16.3: Radical Chain Reactions

Because of their high reactivity, free radicals have the potential to be extremely powerful chemical tools - but as we will see in this chapter, they can also be extremely harmful in a biological/environmental context. Key to understanding many types of radical reactions is the idea of a **radical chain reaction**.

Radical chain reactions have three distinct phases: initiation, propagation, and termination. We'll use a well-known example, the halogenation of an alkane such as ethane, to illustrate. The overall reaction is:

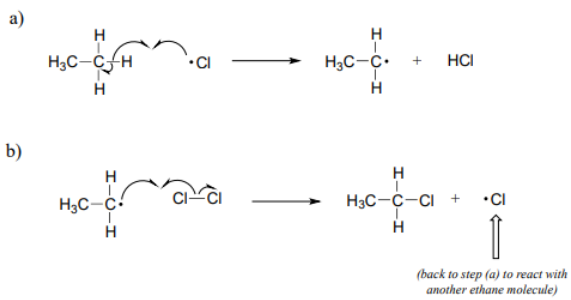
$$CH_3CH_3 + Cl_2 \underset{h\nu \ or \ \Delta}{\rightarrow} CH_3CH_2Cl + HCl \cdots h\nu \text{ means light } \Delta \text{ means heat} \tag{16.3.1}$$

The initiation phase in a radical chain reaction involves the homolytic cleavage of a weak single bond in a non-radical compound, resulting in two radical species as products.

Often, heat or light provides the energy necessary to overcome an energy barrier for this type of event. The initiation step in alkane halogenation is homolysis of molecular chlorine (Cl_2) into two chlorine radicals. Keep in mind that that virtually all radical species, chlorine radicals included, are highly reactive.

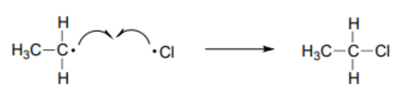
$$Cl \curvearrowleft\curvearrowright Cl \rightarrow 2Cl \tag{16.3.2}$$

The **propagation** phase is the 'chain' part of chain reactions.



Once a reactive free radical (chlorine radical in our example) is generated in the initiation phase, it will react with relatively stable, non-radical compounds to form a new radical species. In ethane halogenation, a chlorine radical generated in the initiation step first reacts with ethane in a hydrogen abstraction step, generating HCl and an ethyl radical (part a above). Then, the ethyl radical reacts with another (non-radical) Cl_2 molecule, forming the chloroethane product and regenerating a chlorine radical (part b above). This process repeats itself again and again, as chlorine radicals formed in part (b) react with additional ethane molecules as in part (a).

The termination phase is a radical combination step, where two radical species happen to collide and react with each other to form a non-radical product and 'break the chain'. In our ethane chlorination example, one possible termination event is the reaction of a chlorine radical with an ethyl radical to form chloroethane.



Exercise 16.3.1

Draw two alternative chain termination steps in the ethane chlorination chain reaction. Which one leads to an undesired product?

Because radical species are so reactive and short-lived, their concentration in the reaction mixture at any given time is very low compared to the non-radical components such as ethane and Cl_2. Thus, many cycles of the chain typically occur before a termination event takes place. In other words, a single initiation event leads to the formation of many product molecules.

Compounds which readily undergo homolytic cleavage to generate radicals are called radical initiators. As we have just seen, molecular chlorine and bromine will readily undergo homolytic cleavage to form radicals when subjected to heat or light. Other commonly used as radical initiators are peroxides and N-bromosuccinimide (NBS).