This is an electron-pair displacement reaction. As this example illustrates, the electrophile in this type of reaction both accepts and releases electrons, but the leaving group only accepts electrons. Therefore, electronegativity is more important for the leaving group. Although the mechanisms of the other addition reactions differ somewhat, we’ll find that the same issues are present.

Because of the similarity of these addition reactions and others like them, they are grouped as a class and referred to as electrophilic additions. An addition reaction is an electrophilic addition when it begins with the donation of an electron pair from a π bond to an electrophile.

**PROBLEM 5.1**

(a) Iodine azide, I—N₃, adds to isobutylene in the following manner:

\[
\begin{align*}
(CH_2)_2C\equiv CH_2 + \begin{array}{c}
\text{iodine azide} \\
\text{iodine azide}
\end{array} & \rightarrow (CH_2)_2C\equiv CH_2 \begin{array}{c}
\text{iodine azide} \\
\text{iodine azide}
\end{array}
\end{align*}
\]

Which group is the electrophilic group to which the π bond donates electrons? How do you know? Does this result fit the electronegativity pattern for electrophilic additions? Explain.

(b) Predict the product of the following electrophilic addition reaction, and explain your reasoning.

\[
(\text{CH}_3)_2C\equiv CH_2 + \begin{array}{c}
\text{iodine bromide} \\
\text{iodine bromide}
\end{array} \rightarrow
\]

**5.2 REACTIONS OF ALKENES WITH HALOGENS**

**A. Addition of Chlorine and Bromine**

Halogens undergo addition to alkenes.

\[
\begin{align*}
\text{cis- or trans-2-butene} & \xrightarrow{\text{CH}_3\text{Cl}_2 \text{ (solvent)}} \text{2,3-dibromobutane} \\
\text{cyclohexene} & \xrightarrow{\text{CCl}_4 \text{ (solvent)}} \text{1,2-dichlorocyclohexane}
\end{align*}
\]

The products of these reactions are vicinal dihalides. Vicinal (Latin vicinus, for “neighborhood”) means “on adjacent sites.” Thus, vicinal dihalides are compounds with halogens on adjacent carbons.

Bromine and chlorine are the two halogens used most frequently in halogen addition. Fluorine is so reactive that it not only adds to the double bond but also rapidly replaces all the hydrogens with fluorines, often with considerable violence. Iodine adds to alkenes at low temperature, but most diiodides are unstable and decompose to the corresponding alkenes and I₂.
at room temperature. Because bromine is a liquid that is more easily handled than chlorine gas, many halogen additions are carried out with bromine. Inert solvents such as methylene chloride (CH₂Cl₂) or carbon tetrachloride (CCl₄) are typically used for halogen additions because these solvents dissolve both halogens and alkenes. The addition of bromine to most alkenes is so fast that when bromine is added dropwise to a solution of the alkene the red bromine color disappears almost immediately. In fact, this discharge of color is a useful qualitative test for alkenes.

Bromine addition can occur by a variety of mechanisms, depending on the solvent, the alkene, and the reaction conditions. One of the most common mechanisms involves a reactive intermediate called a bromonium ion.

\[
\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{Br}_2 \rightleftharpoons \text{CH}_3\text{CH} - \text{CHCH}_3 :\text{Br}^+ \quad (5.10)
\]

A bromonium ion is a species that contains a bromine bonded to two carbon atoms; the bromine has an octet of electrons and a positive charge. Formation of the bromonium ion occurs in a single mechanistic step. However, it is easier to understand how it is formed if we dissect bromonium-ion formation into two fictitious steps. In the first step, the electrons of the π bond are donated to one of the bromines, the other bromine acts as a leaving group, and a carbocation is formed. This is exactly like carbocation formation in the reaction of HBr with an alkene, except that in this case, Br rather than H is the electrophile. In the second step, the carbocation undergoes a Lewis acid–base association reaction with the neighboring bromine.

Step 2 is an intramolecular (internal) Lewis acid–base association reaction. The intramolecular reaction occurs in preference to the intermolecular reaction with bromide ion because the first bromine is “next door” and, unlike the bromide ion, doesn’t have to rely on random diffusion to find the carbocation.

Bromonium ions are favored energetically over carbocations because every atom in a bromonium ion has a full octet of electrons. Although bromonium ions, like carbocations, are reactive intermediates, bromonium ions have been isolated under special conditions. Analogous halonium ions form when chlorine or iodine reacts with alkenes.

The mechanism in Eq. 5.11, through conceptually useful, is fictitious because carbocations are not actual intermediates in most halogen additions. We know this because alkenes that give carbocation rearrangements in HBr addition do not give rearranged products in bromine addition. Other evidence involves stereochemical arguments, which we’ll consider in Chapter 7. Hence, we revise our fictitious mechanism in Eq. 5.11 to show the formation of the bromonium ion in a single step. To do this, we merge the curved arrows of the two steps into a single step.
5.2 REACTIONS OF ALKENES WITH HALOGENS

Bromine addition is completed when the bromide ion donates an electron pair to either one of the ring carbons of the bromonium ion.

This is another electron-pair displacement reaction (Sec. 3.2), in which the nucleophile is bromide ion, the electrophile is the carbon that accepts an electron pair from the nucleophile, and the leaving group is the bromine of the bromonium ion. (The leaving group doesn’t actually leave the molecule, because it is tethered by another bond.) This reaction occurs because the positively charged bromine is very electronegative and readily accepts an electron pair. It also occurs because, as we’ll learn in Chapter 7, three-membered rings are strained, as you can see if you attempt to build a model; opening a three-membered ring releases considerable energy.

B. Halohydrins

In the addition of bromine, the only nucleophile (Lewis base) available to react with the bromonium ion is the bromide ion (Eq. 5.13c). When other nucleophiles are present, they, too, can react with the bromonium ion to form products other than dibromides. A common situation of this type occurs when the solvent itself is a Lewis base. For example, when an alkene is treated with bromine in a solvent containing a large excess of water, a water molecule rather than bromide ion reacts with the bromonium ion.

Loss of a proton from the oxygen in a Brønsted acid–base reaction gives the product.
The product is an example of a bromohydrin: a compound containing both an —OH and a —Br group. Bromohydrins are members of the general class of compounds called halohydrins, which are compounds containing both a halogen and an —OH group. In the most common type of halohydrin, the two groups occupy adjacent, or vicinal, positions.

Halohydrin formation involves the net addition to the double bond of the elements of a hypo-halous acid, such as hypobromous acid, HOBr, or hypochlorous acid, HOCl. Although the products of I₂ addition are unstable (see Sec. 5.2A), iodohydrins can also be prepared.

When the double bond of the alkene is positioned unsymmetrically, the reaction of water with the bromonium ion can give two possible products, each resulting from breakage of a different carbon–bromine bond. The reaction is highly regioselective, however, when one carbon of the alkene contains two alkyl substituents.

The reason for this regioselectivity can be seen from the structure of the bromonium ion (Fig. 5.1). In this structure, about 90% of the positive charge resides on the tertiary carbon, and

![Figure 5.1](image-url)
the bond between this carbon and the bromine is so long and weak that this species is essen-
tially a carbocation containing a weak carbon–bromine interaction.

Water reacts with the bromonium ion at the tertiary carbon, and the weaker bond to the leav-
ing group is broken, to give the observed regioselectivity.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \vdash \quad \text{C} \quad \vdash \quad \text{CH}_2 \\
\text{H}_3\text{C} & \quad \vdash \quad \text{OH}_2
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \vdash \quad \text{C} \quad \vdash \quad \text{CH}_2 \quad \vdash \quad \text{OH}_3 \\
\text{H}_3\text{C} & \quad \vdash \quad \text{Br}
\end{align*}
\]

Water reacts with the bromonium ion at the tertiary carbon, and the weaker bond to the leav-
ing group is broken, to give the observed regioselectivity.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \vdash \quad \text{C} \quad \vdash \quad \text{CH}_2 + \text{H}_3\text{O}^+ \\
\text{H}_3\text{C} & \quad \vdash \quad \text{Br}
\end{align*}
\]  (5.16)

**Study Problem 5.1**

Which of the following chlorohydrins could be formed by addition of Cl\(_2\) in water to an alkene? Explain.

\[
\begin{align*}
\text{Cl} & \quad \text{OH} \\
\text{H}_3\text{C} & \quad \vdash \quad \text{C} \quad \vdash \quad \text{CH}_3 \\
\text{CH}_3 & \quad \vdash \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{Cl} & \quad \text{OH} \\
\text{A} & \quad \vdash \quad \text{C} \quad \vdash \quad \text{CH}_3 \\
\text{CH}_3 & \quad \vdash \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{B} & \quad \vdash \quad \text{C} \quad \vdash \quad \text{CH}_2 \quad \vdash \quad \text{OH}_2 \\
\text{H}_3\text{C} & \quad \vdash \quad \text{Br}
\end{align*}
\]

**Solution** The mechanistic reasoning used in this section shows that the nucleophile (water) reacts with the carbon of the double bond that has more alkyl substituents. In compound \(A\), the carbon bearing the —OH group has fewer alkyl substituents than the one bearing the —Cl. Hence, this compound could not be formed in the reaction of Cl\(_2\) and water with an alkene. Compound \(B\) could be formed by such a reaction, however, because the —OH group is at a carbon with more alkyl substituents than the —Cl. Don’t forget that the carbons of the ring are alkyl groups even though they are part of the ring structure.

**PROBLEMS**

5.2 Give the products, and the mechanisms for their formation, when 2-methyl-1-hexene reacts with each of the following reagents.
(a) Br\(_2\) in H\(_2\)O  (b) Br\(_2\)
(e) iodine azide (I—N\(_3\)) *(Hint: See Problem 5.1a.)*

5.3 Give the structure of the alkene that could be used as a starting material to form chlorohydrin \(B\) in Study Problem 5.1.

5.4 The bromine atom in the bromonium ion in Eq. 5.13 (p. 183) has a positive formal charge. Why can’t this bromine undergo a Lewis acid–base association reaction with a nucleophile?