The $\Delta H^\circ$ of this reaction, called the enthalpy of hydrogenation, can be measured very accurately and can serve as a source of heats of formation. Consider the following enthalpies of hydrogenation: $(E)$-3-hexene, $-117.9$ kJ mol$^{-1}$ (28.2 kcal mol$^{-1}$); $(Z)$-3-hexene, $-121.6$ kJ mol$^{-1}$ (29.1 kcal mol$^{-1}$). Calculate the heats of formation of these two alkenes, given that the $\Delta H^\circ_f$ of hexane is $-167.2$ kJ mol$^{-1}$ (40.0 kcal mol$^{-1}$).

### 4.6 ADDITION REACTIONS OF ALKENES

The remainder of this chapter considers three reactions of alkenes: the reaction with hydrogen halides; the reaction with hydrogen, called catalytic hydrogenation; and the reaction with water, called hydration. These reactions will be used to establish some important principles of chemical reactivity that are very useful in organic chemistry. We’ll study other alkene reactions in Chapter 5.

The most characteristic type of alkene reaction is addition at the carbon–carbon double bond. The addition reaction can be represented generally as follows:

$$
\begin{align*}
\text{bonds broken} & : \quad \text{C} = \text{C} + \text{X} - \text{Y} \\
\text{bonds formed} & : \quad \text{C} - \text{C} - \text{X} - \text{Y}
\end{align*}
$$

In an addition reaction, the carbon–carbon $\pi$ bond of the alkene and the $\text{X} - \text{Y}$ bond of the reagent are broken, and new $\text{C} - \text{X}$ and $\text{C} - \text{Y}$ bonds are formed.

**PROBLEM 4.18** Give the structure of the addition product formed when ethylene reacts with each of the following reagents:
(a) $\text{H} - \text{I}$  
(b) $\text{Br}_2$  
(c) $\text{BH}_3$  
*Hint: Each of the $\text{B} - \text{H}$ bonds undergoes an addition to one molecule of ethylene. That is, three moles of ethylene react with one mole of $\text{BH}_3$.*

### 4.7 ADDITION OF HYDROGEN HALIDES TO ALKENES

The hydrogen halides $\text{H} - \text{F}$, $\text{H} - \text{Cl}$, $\text{H} - \text{Br}$, and $\text{H} - \text{I}$ undergo addition to carbon–carbon double bonds to give products called alkyl halides, compounds in which a halogen is bound to a saturated carbon atom:

$$
\text{CH}_3\text{CH=CHCH}_3 + \text{H} - \text{Br} \rightarrow \text{CH}_3\text{CH} - \text{CHCH}_3
$$

2-butene  
*(Z or E)*

2-bromobutane  
*(an alkyl halide)*

Although the addition of HF has been used for making alkyl fluorides, HF is extremely hazardous and is avoided whenever possible. Additions of HBr and HI are generally preferred to addition of HCl because additions of HBr and HI are faster.
**A. Regioselectivity of Hydrogen Halide Addition**

When the alkene has an unsymmetrically located double bond, two constitutionally isomeric products are possible.

\[
\text{H}_2\text{C}==\text{CH} (\text{CH}_2)_3\text{CH}_3 + \text{HI} \rightarrow \text{H}_3\text{C}==\text{CH} (\text{CH}_2)_2\text{CH}_3 \quad \text{or} \quad \text{CH}_2==\text{CH}_2 (\text{CH}_2)_3\text{CH}_3 \quad (4.16)
\]

1-hexene

As shown in Eq. 4.16, only one of the two possible products is formed from a 1-alkene in significant amount. Generally, the main product is that isomer in which the halogen is bonded to the carbon of the double bond with the greater number of alkyl substituents, and the hydrogen is bonded to the carbon with the smaller number of alkyl substituents.

(Another way to think about this result is to apply the old aphorism, “Them that has, gets.” That is, the carbon with more hydrogens gains yet another hydrogen in the reaction.) When the products of a reaction could consist of more than one constitutional isomer, and when one of the possible isomers is formed in excess over the other, the reaction is said to be a **regioselective reaction**. Hydrogen halide addition to alkenes is a highly regioselective reaction because addition of the hydrogen halide across the double bond gives only one of the two possible constitutionally isomeric addition products.

When the two carbons of the alkene double bond have equal numbers of alkyl substituents, little or no regioselectivity is observed in hydrogen halide addition, even if the alkyl groups are of different size.

\[
\text{H}_2\text{C}==\text{CH} (\text{CH}_2)_2\text{CH}_3
\]

H goes here I goes here

(4.17)

**Markovnikov’s Rule**

In his doctoral dissertation of 1869, the Russian chemist Vladimir Markovnikov (1838–1904; also spelled Markownikoff) proposed a “rule” for regioselective addition of hydrogen halides to alkenes. This rule, which has since become known as Markovnikov’s rule, was originally stated as follows: “The halogen of a hydrogen halide attaches itself to the carbon of the alkene bearing the lesser number of hydrogens and greater number of carbons.”

Markovnikov’s higher education was in political science, economics, and law. During required organic chemistry courses in the Finance curriculum at the University of Kazan, he became infatuated with organic chemistry and eventually completed his now-famous doctoral dissertation. He was appointed to the chair of chemistry at the University of Moscow in 1873, where he was known not only for his chemistry, but also for his openness to students. He was forced to resign this position in 1893 because he would not sign an apology demanded of the faculty by a political official who had been insulted by a student. He was allowed, however, to continue working in the university for the duration of his life.
4.7 ADDITION OF HYDROGEN HALIDES TO ALKENES

PROBLEM 4.19 Using the known regioselectivity of hydrogen halide addition to alkenes, predict the addition product that results from the reaction of:
(a) H—Cl with 2-methylpropene  (b) H—Br with 1-methylcyclohexene

B. Carboxation Intermediates in Hydrogen Halide Addition

For many years the regioselectivity of hydrogen halide addition had only an empirical (experimental) basis. By exploring the underlying reasons for this regioselectivity, we’ll set the stage to develop a broader understanding of not only this reaction but many others as well.

A modern understanding of the regioselectivity of hydrogen halide addition begins with the fact that the overall reaction actually occurs in two successive steps. Let’s consider each of these in turn.

In the first step, the electron pair in the π bond of an alkene is donated to the proton of the hydrogen halide. The electrons of the π bond react rather than the electrons of σ bonds because π electrons have the highest energy (Sec. 4.1A). As a result, the carbon–carbon double bond is protonated on a carbon atom. The other carbon becomes positively charged and electron-deficient:

\[ \text{RCH} = \text{CHR} \rightarrow \text{RCH}^+ \text{CHR} \]

The species with a positively charged, electron-deficient carbon is called a carboxation, pronounced CAR-bo-CAT-ion. (The term carbonium ion was used in earlier literature.) The formation of the carboxation from the alkene is an electron-pair displacement reaction (Sec. 3.2A) in which the π bond acts as a Brønsted base (Sec. 3.4A) toward the Brønsted acid H—Br. The π bond is a very weak base. Nevertheless, it can be protonated to a small extent by a strong acid such as HBr.

The resulting carboxation is a powerful electron-deficient Lewis acid and is thus a potent electrophile. In the second step of hydrogen halide addition, the halide ion, which is a Lewis base, or nucleophile, reacts with the carboxation at its electron-deficient carbon atom:

\[ \text{RCH} = \text{CHR} \rightarrow \text{RCH} = \text{CHR} \]  \[ \text{a nucleophile} \]

This is a Lewis acid–base association reaction (Sec. 3.1B).

The carboxations involved in hydrogen halide addition to alkenes are examples of reactive intermediates or unstable intermediates: species that react so rapidly that they never accumulate in more than very low concentration. Most carboxations are too reactive to be isolated except under special circumstances. Thus, carboxations cannot be isolated from the reactions of hydrogen halides and alkenes because they react very quickly with halide ions.

The complete description of a reaction pathway, including any reactive intermediates such as carboxations, is called the mechanism of the reaction. To summarize the two steps in the mechanism of hydrogen halide addition to alkenes:

1. A carbon of the π bond is protonated.
2. A halide ion reacts with the resulting carboxation.
Now that we understand the mechanism of hydrogen halide addition to alkenes, let’s see how the mechanism addresses the question of regioselectivity. When the double bond of an alkene is not located symmetrically within the molecule, protonation of the double bond can occur in two distinguishable ways to give two different carbocations. For example, protonation of 2-methylpropene can give either the tert-butyl cation (Eq. 4.19a) or the isobutyl cation (Eq. 4.19b):

These two reactions are in competition—that is, one can only happen at the expense of the other because the two reactions compete for the same starting material. Only the tert-butyl cation is formed in this reaction. The tert-butyl cation is formed exclusively because reaction 4.19a is much faster than reaction 4.19b. Because the tert-butyl cation is the only carbocation formed, it is the only carbocation available to react with the bromide ion. Hence, the only product of HBr addition to 2-methylpropene is tert-butyl bromide.

Notice that the bromide ion has become attached to the carbon of 2-methylpropene bearing the greater number of alkyl groups. In other words, the regioselectivity of hydrogen halide addition is due to the formation of only one of two possible carbocations.

To understand why the tert-butyl cation is formed more rapidly than the isobutyl cation in HBr addition, we need to understand the factors that influence reaction rate. The relative stability of carbocations plays an important role in understanding the rate of HBr addition. A discussion of carbocation stability, then, is an essential prelude to a more general discussion of reaction rates.
C. Structure and Stability of Carbocations

Carbocations are classified by the degree of alkyl substitution at their electron-deficient carbon atoms.

\[
\text{primary} \quad \text{secondary} \quad \text{tertiary}
\]

That is, primary carbocations have one alkyl group bound to the electron-deficient carbon, secondary carbocations have two, and tertiary carbocations have three. For example, the isobutyl cation in Eq. 4.19b is a primary carbocation, and the tert-butyl cation in Eq. 4.19a is a tertiary carbocation.

The gas-phase heats of formation of the isomeric butyl carbocations are given in Table 4.2. The data in this table show that alkyl substituents at the electron-deficient carbon strongly stabilize carbocations. (A comparison of the first two entries shows that substituents at other carbons have a much smaller effect on stability.) The relative stability of isomeric carbocations is therefore as follows.

\[
\text{Stability of carbocations: tertiary} > \text{secondary} > \text{primary}
\]

Remember that “greater stability” means “lower energy.”

To understand the reasons for this stability order, consider first the geometry and electronic structure of carbocations, shown in Fig. 4.10 (p. 152) for the tert-butyl cation. The electron-deficient carbon of the carbocation has trigonal planar geometry (Sec. 1.3B) and is therefore \(sp^2\)-hybridized, like the carbons involved in double bonds (Sec. 4.1A); however, in a carbocation, the \(2p\) orbital on the electron-deficient carbon contains no electrons.

The explanation for the stabilization of carbocations by alkyl substituents is in part the same as the explanation for the stabilization of alkenes by alkyl substitution (Sec. 4.5B)—the greater number of \(sp^2–sp^3\) carbon–carbon bonds in a carbocation with a greater number of alkyl substituents. However, if you compare the data in Tables 4.1 (p. 145) and 4.2, you’ll notice that each alkyl branch stabilizes an alkene by about 7 kJ mol\(^{-1}\), but each branch stabilizes a carbocation by nearly 70 kJ mol\(^{-1}\). In other words, the stabilization of carbocations by alkyl substituents is considerably greater than the stabilization of alkenes.

<table>
<thead>
<tr>
<th>Cation structure</th>
<th>Name</th>
<th>Heat of formation</th>
<th>Relative energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3)</td>
<td>butyl cation</td>
<td>845</td>
<td>155</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{CH}_2\text{C}^+)</td>
<td>isobutyl cation</td>
<td>828</td>
<td>138</td>
</tr>
<tr>
<td>(\text{CH}_3\text{C}^+\text{CH}_2\text{CH}_3)</td>
<td>sec-butyl cation</td>
<td>757</td>
<td>67</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{CH}_2\text{C}^+)</td>
<td>tert-butyl cation</td>
<td>690</td>
<td>(0)</td>
</tr>
</tbody>
</table>

*Energy difference between each carbocation and the more stable tert-butyl cation
An additional factor that accounts for the stabilization of carbocations by alkyl branching is a phenomenon called **hyperconjugation**, which is the overlap of bonding electrons from the adjacent $\sigma$ bonds with the unoccupied 2$p$ orbital of the carbocation. In this diagram, the $\sigma$ bond that provides the bonding electrons is a C—H bond. The energetic advantage of hyperconjugation is that it involves **additional bonding**. That is, the electrons in the C—H bonds participate in bonding not only with the C and H, but also with the electron-deficient carbon. Additional bonding is a stabilizing effect. We can show this additional bonding with resonance structures as follows:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\]

The shared electrons are shown in color. (Note that the proton in the right-hand structure hasn’t moved; it’s still part of the molecule.) The double-bond character suggested by the resonance structure on the right is reflected in the lengths of the carbon–carbon bonds in the *tert*-butyl cation. These bonds are considerably shorter (1.442 Å) than the $sp^2$-$sp^3$ C—C bond length in propene because of hyperconjugation, which is discussed below.

Let’s now bring together what you’ve learned about carbocation stability and the mechanism of hydrogen halide addition to alkenes. The addition occurs in two steps. In the first step, protonation of the alkene double bond occurs **at the carbon with the fewer alkyl substituents**.
so that the more stable carbocation is formed—that is, the one with the greater number of alkyl substituents at the electron-deficient carbon. The reaction is completed when the halide ion reacts with the electron-deficient carbon.

An understanding of many organic reactions hinges on an understanding of the reactive intermediates involved. Carbocations are important reactive intermediates that occur not only in the mechanism of hydrogen halide addition, but in the mechanisms of many other reactions as well. Hence, your knowledge of carbocations will be put to use often.

George Olah, a Holiday Party, and a Nobel Prize

Because carbocations are in most cases reactive intermediates that are too unstable to isolate, they remained hypothetical for many years after their existence was first postulated. However, their importance as reactive intermediates led to repeated, unsuccessful efforts to prepare them. In 1966–67, a team of researchers led by Professor George A. Olah (b. 1912), then at Case Western Reserve University, figured out how to prepare a number of pure carbocation salts in solution and studied their properties. For example, they formed a solution of essentially pure tert-butyl cation by protonation of 2-methylpropene at $-80\, ^\circ C$. As the acid, they used HF in the presence of the powerful Lewis acid $\text{SbF}_5$, which actually forms the very strong acid $\text{H}^+\text{SbF}_6$.

The fluoride ion is so tightly held within the $\text{SbF}_6^-$ complex ion that it can't act as a nucleophile towards the tert-butyl cation.

The discovery of this method by Olah’s group was somewhat serendipitous. In 1966, his group had only recently discovered $\text{HSbF}_6$, which they called “magic acid.” Following a holiday party, they put a piece of a holiday candle into magic acid. When they saw that it dissolved, they examined the solution in a nuclear magnetic resonance (NMR) instrument. (You’ll learn about NMR as a method for determining structure in Chapter 13.) They saw unmistakable evidence for carbocations. This was the beginning of a very productive series of investigations in which a number of carbocations were generated and examined structurally. Subsequently, Olah joined the faculty of the University of Southern California. He received the 1994 Nobel Prize in Chemistry for his work in carbocation chemistry.

PROBLEM 4.20  By writing the curved-arrow mechanism of the reaction, predict the product of the reaction of $\text{HBr}$ with 2-methyl-1-pentene.

Study Problem 4.9

Give the structure of an alkene that would give 2-bromopentane as the major (or sole) product of $\text{HBr}$ addition. (The numbers are for reference in the solution.)

\[
\text{an alkene} + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3_3 \quad 2\quad 1
\]

2-bromopentane

Solution  The bromine of the product comes from the H—Br. However, there are many hydrogens in the product! Which ones were there to start with, and which one came from the H—Br?
First, recognize that the carbon bearing the bromine must have originally been one carbon of the double bond. It then follows that the other carbon of the double bond must be an adjacent carbon (because two carbons involved in the same double bond must be adjacent). Use this fact to construct all possible alkenes that might be starting materials. Do this by “thinking backward”: Remove the bromine and a hydrogen from each adjacent carbon in turn.

Remove Br from carbon-2 and H from carbon-3 $\leftrightarrow$ CH$_3$CH$_2$CH=CHCH$_3$

2-pentene (cis or trans)

Remove Br from carbon-2 and H from carbon-1 $\leftrightarrow$ CH$_3$CH$_2$CH$_2$CH=CH$_2$

1-pentene

(The symbol $\leftrightarrow$ means “implies as starting material.”) Which of these is correct? Or are they both correct? You haven’t finished the problem until you’ve mentally carried out the addition of HBr to each compound. Doing this and applying the known regioselectivity of HBr addition leads to the conclusion that the desired alkyl halide could be prepared as the major product from 1-pentene. However, both carbons of the double bond of 2-pentene bear the same number of alkyl groups. Eq. 4.17 (p. 148) indicates that from this starting material we should expect not only the desired product, but also a second product:

CH$_3$CH$_2$CH=CHCH$_3$ + HBr $\rightarrow$ CH$_3$CH$_2$CH$_2$CHCH$_3$ + CH$_3$CH$_2$CHCH$_3$CH$_3$

2-bromopentane 3-bromopentane

Furthermore, the two products should be formed in nearly equal amounts. This means the yield of the desired compound would be relatively low and it would be difficult to separate from its isomer, which has almost the same boiling point. Consequently, 1-pentene is the only alkene that will give the desired alkyl halide as the major product (that is, the one formed almost exclusively).

In solving this type of problem, it isn’t enough to identify potential starting materials. You must also determine whether they really will work, given the known characteristics—in this case, the regioselectivity—of the reaction.

PROBLEM 4.21 In each case, give two different alkene starting materials that would react with H—Br to give the compound shown as the major (or only) addition product.

(a) CH$_3$CH$_3$

(b) CH$_3$

D. Carbocation Rearrangement in Hydrogen Halide Addition

In some cases, the addition of a hydrogen halide to an alkene gives an unusual product, as in the following example.
The minor product is the result of ordinary regioselective addition of HCl across the double bond. The origin of the major product, however, is not obvious. Examination of the carbon skeleton of the major product shows that a \textit{rearrangement} has occurred. In a \textit{rearrangement}, a group from the starting material has moved to a different position in the product. In this case, a methyl group of the alkene (red) has changed positions. As a result, the carbons of the alkyl halide product are connected differently from the carbons of the alkene starting material. Although the rearrangement leading to the second product may seem strange at first sight, it is readily understood by considering the fate of the carbocation intermediate in the reaction.

The reaction begins like a normal addition of HCl—that is, by protonation of the double bond to yield the carbocation with the greater number of alkyl substituents at the electron-deficient carbon.

\begin{equation}
\begin{align*}
\text{CH}_3 & \hspace{1cm} \text{CH}_3 \\
\text{H}_3\text{C} & \hspace{1cm} \text{H}_3\text{C} \\
\text{C} & \hspace{1cm} \text{C} \\
\text{CH}=\text{CH}_2 & \hspace{1cm} \text{CH} \equiv \text{CH}_2 \\
\text{CH}_3 & \hspace{1cm} \text{HCl} \\
\text{CH}_3 & \hspace{1cm} \text{Cl} \\
\text{Cl} & \hspace{1cm} \text{CH}_3 \\
\end{align*}
\end{equation}

(4.25)

(17\% of product) (83\% of product)

Reaction of this carbocation with Cl\textsuperscript{−} occurs, as expected, to yield the minor product of Eq. 4.25. However, the carbocation can also undergo a second type of reaction: it can \textit{rearrange}.

\begin{equation}
\begin{align*}
\text{CH}_3 & \hspace{1cm} \text{CH}_3 \\
\text{H}_3\text{C} & \hspace{1cm} \text{H}_3\text{C} \\
\text{C} & \hspace{1cm} \text{C} \\
\text{CH}=\text{CH}_2 & \hspace{1cm} \text{CH} \equiv \text{CH}_2 \\
\text{CH}_3 & \hspace{1cm} \text{HCl} \\
\text{CH}_3 & \hspace{1cm} \text{Cl} \\
\text{Cl} & \hspace{1cm} \text{CH}_3 \\
\end{align*}
\end{equation}

(4.26)

In this reaction, the methyl group moves \textit{with its pair of bonding electrons} from the carbon adjacent to the electron-deficient carbon. The carbon from which this group departs, as a result, becomes electron-deficient and positively charged. That is, the rearrangement converts one carbocation into another. This is essentially a \textit{Lewis acid–base reaction} in which the electron-deficient carbon is the Lewis acid and the migrating group \textit{with its bonding electron pair} is the Lewis base. The reaction forms a new Lewis acid—the electron-deficient carbon of the rearranged carbocation.

The major product of Eq. 4.25 is formed by the Lewis acid–base association reaction of Cl\textsuperscript{−} with the new carbocation.

\begin{equation}
\begin{align*}
\text{CH}_3 & \hspace{1cm} \text{CH}_3 \\
\text{H}_3\text{C} & \hspace{1cm} \text{H}_3\text{C} \\
\text{C} & \hspace{1cm} \text{C} \\
\text{CH}=\text{CH}_2 & \hspace{1cm} \text{CH} \equiv \text{CH}_2 \\
\text{CH}_3 & \hspace{1cm} \text{HCl} \\
\text{CH}_3 & \hspace{1cm} \text{Cl} \\
\text{Cl} & \hspace{1cm} \text{CH}_3 \\
\end{align*}
\end{equation}

(4.27b)

Why does rearrangement of the carbocation occur? In the case of reaction 4.27a, a more stable tertiary carbocation is formed from a less stable secondary one. Therefore, \textit{rearrangement is favored by the increased stability of the rearranged ion}.
You’ve now learned two pathways by which carbocations can react. They can (1) react with a nucleophile and (2) rearrange to more stable carbocations. The outcome of Eq. 4.25 represents a competition between these two pathways. In any particular case, one cannot predict exactly how much of each different product will be obtained. Nevertheless, the reactions of carbocation intermediates show why both products are reasonable.

Carbocation rearrangements are not limited to the migrations of alkyl groups. In the following reaction, the major product is also derived from the rearrangement of a carbocation intermediate. This rearrangement involves a **hydride shift**, the migration of a hydrogen *with its two bonding electrons*.

The hydride migrates instead of an alkyl group because the rearranged carbocation is tertiary and thus is more stable than the starting carbocation. Migration of an alkyl group would have given another secondary carbocation.

Keep in mind the following points about the rearrangement of carbocation intermediates, all of which are illustrated by the examples in this section.

1. A rearrangement almost always occurs when a more stable carbocation can result.
2. A rearrangement that would give a less stable carbocation generally doesn’t occur.
3. The group that migrates in a carbocation rearrangement comes from a carbon *directly attached* to the electron-deficient, positively charged carbon of the carbocation.
4. The group that migrates in a rearrangement is typically an alkyl group, aryl group (p. 82), or a hydrogen.
5. When there is a choice between the migration of an alkyl group (or aryl group) or a hydrogen from a particular carbon, hydride migration typically occurs because it gives the more stable carbocation.

The First Description of Carbocation Rearrangements
The first clear formulation of the involvement of carbocations in molecular rearrangements was proposed by Frank C. Whitmore (1887–1947) of Pennsylvania State University. (In fact, such rearrangements were once called “Whitmore shifts.”) Whitmore said that carbocation rearrangements result when “an atom in an electron-hungry condition seeks its missing electron pair from the next atom in the molecule.” Whitmore’s description emphasizes the Lewis acid–base character of the reaction. Carbocation rearrangements are not just a laboratory curiosity; they occur extensively in living organisms, particularly in the biological pathways leading to certain cyclic compounds such as steroids.

PROBLEMS
4.22 Which of the following carbocations is likely to rearrange? If rearrangement occurs, give the structure of the rearranged carbocation.

(a) \( \text{H} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \)

(b) \( \text{CH}_3 \quad \text{CH}_3 \quad \text{C} \equiv \text{CH}_3 \quad \text{CH}_3 \)

(c) \( \text{CH}_3 \quad \text{CH}_3 \quad \text{C} \equiv \text{CH}_3 \quad \text{CH}_3 \)

4.23 Draw the curved-arrow mechanism for the reaction in Eq. 4.29 that accounts for the formation of both products.

4.24 Only one of the following three alkyl halides can be prepared as the major product of the addition of HBr to an alkene. Which compound can be prepared in this way? Explain why the other two cannot be prepared in this way.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \quad \text{Br} \quad \text{Br} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{H}_3 \]

4.8 REACTION RATES
Whenever a reaction can give more than one possible product, two or more reactions are in competition. (You’ve already seen examples of competing reactions in hydrogen halide addition to alkenes.) One reaction predominates when it occurs more rapidly than other competing reactions. Understanding why some reactions occur in preference to others, then, is often a matter of understanding the rates of chemical reactions. The theoretical framework for discussing reaction rates is the subject of this section. Although we’ll use hydrogen halide addition to alkenes as our example to develop the theory, the general concepts will be used throughout this text.