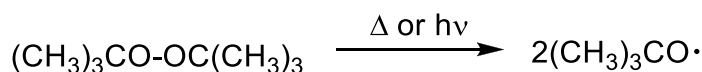


### Exercise 9: - Radical reactions

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



A mixture of methylpropane and  $\text{CCl}_4$  is stable at  $130^\circ\text{C}$ . 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,  $(\text{CH}_3)_3\text{COH}$ , equivalent to the peroxide used, is also formed. Propose a mechanism which explains the formation of these products.

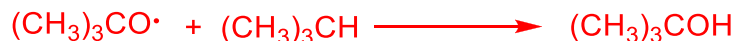
Under the influence of heat or light a molecule of peroxide dissociates:



To determine the fate of the  $(\text{CH}_3)_3\text{CO}\cdot$  we must look at the products and the sentence "A small amount of 2-methyl-2-propanol,  $(\text{CH}_3)_3\text{COH}$ , equivalent to the peroxide used, is also formed" provides the answer. We can start step 2 by writing the following:



To determine the source of the hydrogen we must look at the reactants.  $\text{CCl}_4$  has no hydrogen atoms. Thus the hydrogen of the alcohol must come from the methylpropane:



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



The new intermediate  $(\text{CH}_3)_3\text{C}\cdot$  starts step 3. What is its fate? Look at the products. It must form  $(\text{CH}_3)_3\text{CCl}$ . The chlorine must come from the  $\text{CCl}_4$  hence step 3 is:

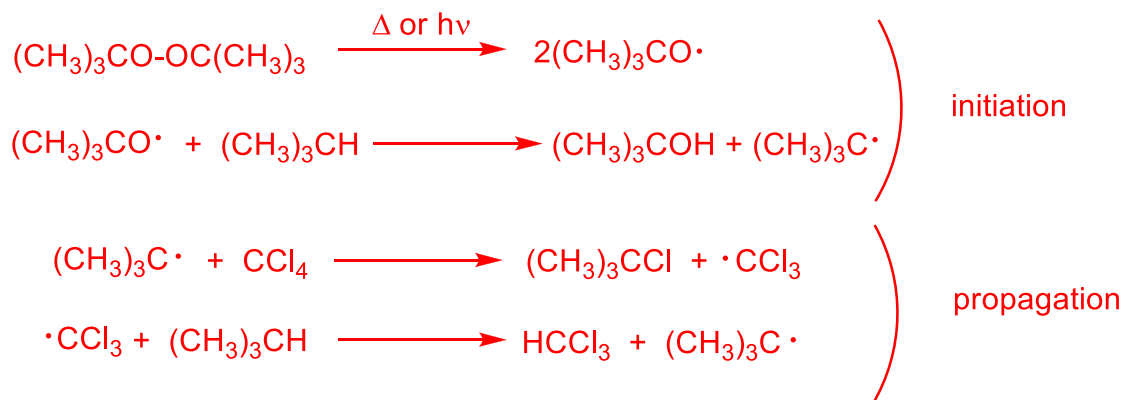


The new intermediate  $\cdot\text{CCl}_3$  starts step 4. What is its fate? Look at the products. It must form  $\text{HCCl}_3$ . The hydrogen must come from the  $(\text{CH}_3)_3\text{CH}$  hence step 4 is:



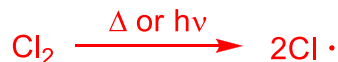
Steps 3 and 4 constitute a chain reaction.

The overall mechanism is:



2. A mixture of  $\text{H}_2$  and  $\text{Cl}_2$  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  $\text{HCl}$  is formed. The photochemical reaction yields as many as a million molecules of  $\text{HCl}$  for each photon absorbed. The presence of a trace of oxygen slows down the reaction. Propose a possible mechanism for this reaction.

initiation



propagation



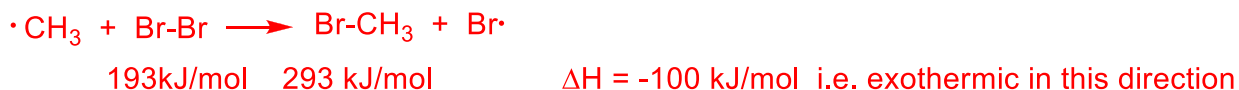
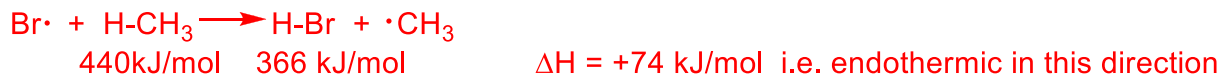
termination



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.



As soon as the  $\text{CH}_3\cdot$  radical forms in the first reaction, it reacts with  $\text{Br}_2$  as the activation energy for the second step is very low.

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



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