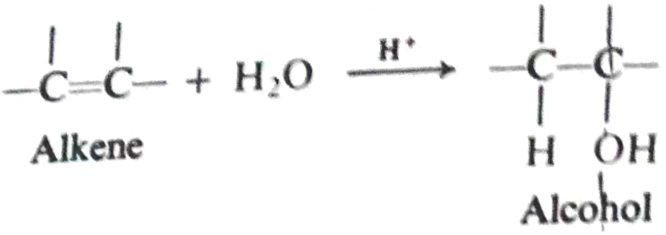
9.8 Addition of water. Hydration

Water adds to the more reactive alkenes in the presence of acids to yi alcohols. Since this addition, too, follows Markovnikov's rule, the alcohols are



$$-\overset{|}{C}=\overset{|}{C}- + H_2O \xrightarrow{H^+} -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{OH}{|}}{\overset{|}{C}}-$$

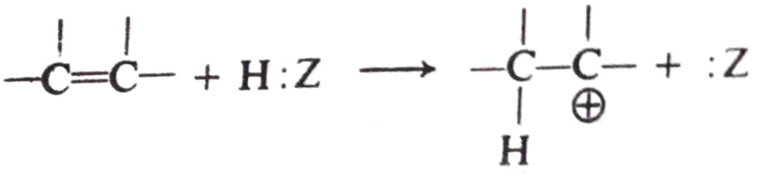
same as those obtained by the two-step synthesis just described. Hydration alkenes, directly or via the alkyl hydrogen sulfates, is the principal industrial sour of those lower alcohols whose formation is consistent with Markovnikov's rule.

9.9 Electrophilic addition: mechanism

Before we take up other reactions of alkenes, let us examine the mechanis of the reactions we have discussed so far. After we have done this, we shall retur to our systematic consideration of alkene reactions, prepared to understand the better in terms of these earlier reactions.

Addition of the acidic reagent, HZ, involves two steps:

(1)

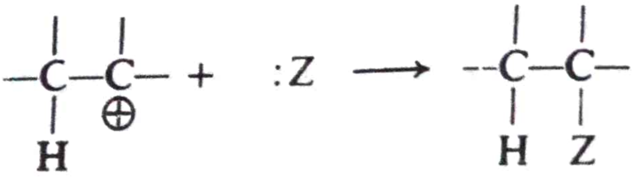


$$-\overset{|}{C}=\overset{|}{C}- + H{:}Z \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\oplus}{\overset{|}{C}}- + {:}Z$$

HZ = HCl, HBr, HI, H_2SO_4, H_3O^+

Slow

(2)



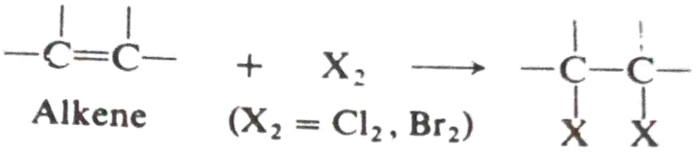
$$-\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\oplus}{\overset{|}{C}}- + {:}Z \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{Z}{|}}{\overset{|}{C}}-$$

:Z = Cl^-, Br^-, I^-, HSO_4^-, H_2O

Fast

9.12 Addition of halogens

Alkenes are readily converted by chlorine or bromine into saturated compounds that contain two atoms of halogen attached to adjacent carbons; iodine generally fails to react.

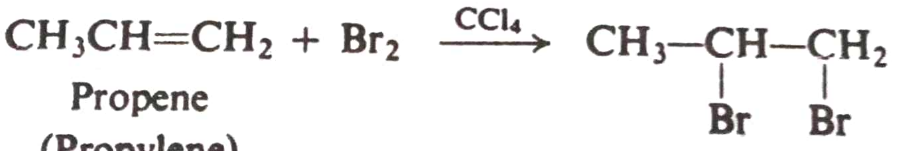


$$-\overset{|}{C}=\overset{|}{C}- \;+\; X_2 \longrightarrow -\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$

Alkene (X$_2$ = Cl$_2$, Br$_2$) Vicinal dihalide

The reaction is carried out simply by mixing together the two reactants, usually in an inert solvent like carbon tetrachloride. The addition proceeds rapidly at room temperature or below, and does not require exposure to ultraviolet light; in fact, we deliberately avoid higher temperatures and undue exposure to light, as well as the presence of excess halogen, since under those conditions substitution might become an important side reaction.

This reaction is by far the best method of preparing **vicinal dihalides**. For example:



$$CH_3CH{=}CH_2 + Br_2 \xrightarrow{CCl_4} CH_3{-}\underset{Br}{\underset{|}{CH}}{-}\underset{Br}{\underset{|}{CH_2}}$$

Propene
(Propylene)

1,2-Dibromopropane

$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{CH_2}}$$

2-Methylpropene (Isobutylene) 1,2-Dibromo-2-methylpropane

Addition of bromine is extremely useful for detection of the carbon–carbon double bond. A solution of bromine in carbon tetrachloride is red; the dihalide, like the alkene, is colorless. Rapid decolorization of a bromine solution is characteristic of compounds containing the carbon–carbon double bond. (However, see Sec. 9.27.)

9.13 Mechanism of addition of halogens

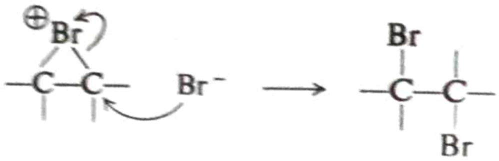
The addition of halogens to alkenes, like the addition of protic acids, is believed to be electrophilic addition, and to involve two steps. Again, the first step involves the formation of a cation. But this cation, in most cases, is not a carbocation, but something new to us: a *halonium ion*. Let us see what a halonium ion is, and what evidence there is for its formation.

Let us use addition of bromine as our example. In step (1) bromine is transferred from a bromine molecule to the alkene: not to just one of the doubly bonded carbons, but to both, forming a cyclic **bromonium ion.**

(1)

A bromonium ion

(2)



Step (1) does indeed represent electrophilic addition. Bromine is transferred as *positive* bromine: that is, without a pair of electrons, which are left behind on the newly formed bromide ion. In step (2) this bromide ion, or more probably another just like it, reacts with the bromonium ion to yield the product, the dibromide.

What is being proposed here is *not* a π-complex (Sec. 14.10), in which the (acidic) bromine molecule is held by the (basic) π cloud of the alkene. Bromine is bonded by two σ bonds—one to each carbon—to form a ring. A π-complex of molecular Br_2 and alkene may, however, be a reversibly formed precursor of the bromonium ion.

The transfer of a proton from a strong acid to an alkene, while new to us, does fit into a familiar framework of acid–base reactions. But how are we to understand the transfer of positive bromine from a bromine molecule? To begin with, it *is* an acid–base reaction—although not in the Lowry–Brønsted sense. Just as alkenes are bases, so halogens are acids, of the Lewis type.

We can understand this reaction better if we change our viewpoint. From the standpoint of a halogen molecule, the reaction with an alkene is nucleophilic substitution. Acting as a nucleophile, the alkene attaches itself to one of the bromines and pushes the other bromine out as bromide ion. Bromide ion is the leaving group; and, as we have seen, bromide ion is a very *good* leaving group.

What are the facts upon which this mechanism is based? They are:

(a) the *effect of the structure of the alkene on reactivity*;

(b) the *effect of added nucleophiles* on the products obtained;

(c) the fact that halogens add with *complete stereoselectivity* and in the *anti* sense;

(d) the *direct observation of halonium ions* under superacid conditions; and

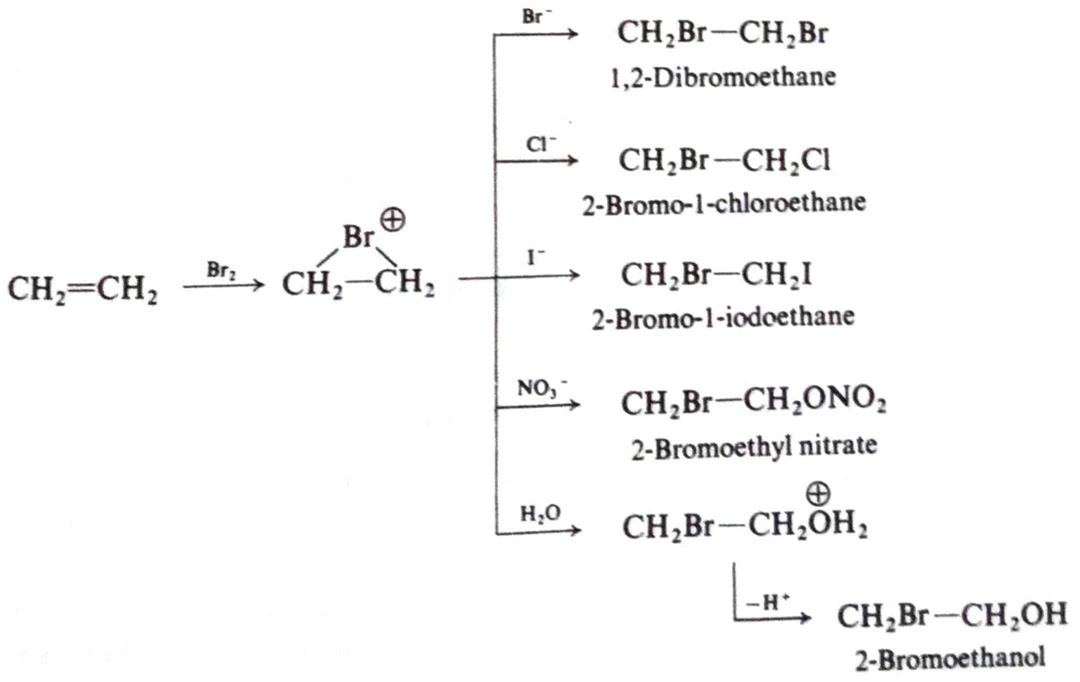
(e) the role played by halonium ions in *neighboring group effects*.

We shall examine each of these pieces of evidence: (a) and (b) now, and (c) and (d) in Secs. 10.2–10.3, and (e) in Secs. 29.2–29.4.

First, there is (a) the *effect of the structure of the alkene on reactivity*. Alkenes show the same order of reactivity toward halogens as toward the acids already studied: electron-releasing substituents activate an alkene, and electron-withdrawing substituents deactivate. This fact supports the idea that addition is indeed electrophilic—that the alkene is acting as an electron source, and that halogen acts as an acid.

Next, there is (b) the *effect of added nucleophiles* on the products obtained. If a halonium ion is the intermediate, and capable of reacting with halide ion, then we might expect it to react with almost any negative ion or basic molecule we care to provide. The bromonium ion formed in the reaction between ethylene and bromine, for example, should be able to react not only with bromide ion but also—if these are present—with fluoride ion, iodide ion, nitrate ion, or water.

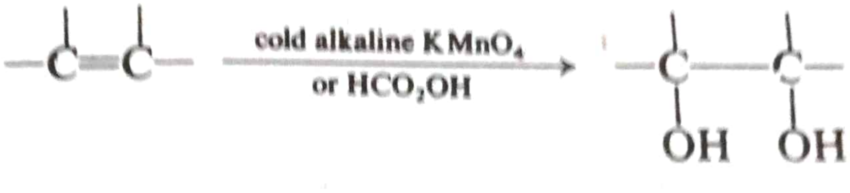
The facts are in complete agreement with this expectation. When ethylene is bubbled into an aqueous solution of bromine and sodium chloride, there is formed not only the dibromo compound but also the bromochloro compound and the bromoalcohol. Aqueous sodium chloride *alone* is completely inert toward ethylene; chloride ion or water can react only after the halonium ion has been formed by the action of bromine. In a similar way bromine and aqueous sodium iodide or sodium nitrate convert ethylene into the bromoiodo compound or the bromonitrate, as well as the dibromo compound and the bromoalcohol. Bromine in water with no added ion yields the dibromo compound and the bromoalcohol.



Now, this elegant work certainly shows that ethylene reacts with bromine to form *something* that can react with these other nucleophiles—but it need not be a bromonium ion. On this evidence alone the intermediate cation could be the simple open carbocation $BrCH_2CH_2^+$. As we shall see in Secs. 10.2–10.3, it was the *stereochemistry* of the reaction that led to the concept of an intermediate bromonium ion, a concept that has since been supported by actual observation of such ions.

9.25 Hydroxylation. Formation of 1,2-diols

Certain oxidizing agents convert alkenes into **1,2-diols**: dihydroxy alcohols containing the two —OH groups on adjacent carbons. (They are also known as *glycols*.) The reaction amounts to addition of two hydroxyl groups to the double bond.



$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{or } HCO_2OH]{\text{cold alkaline } KMnO_4} -\underset{OH}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

A 1,2-diol

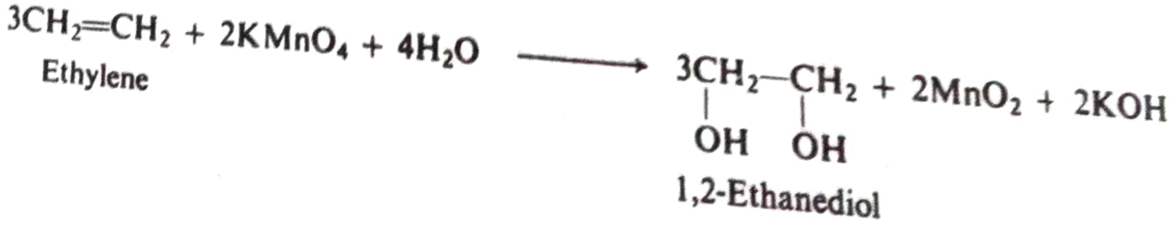
Of the numerous oxidizing agents that bring about hydroxylation, two of th ost commonly used are (a) cold alkaline potassium *permanganate* ($KMnO_4$), a) *peroxy acids*, such as peroxyformic acid (HCO_2OH).

Since permanganate is one of the most important oxidizing agents in organic chemistry, we should perhaps become familiar now with certain of its general characteristics. It is a powerful oxidizing agent, and conditions must be carefully selected—acidity or alkalinity, temperature, quantity of the reagent used—to avoid over-oxidation, that is, taking reaction past the oxidation stage we want. A major problem has been that of solubility: one must get the water-soluble permanganate into contact with the very often water-insoluble substrate. Yet many solvents commonly used to bring polar and non-polar reagents together—alcohols, for example—are themselves oxidized by permanganate. In recent years, this problem has been solved in part by use of phase-transfer catalysts (Sec. 7.7). Quaternary ammonium ions can carry permanganate ions from an aqueous layer into a non-aqueous layer (benzene, say, or dichloromethane) where the substrate awaits. Crown ethers (Sec. 13.19) can complex potassium ions and thus make solid $KMnO_4$ soluble in benzene; the resulting "purple benzene" is an excellent oxidizing agent.

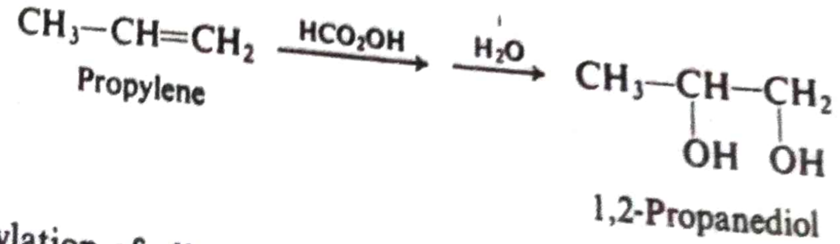
Hydroxylation with permanganate is carried out by stirring together at room temperature the alkene and the aqueous permanganate solution: either neutral—the reaction produces OH^-—or, better, slightly alkaline. Higher yields are sometimes obtained by use of "purple benzene" solutions. *Mild conditions* are the key consideration. Heat and the addition of acid are avoided, since these more vigorous conditions promote further oxidation of the diol, with cleavage of the carbon–carbon double bond (Sec. 9.26).

Hydroxylation with peroxyformic acid is carried out by allowing the alkene to stand with a mixture of hydrogen peroxide and formic acid, HCOOH, for a few hours, and then heating the product with water to hydrolyze certain intermediate compounds.

For example:



$$\underset{\text{Ethylene}}{3CH_2{=}CH_2} + 2KMnO_4 + 4H_2O \longrightarrow \underset{\text{1,2-Ethanediol}}{3\underset{OH}{\underset{|}{C}}H_2{-}\underset{OH}{\underset{|}{C}}H_2} + 2MnO_2 + 2KOH$$



$$\underset{\text{Propylene}}{CH_3{-}CH{=}CH_2} \xrightarrow{HCO_2OH} \xrightarrow{H_2O} \underset{\text{1,2-Propanediol}}{CH_3{-}\underset{OH}{\underset{|}{C}}H{-}\underset{OH}{\underset{|}{C}}H_2}$$

Hydroxylation of alkenes is the most important method for the synthesis of 1,2-diols, with the special feature of permitting *stereochemical control* by the choice of reagent (Problem 10.1, p. 372).

Oxidation by permanganate is the basis of a very useful analytical test known as the Baeyer test (Sec. 9.27).

9.26