This page describes the reactions between alkanes and cycloalkanes with the halogens fluorine, chlorine, bromine and iodine - mainly concentrating on chlorine and bromine.

- **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:

  \[CH_4 + 2F_2 \rightarrow C + 4HF\]

- **The reaction between alkanes and iodine**: Iodine does not 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.

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**Methane and Chlorine**

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 that happen at room temperature. We'll look at the reactions with chlorine, although the reactions with bromine are similar, but evolve more slowly.

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.

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\begin{align*}
\text{CH}_4 + \text{Cl}_2 & \quad \rightarrow \quad \text{CH}_3\text{Cl} + \text{HCl} \\
\text{CH}_3\text{C} + \text{Cl}_2 & \quad \rightarrow \quad \text{CH}_2\text{Cl}_2 + \text{HCl} \\
\text{CH}_2\text{C}_2 + \text{Cl}_2 & \quad \rightarrow \quad \text{CHCl}_3 + \text{HCl} \\
\text{CHCl}_3 + \text{Cl}_2 & \quad \rightarrow \quad \text{CCl}_4 + \text{HCl}
\end{align*}
\]

The original mixture of a colorless 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 vapor, 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. One would not 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 three 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 center carbon atom.

Cycloalkanes

The reactions of the cycloalkanes are generally just the same as the alkanes, with the exception of the very small ones - particularly cyclopropane. In the presence of UV light, cyclopropane will undergo substitution reactions with chlorine or bromine just like a non-cyclic alkane. However, it also has the ability to react in the dark. In the absence of UV light, cyclopropane can undergo addition reactions in which the ring is broken. For example, with bromine, cyclopropane gives 1,3-dibromopropane.

This can still happen in the presence of light - but you will get substitution reactions as well. The ring is broken because cyclopropane suffers badly from ring strain. The bond angles in the ring are 60° rather than the normal value of about 109.5° when the carbon makes four single bonds. The overlap between the atomic orbitals in forming the carbon-carbon bonds is less good than it is normally, and there is considerable repulsion between the bonding pairs. The system becomes more stable if the ring is broken.

Contributors

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