Exercise 9: - Radical reactions

1. *tert*-Butyl peroxide is a source of free radicals:

$$(CH_3)_3CO\text{-}OC(CH_3)_3 \xrightarrow{\Delta \text{ or } h\nu} 2(CH_3)_3CO\cdot$$

A mixture of methylpropane and CCl_4 is stable at 130°C. If a small amount of *tert*-butyl peroxide is added, a reaction occurs that yields 2-chloro-2-methylpropane and chloroform. A small amount of 2-methyl-2-propanol, $(CH_3)_3COH$, equivalent to the peroxide used, is also formed. Propose a mechanism which explains the formation of these products.

Under the influence of heat or light a molecule of peroxide dissociates:

$$(CH_3)_3CO\text{-}OC(CH_3)_3 \xrightarrow{\Delta \text{ or } h\nu} 2(CH_3)_3CO\cdot$$

To determine the fate of the $(CH_3)_3CO\cdot$ we must look at the products and the sentence "A small amount of 2-methyl-2-propanol, $(CH_3)_3COH$, equivalent to the peroxide used, is also formed" provides the answer. We can start step 2 by writing the following:

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_3COH$$

To determine the source of the hydrogen we must look at the reactants. CCl_4 has no hydrogen atoms. Thus the hydrogen of the alcohol must come from the methylpropane:

$$(CH_3)_3CO\cdot + (CH_3)_3CH \longrightarrow (CH_3)_3COH$$

To determine which hydrogen in abstracted, look at the products. 2-Chloro-2-methylpropane can only be formed by abstraction of the tertiary hydrogen. Step 2 is therefore:

$$(CH_3)_3CO\cdot + (CH_3)_3CH \longrightarrow (CH_3)_3COH + (CH_3)_3C\cdot$$

The new intermediate $(CH_3)_3C\cdot$ starts step 3. What is its fate? Look at the products. It must form $(CH_3)_3CCl$. The chlorine must come from the CCl_4 hence step 3 is:

$$(CH_3)_3C\cdot + CCl_4 \longrightarrow (CH_3)_3CCl + \cdot CCl_3$$

The new intermediate $\cdot CCl_3$ starts step 4. What is its fate? Look at the products. It must form $HCCl_3$. The hydrogen must come from the $(CH_3)_3CH$ hence step 4 is:

$$\cdot CCl_3 + (CH_3)_3CH \longrightarrow HCCl_3 + (CH_3)_3C\cdot$$

Steps 3 and 4 constitute a chain reaction.

The overall mechanism is:

$$\left.\begin{array}{l} (CH_3)_3CO\text{-}OC(CH_3)_3 \xrightarrow{\Delta \text{ or } h\nu} 2(CH_3)_3CO\cdot \\ (CH_3)_3CO\cdot + (CH_3)_3CH \longrightarrow (CH_3)_3COH + (CH_3)_3C\cdot \end{array}\right) \text{ initiation}$$

$$\left.\begin{array}{l} (CH_3)_3C\cdot + CCl_4 \longrightarrow (CH_3)_3CCl + \cdot CCl_3 \\ \cdot CCl_3 + (CH_3)_3CH \longrightarrow HCCl_3 + (CH_3)_3C\cdot \end{array}\right) \text{ propagation}$$

2. A mixture of H_2 and Cl_2 does not react at room temperature. At high temperature or under the influence of light (of wavelength absorbed by chlorine) a violent reaction takes place and HCl is formed. The photochemical reaction yields as many as a million molecules of HCl for each photon absorbed. The presence of a trace of oxygen slows down the reaction. Propose a possible mechanism for this reaction.

initiation

$$Cl_2 \xrightarrow{\Delta \text{ or } h\nu} 2Cl\cdot$$

propagation

$$Cl\cdot + H_2 \longrightarrow H\text{-}Cl + H\cdot$$

$$H\cdot + Cl_2 \longrightarrow H\text{-}Cl + Cl\cdot$$

termination

$$2Cl\cdot \longrightarrow Cl_2$$

$$2H\cdot \longrightarrow H_2$$

$$Cl\cdot + H\cdot \longrightarrow HCl$$

3. When a mixture of methane and chlorine is irradiated, reaction begins at once. However, when irradiation is stopped, the reaction gradually slows down; it does not stop immediately. Why?

It is a chain reaction and will continue until all reactive species are consumed.

4. Bromination of methane is slowed down by the addition of fairly large amounts of HBr. Suggest an explanation.

$Br\cdot + H\text{-}CH_3 \longrightarrow H\text{-}Br + \cdot CH_3$

440kJ/mol 366 kJ/mol $\Delta H = +74$ kJ/mol i.e. endothermic in this direction

$\cdot CH_3 + Br\text{-}Br \longrightarrow Br\text{-}CH_3 + Br\cdot$

193kJ/mol 293 kJ/mol $\Delta H = -100$ kJ/mol i.e. exothermic in this direction

As soon as the $CH_3\cdot$ radical forms in the first reaction, it reacts with Br_2 as the activation energy for the second step is very low.

However, as HBr is added, a competing reaction becomes possible:

$H\text{-}Br + \cdot CH_3 \longrightarrow H\text{-}CH_3 + Br\cdot$

This is exothermic and will have a low activation energy. It removes methyl radicals and therefore swlows down the formation of bromomethane.