Pearson

21.6: Hydrocarbon Reactions

One of the most common hydrocarbon reactions is combustion, the burning of hydrocarbons in the presence of oxygen. Hydrocarbon combustion reactions are highly exothermic and are commonly used to warm homes and buildings, to generate electricity, and to power the engines of cars, ships, and airplanes. It is not an exaggeration to say that hydrocarbon combustion makes our current way of life possible. Approximately 90% of the energy produced in the United States is generated by hydrocarbon combustion. Alkanes, alkenes, and alkynes all undergo combustion. In a combustion reaction, the hydrocarbon reacts with oxygen to form carbon dioxide and water:

$$\begin{array}{rcll} \mathrm{CH_3CH_2CH_3}\,(g) + 5\,\mathrm{O_2}\,(g) & \rightarrow & 3\,\mathrm{CO_2}\,(g) + 4\,\mathrm{H_2O}\,(g) & \text{Alkane combustion} \\ \mathrm{CH_2{=}CHCH_2CH_3}\,(g) + 6\,\mathrm{O_2}\,(g) & \rightarrow & 4\,\mathrm{CO_2}\,(g) + 4\,\mathrm{H_2O}\,(g) & \text{Alkene combustion} \\ \mathrm{CH \equiv CCH_3}\,(g) + 4\,\mathrm{O_2}\,(g) & \rightarrow & 3\,\mathrm{CO_2}\,(g) + 2\,\mathrm{H_2O}\,(g) & \text{Alkyne combustion} \end{array}$$

Reactions of Alkanes

In addition to combustion reactions, alkanes also undergo **substitution reactions**, in which one or more hydrogen atoms on an alkane are replaced by one or more other atoms. The most common substitution reaction is *halogen substitution* (also referred to as *halogenation*). For example, methane can react with chlorine gas in the presence of heat or light to form chloromethane:

$$\underset{\text{methane}}{\mathrm{CH_4}\,(g)} + \underset{\text{chlorine}}{\mathrm{Cl_2}\,(g)} \xrightarrow{\text{heat or light}} \underset{\text{chloromethane}}{\mathrm{CH_3Cl}\,(g)} + \mathrm{HCl}\,(g)$$

Ethane also reacts with chlorine gas to form chloroethane:

$$\underset{\text{ethane}}{\mathrm{CH_3CH_3}\,(g)} + \underset{\text{chlorine}}{\mathrm{Cl_2}\,(g)} \xrightarrow{\text{heat or light}} \underset{\text{chloromethane}}{\mathrm{CH_3CH_2Cl}\,(g)} + \mathrm{HCl}\,(g)$$

Multiple halogenation reactions can occur because halogens can replace more than one of the hydrogen atoms on an alkane. For example, chloromethane can react with chlorine, and the product of that reaction can react again (and so on):

$$\underset{\text{chloromethane}}{\mathrm{CH_3Cl}\,(g)} + \underset{\text{chlorine}}{\mathrm{Cl_2}\,(g)} \xrightarrow{\text{heat or light}} \underset{\substack{\text{dichloromethane} \\ \text{(also known as} \\ \text{methylene chloride}}}{\mathrm{CH_2Cl_2}\,(g)} + \mathrm{HCl}\,(g)$$

$$\underset{\text{dichloromethane}}{\mathrm{CH_2Cl_2}\,(g)} + \underset{\text{chlorine}}{\mathrm{Cl_2}\,(g)} \xrightarrow{\text{heat or light}} \underset{\substack{\text{trichloromethane} \\ \text{(also known as} \\ \text{chloroform}}}{\mathrm{CHCl_3}\,(g)} + \mathrm{HCl}\,(g)$$

$$\underset{\text{trichloromethane}}{\mathrm{CHCl_3}\,(g)} + \underset{\text{chlorine}}{\mathrm{Cl_2}\,(g)} \xrightarrow{\text{heat or light}} \underset{\substack{\text{tetrachloromethane} \\ \text{(also known as} \\ \text{carbon tetrachloride}}}{\mathrm{CCl_4}\,(g)} + \mathrm{HCl}\,(g)$$

The general form for halogen substitution reactions is:

$$\underset{\text{alkane}}{\mathrm{R{-}H}} + \underset{\text{halogen}}{\mathrm{X_2}} \xrightarrow{\text{heat or light}} \underset{\text{haloalkane}}{\mathrm{R{-}X}} + \underset{\substack{\text{Hydrogen} \\ \text{halide}}}{\mathrm{HX}}$$

Notice that the halogenation of hydrocarbons requires initiation with heat or light, which causes the chlorine–chlorine bond to break:

$$\mathrm{Cl{-}Cl} \xrightarrow{\text{heat or light}} \mathrm{Cl\cdot + Cl\cdot}$$

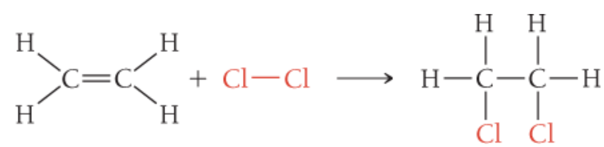
The resulting chlorine atoms are *free radicals* (see Section 5.5), as the dot that represents each chlorine atom's unpaired electron indicates. Chlorine radicals are highly reactive and attack the C—H bond in hydrocarbons. The subsequent reaction proceeds by this mechanism:

$$\begin{aligned} \mathrm{Cl\cdot + R{-}H} &\rightarrow \mathrm{R\cdot + HCl} \\ \mathrm{R\cdot + Cl_2} &\rightarrow \mathrm{R{-}Cl + Cl\cdot} \end{aligned}$$

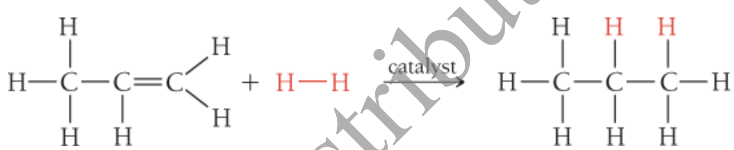
Notice that a chlorine free radical is produced as a product of the last step. This free radical can go on to react again, unless it encounters another chlorine free radical, in which case it reacts with it to re-form Cl_2.

Reactions of Alkenes and Alkynes

Alkenes and alkynes undergo **addition reactions** in which molecules add across (on either side of) the multiple bond. For example, ethene reacts with chlorine gas to form dichloroethane:

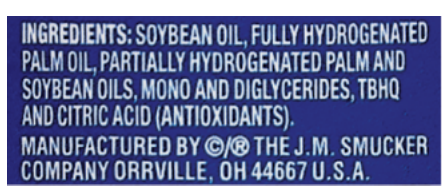


The addition of chlorine converts the carbon–carbon double bond into a single bond because each carbon atom bonds to a chlorine atom. Alkenes and alkynes can also add hydrogen in hydrogenation reactions. For example, in the presence of an appropriate catalyst, propene reacts with hydrogen gas to form propane:



> We often indicate the presence of a catalyst by adding a label over the reaction arrow.

Hydrogenation reactions convert unsaturated hydrocarbons into saturated hydrocarbons. For example, hydrogenation reactions convert unsaturated vegetable oils into saturated fats. Most vegetable oils are unsaturated because their carbon chains contain double bonds. The double bonds put bends into the carbon chains that result in less efficient packing of molecules; thus vegetable oils are liquids at room temperature, while saturated fats are solids at room temperature. When food manufacturers add hydrogen to the double bonds of vegetable oil, the unsaturated fat is converted into a saturated fat, turning the liquid oil into a solid at room temperature. As we have seen so many times, structure determines properties. The words "partially hydrogenated vegetable oil" on a label indicate a food product that contains saturated fats made via hydrogenation reactions.

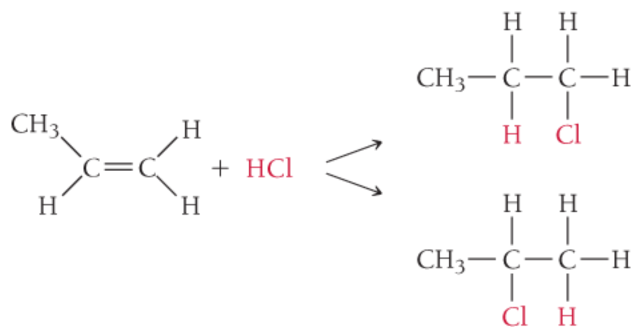


Partially hydrogenated vegetable oil is a saturated fat that is made by hydrogenating unsaturated fats.

Alkenes can also add unsymmetrical reagents across the double bond. For example, ethene reacts with hydrogen chloride to form chloroethane:

chloroethane

If the alkene itself is also unsymmetrical, then the addition of an unsymmetrical reagent leads to the potential for two different products. For example, when HCl reacts with propene, two products are possible:



1-chloropropane (not observed)

2-chloropropane

When this reaction is carried out in the lab, however, only the 2-chloropropane forms. We can predict the product of the addition of an unsymmetrical reagent to an unsymmetrical alkene with *Markovnikov's rule,* which states the following:

> **When a polar reagent is added to an unsymmetrical alkene, the positive end (the least electronegative part) of the reagent adds to the carbon atom that has the most hydrogen atoms.**

In most reactions of this type, the positive end of the reagent is hydrogen; therefore, the hydrogen atom bonds to the carbon atom that already contains the most hydrogen atoms.

Example 21.6 Alkene Addition Reactions

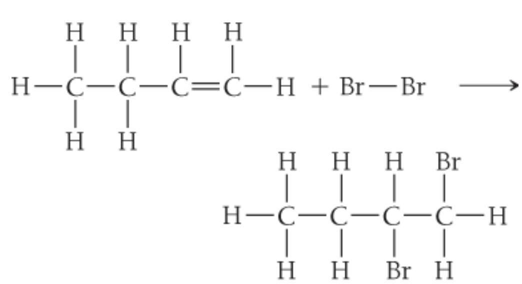
Determine the products of the reactions.

a. $CH_3CH_2CH{=}CH_2 + Br_2 \rightarrow$

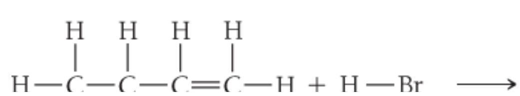
b. $CH_3CH_2CH{=}CH_2 + HBr \rightarrow$

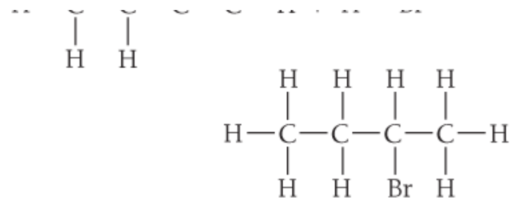
SOLUTION

a. The reaction of 1-butene with bromine is an example of a symmetric addition. The bromine adds across the double bond, and each carbon forms a single bond to a bromine atom.



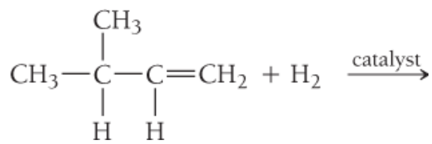
b. The reaction of 1-butene with hydrogen bromide is an example of an unsymmetrical addition. Apply Markovnikov's rule to determine which carbon the hydrogen bonds with and which carbon the bromine atom bonds with. Markovnikov's rule predicts that the hydrogen bonds to the end carbon in this case.





FOR PRACTICE 21.6 Determine the products of the reactions.

a.



b.