen molecule to form free radicals.
- **Radicals Involved:** The reaction proceeds through a chain mechanism involving radicals such as Cl^\cdot , CH_3^\cdot , and other intermediate radicals.
- **Propagation Cycle:** Once initiated, the radicals react with other molecules to propagate the reaction.
- **Light or Heat Initiation:** The reaction is often initiated by UV light or heat, which provides the energy needed to break the halogen-halogen bond.

Relevance

Free radical substitution reactions are important in organic chemistry for the functionalization of alkanes, leading to halogenated compounds which are precursors to many other organic syntheses.