CHAPTER-3

FREE RADICAL CHAIN REACTION OF ALKANE

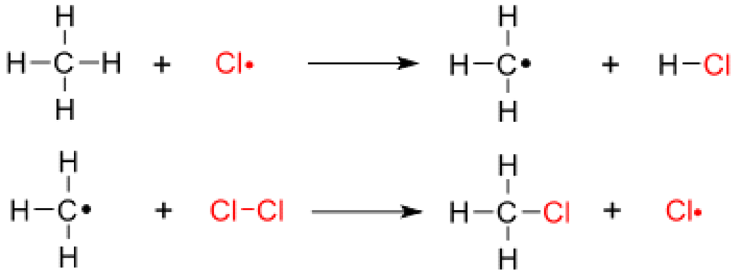
FREE RADICAL:

- **Radicals** (often referred to as **free radicals**) are atoms, molecules, or ions with unpaired electrons or an open shell configuration.
- Free radicals may have positive, negative, or zero charge. With some exceptions, these unpaired electrons cause radicals to be highly chemically reactive.
- Free radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes.
- In living organisms, superoxide and nitric oxide and their reaction products regulate many processes, such as control of vascular tone and thus blood pressure.
- They also play a key role in the intermediary metabolism of various biological compounds.
- Such radicals can even be messengers in a phenomenon dubbed redox signaling.
- A radical may be trapped within a *solvent cage* or be otherwise bound.

General mechanism

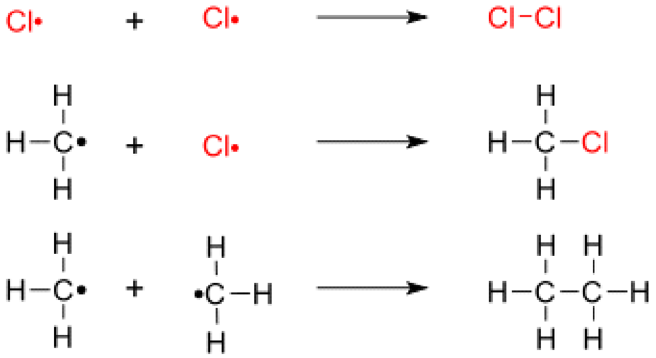
- The chain mechanism is as follows, using the chlorination of methane as a typical example:
  - **Initiation**: Splitting or homolysis of a chlorine molecule to form two chlorine atoms, initiated by UV Radiation or sunlight. A chlorine atom has an unpaired electron and acts as a free radical.

2. Chain propogation (two steps): a hydrogen atom is pulled off from methane leaving a 1° methyl radical. The methyl radical then pulls a Cl· from Cl_2.



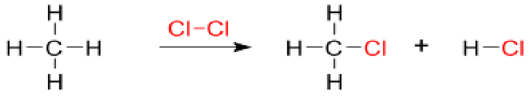
- This results in the desired product plus another chlorine radical.
- This radical will then go on to take part in another propagation reaction causing a chain reaction.
- If there is sufficient chlorine, other products such as CH_2Cl_2 may be for Cl_2.

Chain Termination:



- The last possibility in the termination step will result in an impurity in the final mixture; notably this results in an organic molecule with a longer carbon chain than the reactants.

- The net reaction is:



or $CH_4 + Cl_2 \xrightarrow{uv\ light} CH_3Cl + HCl$

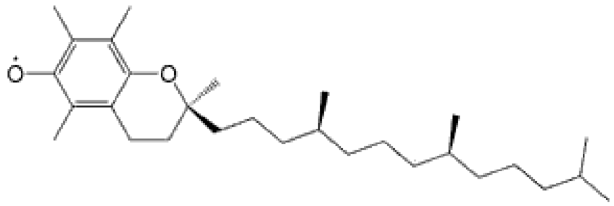
  - In the case of methane or ethane, all the hydrogen atoms are equivalent and thus have an equal chance of being replaced.
  - This leads to what is known as a *statistical product distribution.*
  - For propane and higher alkanes, the hydrogen atoms which form part of CH_2 (or CH) groups are preferentially replaced.
  - The reactivity of the different halogens varies considerably. The relative rates are: flourine (108) > chlorine (1) > bromine(7×10^{-11}) > iodine (2×10^{-22}).
  - Hence the reaction of the alkanes with fluorine is difficult to control, that with chlorine is moderate to fast, that with bromine is slow and requires high levels of UV irradiation while the reaction with iodine is practically non-existent and thermodynamically unfavorable.
  - A common method in organic synthesis employing *N*-bromosuccinimide, which can undergo homolysis to yield a bromine radical and is a free-radical halogenation variant, is the Wohl-Ziegler reaction.

Reactivivity

- Radical alkyl intermediates are stabilized by similar physical processes to carbocations: as a general rule, the more substituted the radical center is, the more stable it is.
- This directs their reactions. Thus, formation of a tertiary radical ($R_3C\cdot$) is favored over secondary ($R_2HC\cdot$), which is favored over primary ($RH_2C\cdot$).
- Likewise, radicals next to functional groups such as carbonyl, nitrile, and ether are more stable than tertiary alkyl radicals.
- Radicals attack double bonds. However, unlike similar ions, such radical reactions are not as much directed by electrostatic interactions.
- For example, the reactivity of nucleophilic ions with α,β-unsaturated compounds (C=C–C=O) is directed by the electron-withdrawing effect of the oxygen, resulting in a partial positive charge on the carbonyl carbon.
- There are two reactions that are observed in the ionic case: the carbonyl is attacked in a direct addition to carbonyl, or the vinyl is attacked in conjugate addition, and in either case, the charge on the nucleophile is taken by the oxygen.
- Radicals add rapidly to the double bond, and the resulting α-radical carbonyl is relatively stable; it can couple with another molecule or be oxidized.
- Nonetheless, the electrophilic/neutrophilic character of radicals has been shown in a variety of instances.
- One example is the alternating tendency of the copolymerization of maleic anhydride(electrophilic) and styrene (slightly nucleophilic).

- In intramolecular reactions, precise control can be achieved despite the extreme reactivity of radicals.
- In general, radicals attack the closest reactive site the most readily.
- Therefore, when there is a choice, a preference for five-membered rings is observed: four-membered rings are too strained, and collisions with carbons six or more atoms away in the chain are infrequent.
- Carbenes and nitrenes, which are diradicals, have distinctive chemistry.

Persistence and stability



- The radical derived from *α-tocopherol*
- Although radicals are generally short-lived due to their reactivity, there are long-lived radicals. These are categorized as follows:

Stable radicals

- The prime example of a stable radical is molecular dioxygen (O_2).
- Another common example is nitric oxide (NO). Organic radicals can be long lived if they occur in a conjugated π

system, such as the radical derived from α-tocopherol (vitamin E).

- There are also hundreds of examples of thiazyl radicals, which show remarkable kinetic and thermodynamic stability with only a very limited extent of π resonance stabilization.

Persistent radicals

- Persistent radical compounds are those whose longevity is due to steric crowding around the radical center, which makes it physically difficult for the radical to react with another molecule.
- Examples of these include Gomberg's triphenylmethyl radical, Fremy's salt (Potassium nitrosodisulfonate, $(KSO_3)_2NO\cdot$), nitroxides, (general formula $R_2NO\cdot$) such as TEMPO, TEMPOL, nitronyl nitroxides, and azephenylenyls and radicals derived from PTM (perchlorophenylmethyl radical) and TTM (tris(2,4,6-trichlorophenylmethyl radical).
- Persistent radicals are generated in great quantity during combustion, and "may be responsible for the oxidative stress resulting in cardiopulmonary disease and probably cancer that has been attributed to exposure to airborne fine particles."

Diradicals

- Diradicals are molecules containing two radical centers. Multiple radical centers can exist in a molecule.

- Atmospheric oxygen naturally exists as a diradical in its ground state as tripletoxygen.
- The low reactivity of atmospheric oxygen is due to its diradical state.
- Non-radical states of dioxygen are actually less stable than the diradical.
- The relative stability of the oxygen diradical is primarily due to the nature of the triplet-singlet transition required for it to grab electrons, i.e., "oxidize".
- The diradical state of oxygen also results in its paramagnetic character, which is demonstrated by its attraction to an external magnet.

By

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