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Free Radical Mechanism

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Abstract

Free radical reactions are a class of chemical reactions that involve highly reactive intermediates known as free radicals. These species possess unpaired electrons, making them extremely unstable and eager to form stable bonds. Free radical mechanisms are fundamental processes in chemistry, playing a significant role in a variety of chemical reactions, including polymerization, combustion, and biological processes. The mechanism typically involves three primary stages: initiation, propagation, and termination. In the initiation step, free radicals are generated through processes such as homolytic bond cleavage, often induced by heat, light, or chemical catalysts. During propagation, these radicals react with stable molecules to form new radicals, sustaining a chain reaction. The termination step occurs when two radicals combine, neutralizing their reactivity and halting the chain process. Free radical mechanisms are critical in synthetic chemistry, especially in the production of polymers through free radical polymerization. However, uncontrolled free radical activity can be harmful, as observed in biological systems where oxidative stress leads to cell damage. Antioxidants play a crucial role in mitigating such damage by scavenging free radicals. This paper will investigate into the fundamental mechanism of free radical reactions, encircling the key steps involved and the factors influencing their reactivity.

Key Words: Free radical, initiation, propagation, termination, heat, photon, unpaired electron, intermediate, polymerization, homolytic cleavage

Introduction

Free radical reactions are ubiquitous in nature, playing crucial roles in various biological and industrial processes. They are involved in phenomena such as combustion, atmospheric chemistry, polymerization, and even aging. Understanding the mechanism of these reactions is essential for controlling and manipulating them for beneficial purposes, such as in the synthesis of polymers and pharmaceuticals.

Mechanism of Free Radical Reactions

Free radical reactions typically proceed through a chain mechanism, consisting of three primary steps:

I. Initiation:

This step involves the formation of the initial free radicals.

It can be triggered by various means, such as heat, light, or the introduction of a radical initiator.

Initiators: Certain compounds, known as radical initiators, readily decompose to form free radicals under relatively mild conditions. Common examples include peroxides (e.g., dibenzoyl peroxide) and azo compounds (e.g., azobisisobutyronitrile). A common example is the homolytic cleavage of a bond in a molecule, resulting in two free radicals.

Example: Chlorination of Methane

One classic example of free radical initiation involves the chlorination of methane. In the presence of ultraviolet (UV) light, a chlorine molecule (Cl_2) undergoes homolytic cleavage:



Here, " $h\nu$ " represents a photon of light. The resulting chlorine atoms ($\text{Cl}\cdot$) are highly reactive free radicals, ready to initiate the chain reaction.

II. Propagation:

This is the chain-carrying step where the free radical reacts with a molecule to form a new product and another free radical. This new radical can then participate in further propagation steps, leading to a chain reaction. The reactivity of the free radical and the stability of the resulting product influence the rate and selectivity of this step.

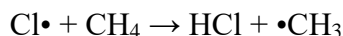
Key Characteristics:

- 1. Chain-Carrying Steps:** Propagation involves a series of reactions where one free radical is consumed, and another is generated. This cyclical nature sustains the chain reaction, allowing it to continue as long as reactants are available.
- 2. Two or More Steps:** Propagation typically consists of two or more distinct steps, each involving a different type of reaction. These steps often involve:
- 3. Hydrogen Abstraction:** A free radical abstracts a hydrogen atom from a molecule, forming a new free radical and a stable molecule (e.g., in the chlorination of methane).
- 4. Addition to a Double Bond:** A free radical adds to a carbon-carbon double bond, forming a new carbon-centered radical. This is crucial in polymerization reactions.

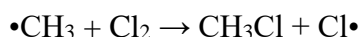
Example: Chlorination of Methane

The propagation steps are as follows:

Step 1: A chlorine radical ($\text{Cl}\cdot$) abstracts a hydrogen atom from methane (CH_4), forming hydrogen chloride (HCl) and a methyl radical ($\cdot\text{CH}_3$):



Step 2: The methyl radical ($\cdot\text{CH}_3$) reacts with a chlorine molecule (Cl_2), forming chloromethane (CH_3Cl) and another chlorine radical ($\text{Cl}\cdot$):



These two steps constitute a cycle. The chlorine radical generated in step 2 can then go on to abstract another hydrogen atom from methane in step 1, and the cycle repeats. This chain reaction continues until the reactants are depleted or termination reactions occur.

Significance:

1. Chain Reactions: Propagation steps are responsible for the chain-like nature of free radical reactions, leading to the rapid consumption of reactants.

2. Product Formation: These steps directly lead to the formation of the desired products in many free radical reactions, such as substitution reactions and polymerization.

III. Termination:

This step involves the combination of two free radicals to form a stable molecule. It terminates the chain reaction, reducing the concentration of free radicals. Termination can occur through various pathways, such as radical-radical coupling or disproportionation.

Key Characteristics:

Radical-Radical Combination: Termination involves the reaction between two free radicals. This can occur in several ways:

- 1. Coupling:** Two identical radicals combine to form a single molecule.
- 2. Disproportionation:** Two radicals undergo a hydrogen atom transfer, resulting in one saturated molecule and one unsaturated molecule.
- 3. Chain Interruption:** Termination steps effectively break the chain reaction, reducing the concentration of free radicals and halting the propagation cycle.

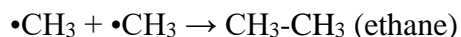
Example: Chlorination of Methane

In the chlorination of methane, some possible termination steps include:

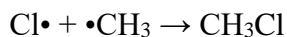
- Combination of two chlorine radicals:



- Combination of two methyl radicals:



- Combination of a chlorine radical and a methyl radical:



Significance:

- 1. Chain Reaction Control:** Termination steps play a crucial role in controlling the length of the chain reaction.
- 2. Product Formation:** While termination steps generally reduce the yield of the desired product, they also contribute to the formation of side products.

Factors Influencing Free Radical Reactivity

Several factors can influence the reactivity of free radicals:

- 1. Bond dissociation energy:** Weaker bonds are more susceptible to homolytic cleavage, leading to easier formation of free radicals.
- 2. Stability of the radical:** More stable radicals are less reactive and tend to participate in slower reactions.
- 3. Polar effects:** The presence of electron-withdrawing or electron-donating groups can influence the electron density around the radical center, affecting its reactivity.
- 4. Steric hindrance:** Bulky groups around the radical center can hinder its approach to other molecules, reducing its reactivity.

Applications of Free Radical Reactions

Free radical reactions have numerous applications in various fields:

- 1. Polymerization:** Free radical polymerization is a widely used method for producing polymers, such as polyethylene and polystyrene.
- 2. Combustion:** The burning of fuels involves complex free radical reactions.
- 3. Atmospheric chemistry:** Free radicals play a significant role in atmospheric reactions, such as the formation of ozone and smog.
- 4. Biological systems:** Free radicals are involved in various biological processes, including oxidative stress and cellular signaling.

Conclusion:

Free radical reactions are fundamental to many chemical processes, both natural and synthetic. Understanding their mechanism and the factors influencing their reactivity is crucial for controlling and utilizing them for various applications. Continued research in this area will undoubtedly lead to further advancements in fields such as materials science, medicine, and environmental science.

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