Free Radicals Chain Reactions of Alkane

Free Radical Reactions of Alkanes

Introduction to Free Radical Reactions of Alkanes

- Alkanes are saturated hydrocarbons with only single bonds between carbon atoms. Due to the strength and non-polar nature of the C–C and C–H sigma bonds, they are generally considered chemically inert under normal conditions.
- However, they do undergo reactions under specific conditions — one of the most important being free radical halogenation, typically involving chlorine or bromine.
- The free radical chain reaction is a characteristic mechanism for such reactions and is one of the foundational mechanisms in organic chemistry.
- It explains how relatively unreactive molecules like alkanes can be transformed into more functionalized compounds, such as haloalkanes.

General Example: Halogenation of Alkanes

- For the sake of clarity, let's consider the chlorination of methane as the simplest example:



- This reaction is light or heat initiated and proceeds via a free radical chain mechanism, which includes three main stages:
  - Initiation Step
  - Propagation Steps
  - Termination Steps

Mechanism of Free Radical Chain Reactions

- The free radical reaction of alkanes typically follows a three-step mechanism: **Initiation, Propagation, and Termination**.
- This is often exemplified by the halogenation of alkanes, particularly chlorination or bromination of methane.

1. Initiation Step

- This is the first step where the chain reaction is started by the formation of free radicals. This step requires energy, usually provided by heat or ultraviolet (UV) light.
- **For chlorination**:

$$Cl_2 \xrightarrow{h\nu} Cl^{\cdot} + Cl^{\cdot}$$



- Here, UV light breaks the chlorine molecule via **homolytic cleavage** (both atoms get one electron from the bond), generating two chlorine free radicals. These chlorine atoms are highly reactive due to the presence of an unpaired electron.
- **Note**: This step is non-chain propagating, meaning it happens only once per initiation event but is necessary to generate the reactive species.

2. Propagation Steps

- These are the chain-carrying steps. In this stage, the free radicals generated in initiation continue to react with stable molecules to produce new radicals, which further continue the chain.

A. Step 1:

- Here, the chlorine radical abstracts a hydrogen atom from methane, forming methyl radical and hydrogen chloride.

$$Cl^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + HCl$$



- The abstraction of hydrogen is a key step; it determines the site of substitution.

B. Step 2:

- Now the methyl radical reacts with another chlorine molecule, producing **chloromethane (CH_3Cl)** and regenerating a chlorine radical, which can then continue the chain.

$$CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$$

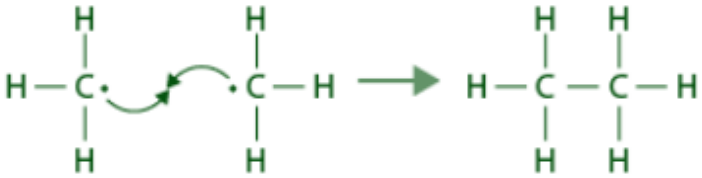


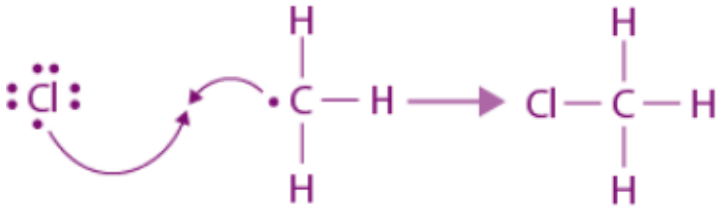
- These propagation steps may repeat thousands of times, making the reaction highly efficient once initiated.

3. Termination Steps

- These are reactions where two free radicals combine, effectively ending the chain.
- These steps are rare compared to propagation because the concentration of radicals is typically low, but they are crucial for stopping the reaction.
- **Examples:**







- These reactions remove reactive species from the system, decreasing the rate of reaction over time.

Relative Reactivity of Alkanes in Radical Reactions

- Reactivity of different alkanes depends on the ease of hydrogen abstraction from carbon atoms.
- **C–H bond strength varies depending on the type of carbon:**
  - **Primary (1°) hydrogen:** Hydrogen attached to a carbon bonded to only one other carbon.
  - **Secondary (2°) hydrogen:** Attached to a carbon bonded to two other carbons.
  - **Tertiary (3°) hydrogen:** Attached to a carbon bonded to three other carbons.
- **Order of Ease of Hydrogen Abstraction:**

$$3^\circ > 2^\circ > 1^\circ > CH_4$$

- **This means that:**
  - Tertiary hydrogens are more easily abstracted due to the greater stability of the resulting tertiary free radical.
  - The reactivity increases as the stability of the resulting radical increases.

Experimental Reactivity Ratios (for chlorination):

- On average, the relative reactivities of hydrogen atoms towards chlorine radicals are approximately:

$$3^\circ : 2^\circ : 1^\circ \approx 5 : 3.8 : 1$$

- So, if you halogenate a molecule like propane ($CH_3–CH_2–CH_3$):
  - There are **six primary hydrogens** (on the CH_3 groups).

- There are **two secondary hydrogens** (on the CH_2 group).

- Based on reactivity, more substitution happens at the **secondary position**.

Reactivity in Bromination vs. Chlorination:

- Chlorination is less selective but more reactive.
- Bromination is more selective but less reactive.

This is because:

- **In chlorination**, both propagation steps are moderately exothermic, so the reaction is under kinetic control — it proceeds quickly and with little selectivity.
- **In bromination**, the first propagation step is endothermic, and the transition state resembles the products more than the reactants — so the stability of the radical has a much larger effect. This makes bromination highly selective for more stable radicals (tertiary > secondary > primary).

- **Reactivity ratios for bromination** are approximately:

$$3^\circ : 2^\circ : 1^\circ \approx 1600 : 80 : 1$$

- This huge difference explains why bromination is more useful for selective functionalization.

Factors Influencing Relative Reactivity

- **Bond Strengths**: Weaker C–H bonds (e.g., tertiary) break more easily.
- **Radical Stability**: More stable radicals are formed preferentially.
- **Transition State Theory**: Selectivity increases when the rate-determining step is product-like (endothermic reactions).
- **Steric Effects**: Less important in radical reactions compared to ionic mechanisms.
- **Temperature**: Higher temperatures can decrease selectivity by giving more energy to overcome activation barriers.

Persistence / Stability of Radicals

- The persistence or stability of a radical refers to how long-lived it is and how resistant it is to reacting with other molecules or itself.
- **In the context of alkyl radicals formed in chain reactions, their stability affects both:**
  - The regioselectivity of substitution
  - The efficiency and control of the chain process

General Radical Stability Order

- Alkyl radical stability follows this trend:

$$\mathbf{3^\circ > 2^\circ > 1^\circ > methyl}$$

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