

Reactions of Alkanes: Generally speaking, alkanes are fairly **inert** (i.e non-reactive). A bottle full of an alkane can sit forever without decomposing or reacting with air-borne chemicals. Paraffin Wax, which is made of very large alkanes, is used in home canning because it is not affected by the food being canned.

However, there are three very important classes of reactions that alkanes do take part in. The first is **combustion** and the second is **halogenation**. The first consists of oxidizing the alkane in the presence of O₂ (oxygen gas) to produce CO₂ and H₂O. The internal combustion engines of automobiles are devices that use these reactions to propel cars. Gas burning stoves use combustion of hydrocarbons to produce the heat required to cook.

On the other hand, halogenation is very important. In this type of reaction, halogen gases (F₂, Cl₂, Br₂, and I₂) are reacted with the alkanes (in the presence of light or heat) to produce a *halo-alkane*, or **alkyl halides**. This is an alkane where one of the hydrogen atoms has been replaced by the halogen atom. The other product of this reaction would be the hydrogen halide (i.e. H-X, where X could be F, Cl, Br, or I).

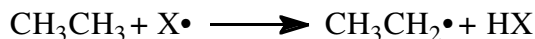
Alkyl halides are very important in the "synthesis" of other alkanes and organic molecules in general. Therefore, we will spend a little more time talking about the reactions that produce them. But first, we should mention the third class of reaction. These reactions are called **pyrolysis** or "**cracking**" reactions, and are very important in the petro-chemical industry. In these reactions, large alkanes are heated to extremely high temperatures (in the absence of O₂), and the products are smaller alkanes. These are kind of "hit or miss" reactions, where the products are not easily predicted.

Free Radical Halogenation: Even though F₂ and I₂ are halogens, their reactivities with alkanes are not too great, namely due to the size of the iodine atoms and the strength of the fluorine-fluorine bond. We will restrict ourselves, therefore, to chlorine and bromine.

In these reactions, the halogen molecule is split into two atoms (known as **free radicals** due to the unpaired electron each has) using heat or light energy. The reaction can be written as:



The halogen free radical is quite reactive. It will try to react with anything it comes into contact with. If, by chance, it comes in contact with an alkane molecule, it will pull off a hydrogen atom to produce HX and a free radical alkyl. For example, if the alkane in question were ethane, we would get:

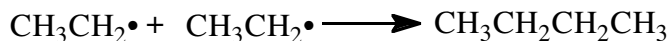
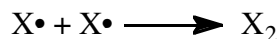
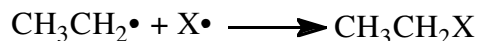


The alkyl radical can run into an un-split X₂ molecule, and extract an X, producing another X• and alkyl halide. In our example of ethane, this reaction is:



These two steps are referred to as **chain propagation steps** since they can continue as long as there is X₂ and ethane available, assuming nothing interferes with them. In other

words, if two free radicals come together, they will form a bond. By forming a bond, they are removing themselves from the cycle. Three possible **chain termination** steps are:



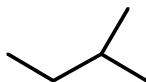
The overall reaction, therefore, is called a "chain reaction".

Another interesting **side** reaction is the multiple halogenation reaction. In this case, the halogen free radical pulls off a hydrogen atom from an alkyl halide. The alkyl halide radical can then go through the propagation steps. However, the likelihood of this occurring when there are still unhalogenated alkanes around is small. As it turns out, it is easier to remove a hydrogen atom from an alkane than from an alkyl halide. If there is A LOT of halogen, then multiple halogenation can, and does, occur.

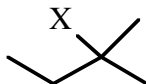
Selectivity and Reactivity: We chose ethane for our example for a good reason. It is a typical alkane, and all the hydrogen atoms on it are equivalent. What if we chose propane? Are all the hydrogen atoms equivalent?

They are not. The central carbon only has two hydrogen atoms, while the outer methyl groups have three, the hydrogen atoms on the central atom are inherently different than the ones on the methyl groups. We refer to the hydrogen atoms on the methyl groups as **primary** (given the symbol 1°), meaning that they are on a carbon that is connected to only 1 other carbon. The hydrogen atoms on the central carbon are called **secondary** (or 2°), meaning the carbon is connected to 2 carbons. Carbons that are connected to 3 other carbons (as in 2-methylpropane) are called **tertiary** (or 3°). In terms of ease of halogenation, the easiest is 3° , then 2° , and finally 1° . Methane is not really a primary carbon, and, as it turns out, is even harder to halogenate.

Therefore, if we tried halogenating 2-methylbutane:



which has 1° , 2° , and 3° carbons, we would expect the product of the halogenation to be:

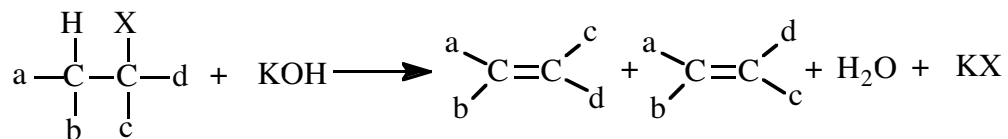


For larger alkanes with many 2° and 3° carbons, there is no way to accurately predict where the halogenation will take place.

One final word about halogenation is that Cl_2 is more reactive than Br_2 . Therefore, it is easier to have a controlled bromination than chlorination.

In the next chapter we will revisit halogenation, but from the point of view of alkenes and alkynes.

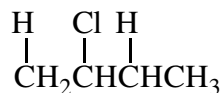
Elimination Reactions: The reactions that produce alkenes from saturated hydrocarbons all share one thing in common: all of them "eliminate" an atom (or group of atoms) in order to produce the desired double bond. The first set of reactions involves the treatment of an halo alkane with a strong base (namely KOH). The reaction can be written as follows:



Note that both the *cis* and the *trans* isomers are formed. This is because the starting alkane has free rotation about the bond, and the orientation of the four things (labeled a,b,c, and d) can vary during the reaction.

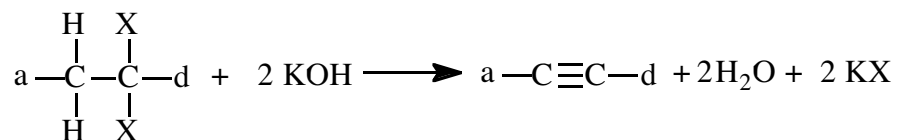
The way the reaction is believed to take place is via an acid-base type reaction. The OH⁻ of the KOH is an Arrhenius base, and it combines with a hydrogen atom from the alkane. The halogen, X, then leaves the molecule as X⁻, and the alkane forms the double bond to re-establish the octets on the two carbons. This type of reaction is also called a **dehydrohalogenation**, because, overall, a molecule of HX (a hydrohalogen) is released.

Consider the example of 2-chlorobutane. The extended formula is:



Note that there are two possible hydrogen atoms that can be pulled off by the OH⁻. Which actually gets pulled off? The answer is BOTH! However, the proportions of products are uneven. Removing the hydrogen from carbon 1 (a "primary" or 1° carbon) is more likely to occur, because the resulting carbanion is more stable. Removing the hydrogen from carbon 3 (a "secondary" or 2° carbon) occurs less readily. Experimentally, the ratio of 1° to 2° alkene is about 4:1. Of course, the 2° alkene has two isomers (*cis* and *trans*), but the ratio of those two in this example is close to 1:1. The take home lesson is that many things can happen in organic chemistry!

Before we talk about other elimination reactions, we should point out that dehydrohalogen-ation is also used to produce alkynes. In this case, the starting material is a dihalogenated alkane, and the elimination reaction is run twice:

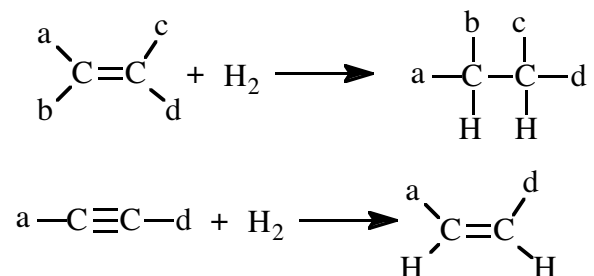


The starting material does not have to have the two halogens on the same carbon for this to work, but other possible products can form as well.

Reactions of Alkenes and Alkynes: Going in the opposite direction, alkenes and alkynes react with H₂ and a catalyst to form alkanes. This is done by **hydrogenation** (also called

"reduction") of the multiple bond. This type of reaction falls into the general class called **addition reactions**.

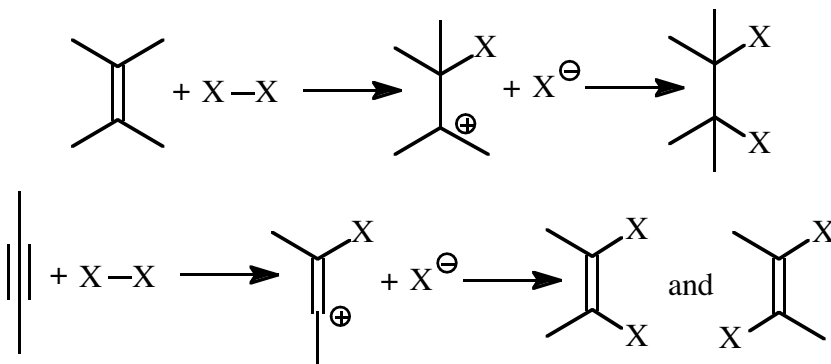
The most common way to complete this reaction is to expose the alkyne or alkene to hydrogen gas in the presence of platinum metal. The hydrogen molecule "sticks" to the multiple bond, and in one swoop breaks the H-H bond and forms the two C-H bonds. This is illustrated below for both the alkene and the alkyne:



The first reaction is not very interesting in that the product is very predictable. The second, however, is very interesting. The **ONLY** product of the single hydrogenation of the alkyne **IS** the *cis* isomer.

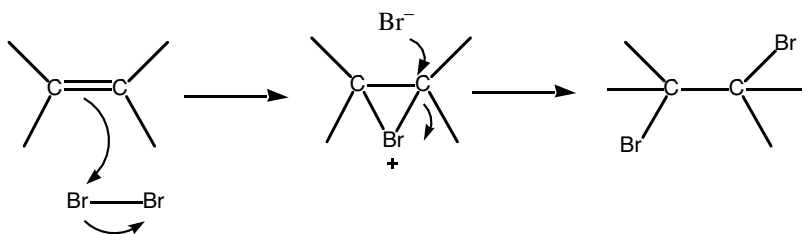
Other things that can add across the multiple bonds are, again not surprisingly, halogens, hydrohalogens, and water. The reason these should not be surprising is that these correspond to the reverse reactions of the multiple bond formation reactions.

Halogenation can occur as follows:



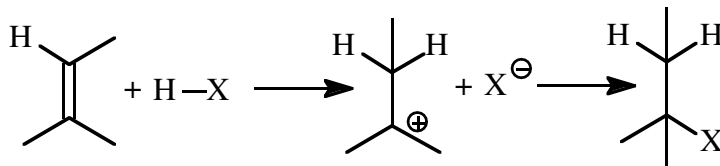
It is interesting to note that both *cis* and *trans* isomers are produced by the halogenation of the alkyne. It should also be pointed out that these reactions must be done **IN THE ABSENCE OF WATER!** Otherwise, the product is a **halohydrin** - a compound that has both a halogen and an -OH.

In the case of bromine being the halogen it is more likely that the reaction will progress through the following mechanism:



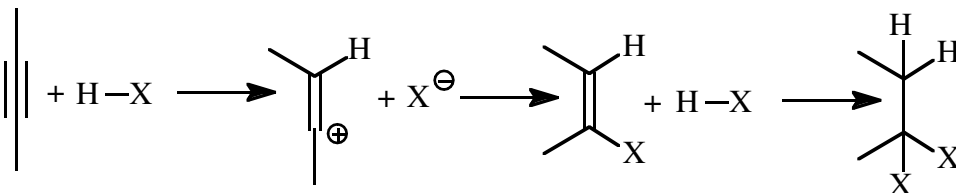
Note the cyclic bromonium ion intermediate. The bromine anion produced in the first step can now attach at either carbon of the newly formed three membered ring. It is possible that reactions involving bromine can follow the first mechanism presented, but studies have shown that the majority of them follow that just presented.

The second reaction, the **hydrohalogenation** occurs in a similar manner. In 1869, Vladimir Markovnikov noticed that the general trend for this is that the H adds to the atom in the double (or triple) bond that has more hydrogen atoms bound to it. This observation is called the **Markovnikov rule**. We can write the mechanism as:



As it turns out, the mechanism above is an over-simplification of the process. Recent evidence indicates that the reaction actually involves at least 2 H-X molecules: one that donates an H⁺, and another that carries the X⁻ to the **carbocation**. This is an example of how long accepted mechanisms are not always right. Remember, "only if we could shrink ourselves to the size of atoms, and observe these reactions first hand could we know how they happen". At any rate, we will treat the reaction as occurring via the mechanism above, for the sake of simplicity.

Markovnikov's rule is especially important when alkynes are doubly hydro-halogenated, because the two halogens ALWAYS end up on the same atom. Thus, we can draw (using the simplified mechanism):

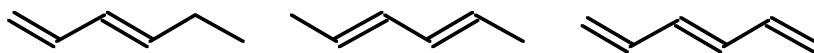


The last addition reaction, **hydration**, involves the adding of water (H₂O) across the double bond. This must be done in the presence of an Arrhenius acid (source of H⁺). This also obeys the Markovnikov rule. However, this does not work as expected for alkynes, since having two -OH groups on the same carbon is very unstable.

Other Reactions: There are many other reactions that involve double and triple bonds. For the sake of time, we will not discuss most of them. However, there is an important side reaction that we should mention, and that is **rearrangement**. In any reaction where a positive charge is placed on a carbon (aka a **carbocation**), the most stable position for the positive charge is at a 2° carbon, not at a 1° one. The most stable place is at a 3° carbon. If, however there is a 3° or 4° carbon next to a 2° carbon that has a positive charge, the 3° or 4° carbon can **shift** an alkyl group to the 2° carbocation.

Polyenes and Conjugation: Although it seems as though having a double bond in a hydrocarbon molecule is unfavorable due to the reactivity of the double bond, the idea of having many double bonds seems even stranger! However, there are many organic molecules that have multiple double bonds. These compounds are referred to as polyenes.

If we examine the common polyenes, we find a very interesting trend. For the most part, the double bonds that comprise the polyene are separated from each other by one single bond. In other words, if we looked at the common (i.e. most stable) hexadiene and heptatriene, we would see:



This particular spatial placement is seen over and over again. The stability imparted by this arrangement is referred to as **resonance** stabilization. This comes from the atomic orbitals that contribute to the double bond; the bonds can switch between adjacent pairs of orbitals. This phenomenon is known as resonance. The order of the bonds, i.e. double bond-single bond-double bond-etc., is called **conjugation**. The conjugated polyenes exhibit an unusual stability.

Another very interesting feature of conjugated polyenes is their color. Most common fabric dyes are composed of conjugated polyenes of some sort.