

## 4.13: REACTIONS OF ALKANES - A BRIEF OVERVIEW

### Learning Objective

- recognize and distinguish between the two major reactions of alkanes - combustion and halogenation

### COMBUSTION

Complete combustion (given sufficient oxygen) of any hydrocarbon produces *carbon dioxide* and *water*. It is quite important that you can write properly balanced equations for these reactions, because they often come up as a part of thermochemistry calculations. Some are easier than others. For example, with alkanes, the ones with an even number of carbon atoms are marginally harder than those with an odd number!

#### Example: Propane Combustion

For example, with propane ( $C_3H_8$ ), you can balance the carbons and hydrogens as you write the equation down. Your first draft would be:



Counting the oxygens leads directly to the final version:



#### Example: Butane Combustion

With butane ( $C_4H_{10}$ ), you can again balance the carbons and hydrogens as you write the equation down.



Counting the oxygens leads to a slight problem - with 13 on the right-hand side. The simple trick is to allow yourself to have "six-and-a-half"  $O_2$  molecules on the left.



If that offends you, double everything:



The hydrocarbons become harder to ignite as the molecules get bigger. This is because the bigger molecules don't vaporize so easily - the reaction is much better if the oxygen and the hydrocarbon are well mixed as gases. If the liquid is not very volatile, only those molecules on the surface can react with the oxygen. Bigger molecules have greater Van der Waals attractions which makes it more difficult for them to break away from their neighbors and turn to a gas.

Provided the combustion is complete, all the hydrocarbons will burn with a blue flame. However, combustion tends to be less complete as the number of carbon atoms in the molecules rises. That means that the bigger the hydrocarbon, the more likely you are to get a yellow, smoky flame. Incomplete combustion (where there is not enough oxygen present) can lead to the formation of carbon or carbon monoxide. As a simple way of thinking about it, the hydrogen in the hydrocarbon gets the first chance at the oxygen, and the carbon gets whatever is left over! The presence of glowing carbon particles in a flame turns it yellow, and black carbon is often visible in the smoke. Carbon monoxide is produced as a colorless poisonous gas.

#### Note: Why carbon monoxide is poisonous

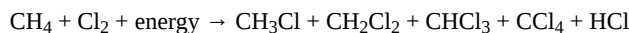
Oxygen is carried around the blood by hemoglobin, which unfortunately binds to exactly the same site on the hemoglobin that oxygen does. The difference is that carbon monoxide binds irreversibly (or very strongly) - making that particular molecule of hemoglobin useless for carrying oxygen. If you breath in enough carbon monoxide you will die from a sort of internal suffocation.

### HALOGENATION OF ALKANES

Halogenation is the replacement of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine or iodine). Unlike the complex transformations of combustion, the halogenation of an alkane appears to be a simple **substitution reaction** in which a C-H bond is broken and a new C-X bond is formed. The chlorination of methane, shown below, provides a simple example of this reaction.



Since only two covalent bonds are broken (C-H & Cl-Cl) and two covalent bonds are formed (C-Cl & H-Cl), this reaction seems to be an ideal case for mechanistic investigation and speculation. However, one complication is that all the hydrogen atoms of an alkane may undergo substitution, resulting in a mixture of products, as shown in the following unbalanced equation. The relative amounts of the various products depend on the proportion of the two reactants used. In the case of methane, a large excess of the hydrocarbon favors formation of methyl chloride as the chief product; whereas, an excess of chlorine favors formation of chloroform and carbon tetrachloride.



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.



chloromethane



dichloromethane



trichloromethane



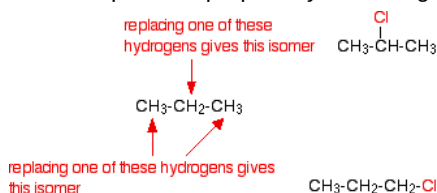
tetrachloromethane

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

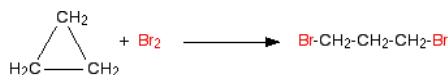
You would again get a mixture of substitution products, but it is worth just looking briefly at what happens if only one of the hydrogen atoms gets substituted (monosubstitution) - just to show that things aren't always as straightforward as they seem! For example, with propane, you could get one of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

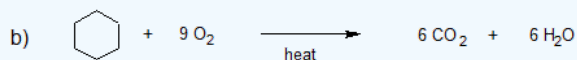
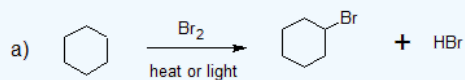


This can still happen in the presence of light - but you will get substitution reactions as well. The ring is broken because cyclopropane suffers badly from ring strain. The bond angles in the ring are 60° rather than the normal value of about 109.5° when the carbon makes four single bonds. The overlap 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.

### Exercise

1. Classify the following reactions as combustion or halogenation.



### Answer

1. a) halogenation
- b) combustion

### CONTRIBUTORS AND ATTRIBUTIONS

- Jim Clark ([Chemguide.co.uk](http://Chemguide.co.uk))
- William Reusch, Professor Emeritus ([Michigan State U.](http://Michigan State U.)), [Virtual Textbook of Organic Chemistry](#)

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