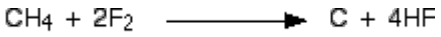
THE HALOGENATION OF ALKANES

Let's discuss the reactions between alkanes with the halogens fluorine, chlorine, bromine and iodine - mainly concentrating on chlorine and bromine.

Alkanes

The reaction between alkanes and fluorine

This reaction is explosive even in the cold and dark, and you tend to get carbon and hydrogen fluoride produced. It is of no particular interest. For example:



The reaction between alkanes and iodine

Iodine doesn't react with the alkanes to any extent - at least, under normal lab conditions.

The reactions between alkanes and chlorine or bromine

There is no reaction in the dark.

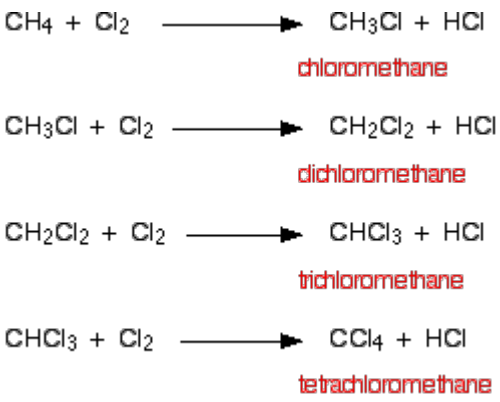
In the presence of a flame, the reactions are rather like the fluorine one - producing a mixture of carbon and the hydrogen halide. The violence of the reaction drops considerably as you go from fluorine to chlorine to bromine.

The interesting reactions happen in the presence of ultra-violet light (sunlight will do). These are ***photochemical reactions***, and happen at room temperature.

We'll look at the reactions with chlorine. The reactions with bromine are similar, but rather slower.

Methane and chlorine

Substitution reactions happen in which hydrogen atoms in the methane are replaced one at a time by chlorine atoms. You end up with a mixture of chloromethane, dichloromethane, trichloromethane and tetrachloromethane.



The original mixture of a colourless and a green gas would produce steamy fumes of hydrogen chloride and a mist of organic liquids. All of the organic products are liquid at room temperature with the exception of the chloromethane which is a gas.

If you were using bromine, you could either mix methane with bromine vapour, or bubble the methane through liquid bromine - in either case, exposed to UV light. The original mixture of gases would, of course, be red-brown rather than green.

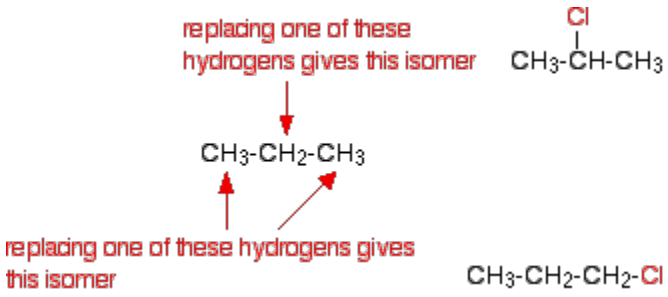
You wouldn't choose to use these reactions as a means of preparing these organic compounds in the lab because the mixture of products would be too tedious to separate.

The mechanisms for the reactions are explained on separate pages.

Larger alkanes and chlorine

You would again get a mixture of substitution products, but it is worth just looking briefly at what happens if only one of the hydrogen atoms gets substituted (monosubstitution) - just to show that things aren't always as straightforward as they seem!

For example, with propane, you could get one of two isomers:



If chance was the only factor, you would expect to get 3 times as much of the isomer with the chlorine on the end. There are 6 hydrogens that could get replaced on the end carbon atoms compared with only 2 in the middle.

In fact, you get about the same amount of each of the two isomers.

If you use bromine instead of chlorine, the great majority of the product is where the bromine is attached to the centre carbon atom.

THE REACTION BETWEEN METHANE AND CHLORINE

A Free Radical Substitution Reaction

This page gives you the facts and a simple, uncluttered mechanism for the free radical substitution reaction between methane and chlorine. If you want the mechanism explained to you in detail, there is a link at the bottom of the page.

The facts

If a mixture of methane and chlorine is exposed to a flame, it explodes - producing carbon and hydrogen chloride. This isn't a very useful reaction!

The reaction we are going to explore is a more gentle one between methane and chlorine in the presence of ultraviolet light - typically sunlight. This is a good example of a photochemical reaction - a reaction brought about by light.

The organic product is chloromethane.

One of the hydrogen atoms in the methane has been replaced by a chlorine atom, so this is a substitution reaction. However, the reaction doesn't stop there, and all the hydrogens in the methane can in turn be replaced by chlorine atoms. Multiple substitution is dealt with on a separate page, and you will find a link to that at the bottom of this page.

The mechanism

The mechanism involves a ***chain reaction.*** During a chain reaction, for every reactive species you start off with, a new one is generated at the end - and this keeps the process going.

The over-all process is known as ***free radical substitution,*** or as a ***free radical chain reaction.***

Chain initiation
The chain is initiated (started) by UV light breaking a chlorine molecule into free radicals.

Chain propagation reactions
These are the reactions which keep the chain going.

Chain termination reactions
These are reactions which remove free radicals from the system without replacing them by new ones.