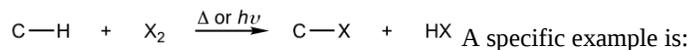


9.2: Halogenation Reaction of Alkanes

When alkanes react with halogen (Cl_2 or Br_2), with heat or light, hydrogen atom of the alkane is replaced by halogen atom and alkyl halide is produced as product. This can be generally shown as:

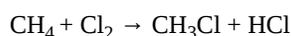


(multi-chlorination products are possible for the reaction)

Such type of reaction can be called as substitution because hydrogen is substituted by halogen; can also be called halogenation because halogen is introduced into the product. For this book, both terms are used in this chapter, interchangeably.

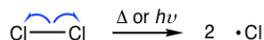
The net reaction for halogenation seems straightforward, the mechanism is more complicated though, it go through multiple steps that include **initiation**, **propagation** and **termination**.

We will take the example of mono-chlorination of methane, for the discussion of reaction mechanism.



Mechanism for mono-chlorination of methane:

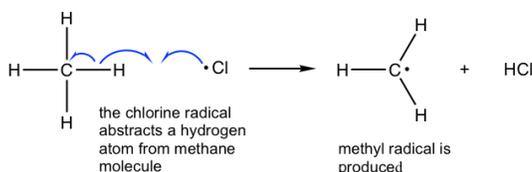
Initiation: Production of radical



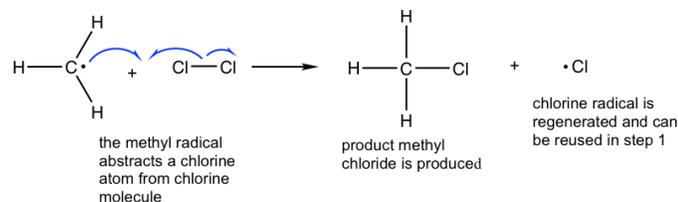
With the energy provided from heat or light, chlorine molecule dissociates homolytically, each chlorine atom takes one of the bonding electrons, and two highly reactive chlorine radicals, $\text{Cl}\cdot$, are produced.

Propagation: Formation of product and regeneration of radical

step 1:



step 2:



The propagation step involve two sub-steps. In the 1st step, the $\text{Cl}\cdot$ takes a hydrogen atom from the methane molecule (this is also called as **hydrogen abstraction** by $\text{Cl}\cdot$), and C-H single bond breaks homolytically. A new σ bond is formed by Cl and H each donate one electron and HCl is produced as the side product. The CH_3 radical, $\text{CH}_3\cdot$, the critical intermediate for the formation of product in next step, is formed as well.

In the 2nd step, the $\text{CH}_3\cdot$ abstracts a chlorine atom to give final CH_3Cl product, together with another $\text{Cl}\cdot$. The regenerated $\text{Cl}\cdot$ can attack another methane molecule and cause the repetition of step 1, then step 2 is repeated, and so forth. Therefore the regeneration of the $\text{Cl}\cdot$ is particularly significant, it makes the propagation step self-repeat hundreds or thousands of time. The propagation step is therefore called the self-sustaining step, only small amount of $\text{Cl}\cdot$ is required at the beginning to promote the process.

Initiation and propagation are productive steps for the formation of product. This type of sequential, step-wise mechanism in which the earlier step generate the intermediate that cause the next step of the reaction to occur, is call the **chain reaction**.

The chain reaction will not continue forever though, because of the termination steps.

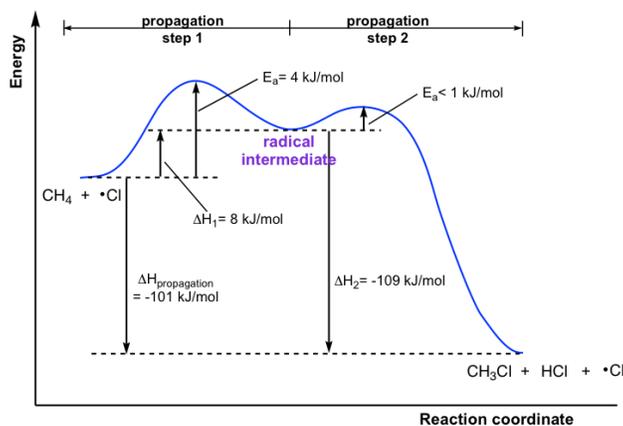
Termination: Consumption of radicals



$\cdot\text{CH}_3 + \cdot\text{CH}_3 \longrightarrow \text{CH}_3\text{CH}_3$ When two radicals in the reaction mixture meet with each other, they combine to form a stable molecule. The combination of radicals lead to the decreasing of the number of radicals available to propagating the reaction, and the reaction slows and stops eventually, so the combination process is called termination step. A few examples of termination are given above, other combinations are possible as well.

The propagation steps are the core steps in halogenation. The energy level diagram helps to provide further understanding of the propagation process.

The 1st step in propagation is endothermic, while the energy absorbed can be offset by the 2nd exothermic step. Therefore the overall propagation is exothermic process and the products are in lower energy level than reactants.



Energy diagram of mono-chlorination of methane

The reaction heat (enthalpy) for each of the propagation step can also be calculated by referring to the homolytic bond dissociation energies (**Table 9.1**). For such calculation, energy absorbed for bond-breaking step, so the bond energy was given “+” sign, and energy released for bond-forming step, and the “-” sign applied.

Bond	kJ/mol	Bond	kJ/mol	Bond	kJ/mol
A — B → A • + B •					
F — F	159	H — Br	366	CH ₃ — I	240
Cl — Cl	243	H — I	298	CH ₃ CH ₂ — H	421
Br — Br	193	CH ₃ — H	440	CH ₃ CH ₂ — F	444
I — I	151	CH ₃ — F	461	CH ₃ CH ₂ — Cl	353
H — F	570	CH ₃ — Cl	352	CH ₃ CH ₂ — Br	295
H — Cl	432	CH ₃ — Br	293	CH ₃ CH ₂ — I	233

Table 9.1 Homolytic Bond Dissociation Energies for Some Single Bonds

Examples

Calculation reaction energy for the propagation step of mono-chlorination of methane (referring to the corresponding bond energies in Table 9.1.)

Solution:



The $\text{H} - \text{CH}_3$ bond broken, absorb energy, so +440 kJ

The $\text{H} - \text{Cl}$ bond formed, release energy, so - 432 kJ

$$\Delta H_1 = +440 + (-432) = +8 \text{ kJ}$$



The $\text{Cl} - \text{Cl}$ bond broken, absorb energy, so +243 kJ

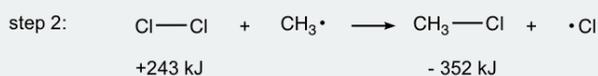
The $\text{CH}_3 - \text{Cl}$ formed, release energy, so -352kJ

$$\Delta H_2 = +243 + (-352) = -109 \text{ kJ}$$

$$\Delta H_{\text{propagation}} = \Delta H_1 + \Delta H_2 = +8 + (-109) = -101 \text{ kJ}$$



$$\Delta H_1 = +440 + (-432) = +8 \text{ kJ}$$



$$\Delta H_2 = +243 + (-352) = -109 \text{ kJ}$$

$$\Delta H_{\text{propagation}} = \Delta H_1 + \Delta H_2 = +8 + (-109) = -101 \text{ kJ}$$

The calculated data does match with the data from the energy diagram.

Reactivity Comparison of Halogenation

The energy changes for halogenation (substitution) with the other halogens can be calculated in the similar way, the results are summarized in **Table 9.2**.

Reaction	F ₂	Cl ₂	Br ₂	I ₂
Step 1: $\text{H} - \text{CH}_3 + \cdot\text{X} \rightarrow \text{CH}_3\cdot + \text{H} - \text{X}$	-130	+8	+74	-142
Step 2: $\text{X} - \text{X} + \text{CH}_3\cdot \rightarrow \text{CH}_3 - \text{X} + \cdot\text{X}$	-322	-109	-100	-89
Overall propagation: $\text{H} - \text{CH}_3 + \text{X} - \text{X} \rightarrow \text{CH}_3 - \text{X} + \text{HX}$	-452	-101	-26	+53

Table 9.2. Enthalpy of the Propagation Steps in Mono-halogenation of Methane (kJ/mol)

The data above indicate that the halogen radicals have different reactivity, fluorine is most reactive and iodine is least reactive. The iodine radical is very unreactive with overall “+” enthalpy, so iodine does not react with alkane at all. On the other side, the extreme high reactivity of fluorine is not a benefit either, the reaction for fluorine radical is so vigorous or even dangerous with lots heat released, and it is not practical to apply this reaction for any application because it is hard to control it. So Cl₂ and Br₂, with reactivity in the medium range, are used for halogen substitutions of alkanes. Apparently Cl₂ is more reactive than Br₂, and this leads to the different selectivity and application between the two halogens, more discussions in **section 9.4**.

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