Mechanism of Halogenation

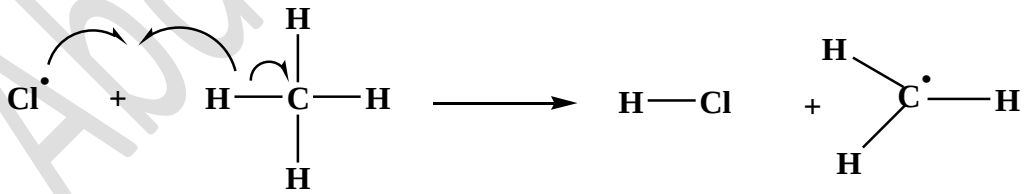
The halogenation reactions of alkanes take place by a radical mechanism. Let's take the example of chlorination of Methane that takes place in the gas phase. Some important experimental observations can be made about this reaction

1. The reaction is promoted by heat or light. Methane and chlorine do not react at room temperature at an appreciable rate if the mixture is kept away from light. However, these do react at room temperature if the gaseous reaction is irradiated with UV light. Methane and chlorine also react in the dark if the gaseous mixture is heated to temperatures greater than 100°C.
2. The light promoted reaction is highly efficient. Relatively small number of photons permits the formation of relatively large amount of chlorinated product.

The reaction takes place in following steps:

1. The first step in the mechanism involves the fragmentation of chlorine molecules, by heat or light, into chlorine atoms or radicals. This step is called the chain initiating step.

2. In step 2, a chlorine atom abstracts a hydrogen atom from a methane molecule. This step produces a molecule of hydrogen chloride and a methyl radical.



3. In step 3 a methyl radical abstracts a chlorine atom from a chlorine molecule and produces a molecule of methyl chloride and chlorine atom. The chlorine atom can now cause a repetition of step 2. Steps 2 and 3 are called chain propagating steps. In these steps one radical generates another.

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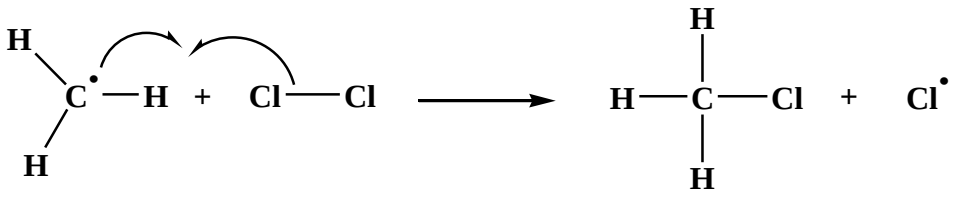
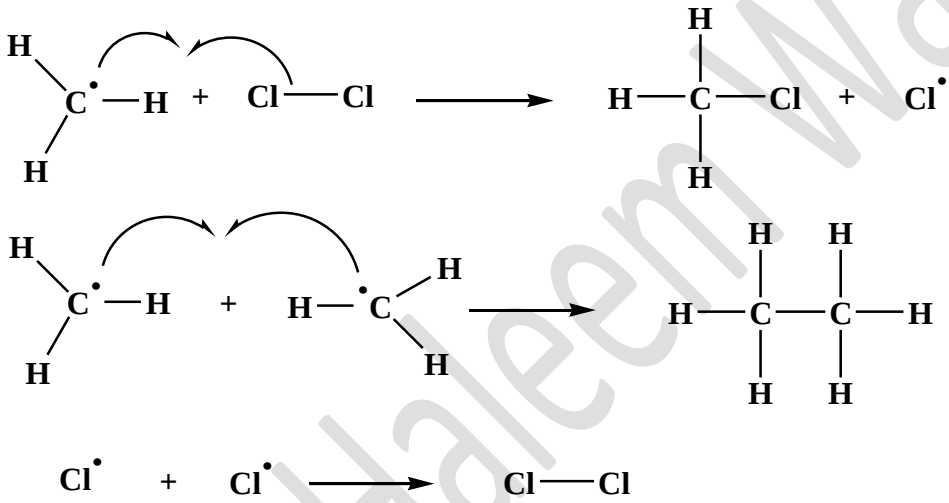
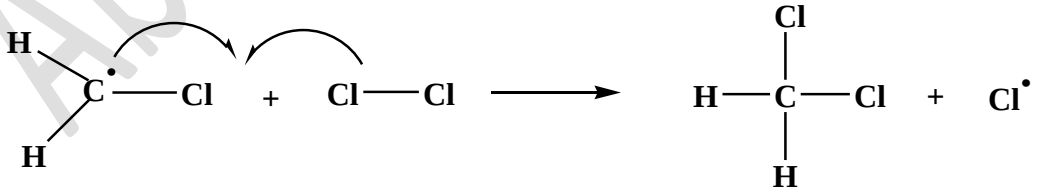


4. The last step is called the chain terminating step. In this step one or both of the already formed reactive intermediates are used up which leads to the chain termination. the Methyl and chloride radicals combine to form methyl chloride. Two methyl radicals combine to form a molecule of ethane. The chlorine radicals combine form a chlorine molecule.



5. As the reaction progresses chloromethane accumulates in the mixture and its hydrogen atoms are also abstracted by chlorine leading to the formation of chloromethyl radicals. Chloromethyl radicals combine with chlorine to produce dichloromethane. Trichloro and tetrachlomethane are also produced similarly.



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