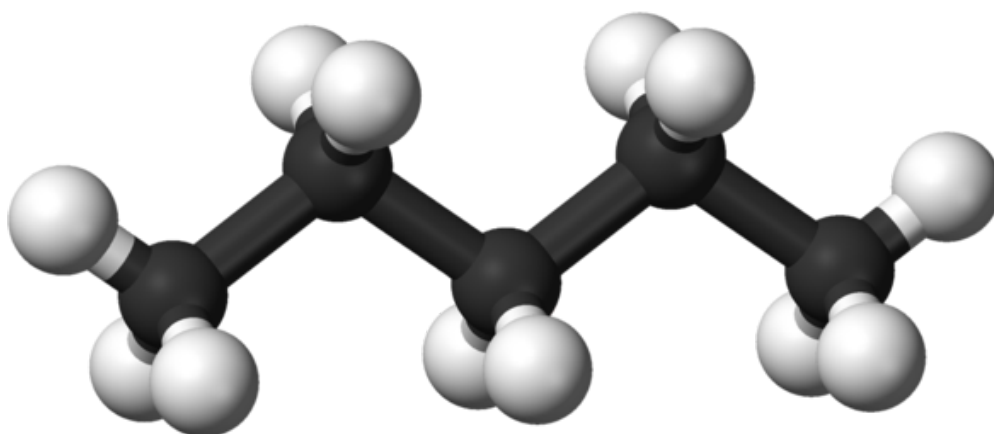


## Hydrocarbons: Alkanes and Alkenes

[See online here](#)

The hydrocarbons are organic compounds classified by the presence of bonds and their unsaturation degree. They are composed of carbon and hydrogen. They may be: 'saturated hydrocarbons' (alkanes and cycloalkanes) in which all their carbons have simple bonds and 'unsaturated hydrocarbons' with a double bond (alkenes) or triple bond (alkynes) in their carbons. The alkanes can be obtained through a process called hydrogenation of alkenes. Some hydrocarbons have electrophilic and nucleophilic properties, depending on their ability to donate or receive electrons.



## Hydrocarbons

Hydrocarbons are organic compounds that only contain hydrogen and [carbon](#) in its structure. They are **classified according to their degree of unsaturation or presence of single, double or triple bonds**. Hydrocarbons, containing only single bonds in their structure, are called saturated hydrocarbons. Saturated hydrocarbons are further classified as alkanes or cycloalkanes. The only difference between the two is that cycloalkanes are cyclic, while alkanes are open-chain compounds.

There are also unsaturated hydrocarbons, or hydrocarbons containing at least one double or triple bond. Simple unsaturated hydrocarbons, containing a double bond, are called an alkene, while simple hydrocarbons containing triple bonds are called alkynes.

## Alkanes

Alkanes are considered the simplest hydrocarbons because of the saturation of the C atoms. They **contain strong carbon-hydrogen and carbon-carbon single bonds**. Because of the very low polarity of the carbon-hydrogen bond and the non-polar bond

between the carbon-carbon, members of this family of compounds have very low reactivities. The reactions of alkanes are only limited to oxidation, halogenation under UV light, and hydrocarbon cracking.

## Electrophilic Addition Reactions

Double bonds and triple bonds in a hydrocarbon are considered electron-rich areas.

**Note:** Because of its high electron density nature, compounds can donate electron pairs through the double and triple bonds. Because of this, alkenes and alkynes are susceptible to electrophilic addition reactions.

These specific types of reactions show the interactions between the nucleophilic double bonds of alkenes and an incoming electrophile.

## Electrophiles vs. Nucleophiles

An important concept, studied in an organic reaction, is the concept of electrophiles and [nucleophiles](#). This is because most reactions occur between the interactions of high and low electron density areas in reactants. Electrophiles are an electron-loving chemical species. **Their electrophilic nature is due to having a positively polarized and electron-poor atom**, which can form new bonds by accepting electron pairs from a nucleophile.

On the other hand, a nucleophile is a chemical species that is nucleus-loving. They are said to be nucleus-loving as they have negatively-polarized electron-rich atoms which are said to be attracted to positively charged nuclei. The interaction between an electrophile and a nucleophile is the one involved also reactions of an alkene.

## Electrophilic Attack

The usual pathway for an electrophilic attack is that **electrons move from a nucleophilic source to an electrophilic sink**. The source of the electrons to be donated from the nucleophile can be an [electron pair in the structure](#),  $\pi$  electrons from multiple bonds, or localized negative charges in the structure. The electrophilic sink, on the other hand, must be readily available to accept electron pairs through a positively charged atom in the structure, or a positively polarized atom in a functional group.

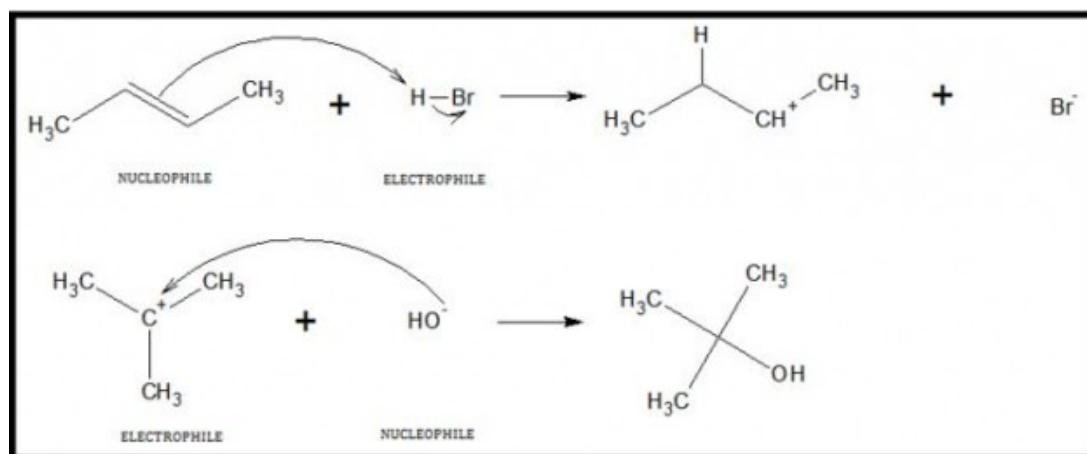
Nucleophiles can be either negatively charged or neutral molecules.

## Negatively charged nucleophiles

For negatively charged nucleophiles, an **electrophilic attack will lead to a formation of a neutral molecule**, while neutral molecules produce a positively charged species after an electrophilic attack.

## Neutral molecules

The electrophiles, on the other hand, can be positively charged or neutral molecules. In a reaction, if the electrophile is positively-charged, it becomes neutral in the process, while neutral electrophiles become negatively-charged after an electrophilic attack.



Electrophilic attack of Nucleophilic OH<sup>-</sup> to a tertiary carbocation. (Figure credits to Mark Xavier Bailon)

## Stability of Carbocation

### Types of carbocations

Carbocations are molecules where a carbon atom in the structure bears three bonds and a positive charge. Carbocations exist in different forms **depending on the number of alkyl substituents present**. The simplest carbocation is the methyl carbocation since there is only one carbon atom present in its structure.

### Primary, secondary and tertiary carbocations

The other possible forms of carbocations are the primary (1°), secondary (2°), and tertiary (3°) carbocations. The difference in the three is the number of alkyl substituents. Primary carbocation has only one alkyl substituent, while the secondary carbocation has two, and the tertiary carbocation has three. **Different types of carbocation have different relative stabilities.**

### Hydrocarbons

For hydrocarbons, the factor to be considered when predicting the stability of a carbocation is the **number of carbon atoms attached to the carbon carrying the positive charge**. The number of bonding electrons around the cation helps 'neutralize' the positive charge through an overlap between  $\sigma$  bonds and the unoccupied p-orbital of the carbocation. This phenomenon is called hyperconjugation.

Because of the overlap, the electron density is somehow supplied to the electron-deficient carbocation carbon increasing its stability. The higher the number of hyperconjugated interactions, the higher is the stability of the carbocation. This would mean that the higher the number of alkyl groups around a carbocation carbon, the more stable is the carbocation. This would translate to having the following trends for the carbocation stability as increasing substitution, increases stability.

**Stability of carbocation:**  $\text{CH}_3^+$  (methyl) <  $\text{RCH}_2^+$  (1°) <  $\text{R}_2\text{CH}^+$  (2°) <  $\text{R}_3\text{C}^+$  (3°)

## Addition of Halogen

Preparation of alkyl halides can be achieved by electrophilic addition reactions using halo acids as the electrophiles. **Electrophilic addition of HX to an alkene is regioselective**, that is, the addition may occur in one of two possible orientations. In the reaction, a carbocation is produced. Most of these reactions usually proceed in the mechanism producing the most stable carbocation. Reactions are usually governed by the Markovnikov's rule.

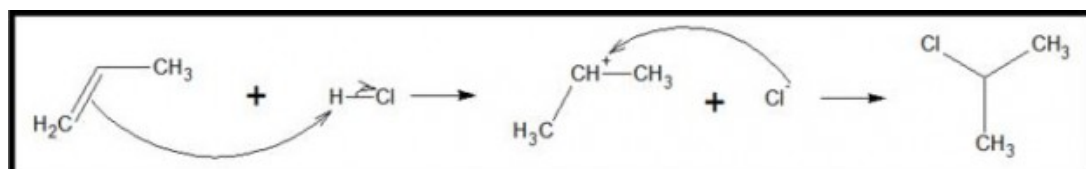
Vladimir Markovnikov proposed in 1869 that, in the addition of HX to an alkene, the H atom attaches to the carbon with fewer alkyl substituents producing the most stable carbocation that can receive the electrons from the remaining negatively-charged X<sup>-</sup> ion.

### Example

For example, the reaction between propene and HCl would yield 2-chloropropane. In this reaction, the HCl is a highly polar compound with the partially negative end in Cl and a partially positive end in H. The **reaction begins with the positive end of HCl attacking the nucleophilic  $\pi$  bonds**. The  $\pi$  bonds donate 2 electrons to form a new  $\sigma$  bond between the hydrogen and the alkene carbon. Hydrogen may attach to either carbon 1 or 2 of the propene molecule but, following Markovnikov's rule, the hydrogen will attach to Carbon 1 to produce a more stable carbocation.

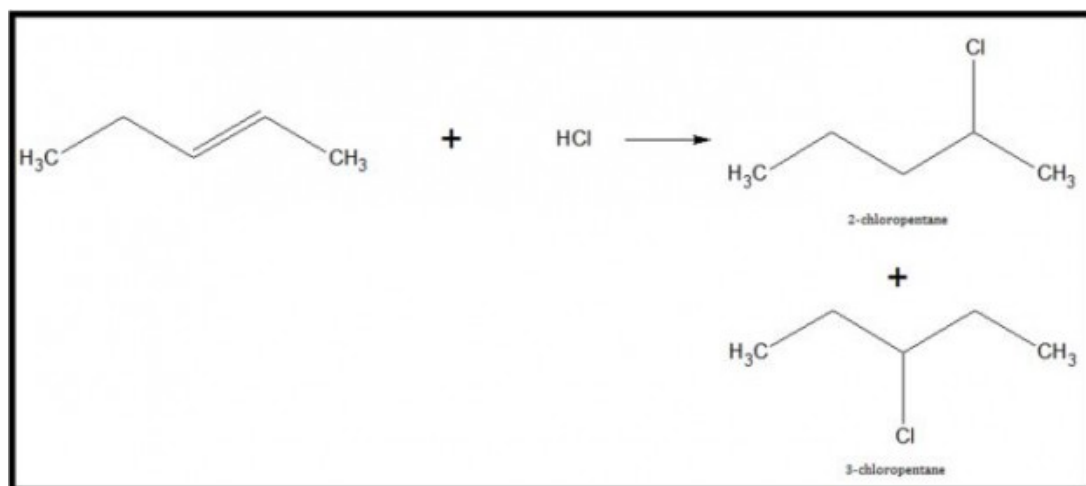
**Note:** The carbocation produced in the process is electrophilic because of the positive charge and can readily receive an electron-pair from the nucleophilic Cl<sup>-</sup> ion to form a C-Cl bond, eventually forming the alkyl halide.

The mechanism for the reaction is summarized in the reaction below.



Electrophilic addition of HCl to propene. (Figure credits to Mark Xavier Bailon)

In cases, wherein the double-bond carbon atoms have the same number of alkyl groups around them, a mixture of additional products will be produced. Such is the reaction of 2-pentene with HCl. In the reactions, **the H and Cl may attach itself in either Carbons 2 or 3 since the two carbons have the same degree of substitution**. In the process, a mixture of 2-chloropentane and 3-chloropentane is produced.

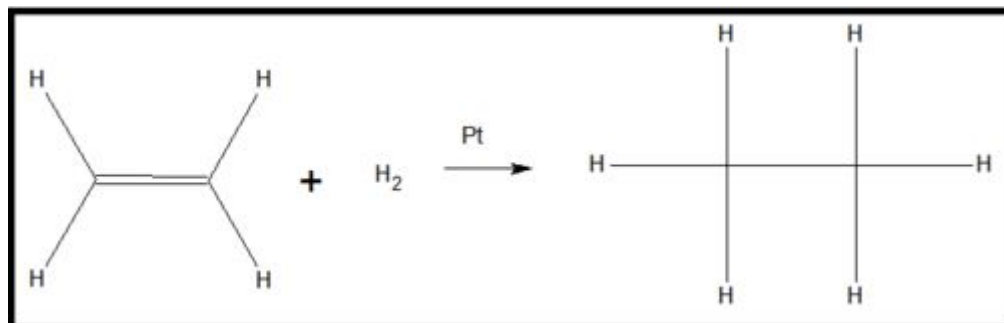


Electrophilic addition of HCl to 2-pentene. (Figure Credits to Mark Xavier Bailon)

## Other Addition Reactions

### Hydrogenation of alkenes

Hydrogenation is the addition of H<sub>2</sub> to the double bond of the alkene and, in the process, produces an alkane. This reaction is very slow, and so there is a need to use metal catalysts like Pt, Pd, and Ni to speed up the reaction.

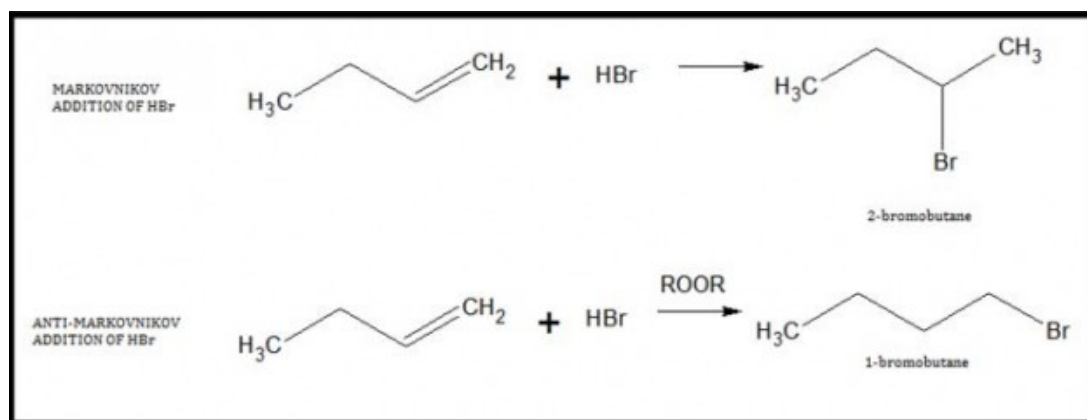


Catalytic hydrogenation of ethene. (Figure credits to Mark Xavier Bailon)

### Free-radical addition of hydrogen bromide

The addition of Hydrogen bromide to propene may follow, or not, the Markovnikov's rule.

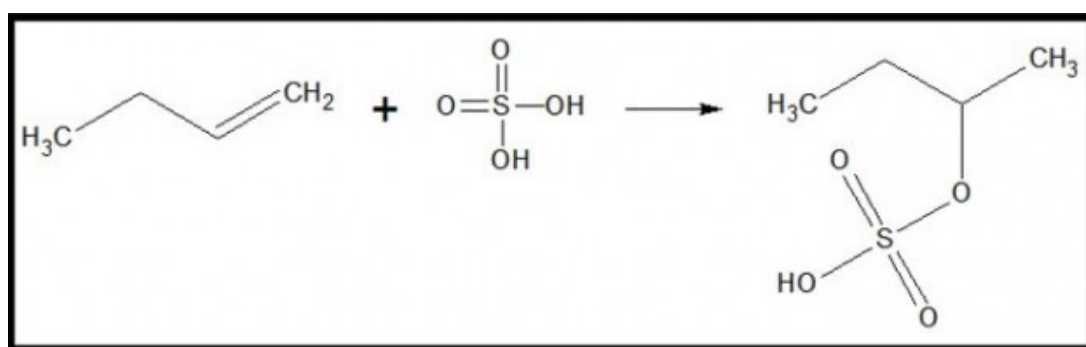
**Ordinary reaction conditions would yield 2-bromobutane following the Markovnikov's rule.** However, in the presence of peroxide, the reactions follow an anti-Markovnikov mechanism producing 1-bromobutane.



Addition reaction of HBr and 1-butene. (Figure credits to Mark Xavier Bailon)

## Addition of sulfuric acid to alkenes

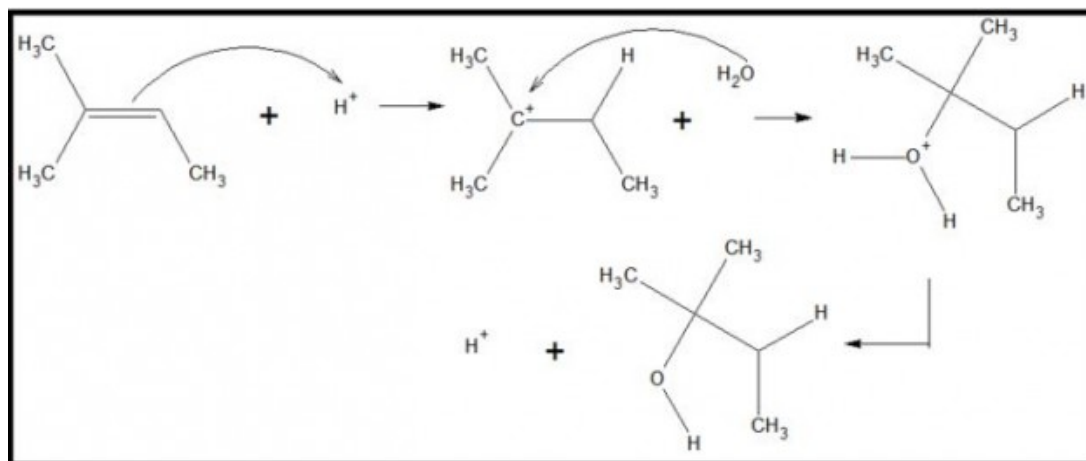
The addition of sulfuric acid,  $\text{H}_2\text{SO}_4$ , follows Markovnikov's rule. **The proton coming from the acid is added to the carbon** having the greater number of hydrogen atoms, while the hydrogen sulfate ion,  $\text{HSO}_4^-$ , attaches to the carbon having a less number of hydrogen atoms.



The addition of sulfuric acid to 1-butene. (Figure credits to Mark Xavier Bailon)

## Acid-catalyzed hydration of alkenes

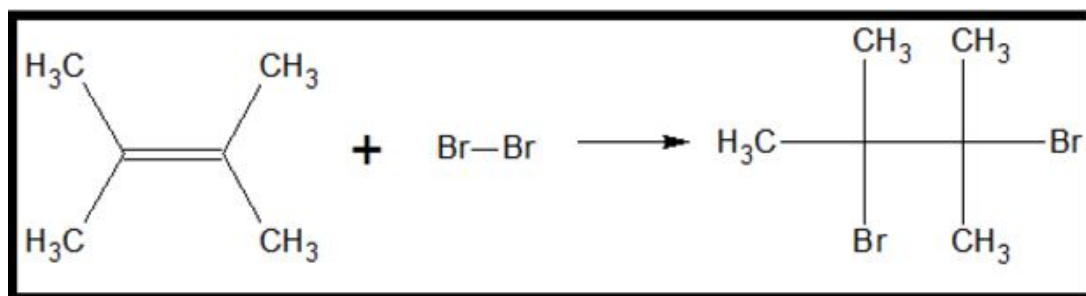
Acid-catalyzed hydration of Alkenes also follows Markovnikov's rule. The first step of the reaction is a proton transfer to a less substituted carbon forming the most stable carbocation. The **water molecules then act as a nucleophile attaching itself to the carbocation** by donating an electron pair from the oxygen atom of the water molecule. The last step is the removal of one of the H atoms attached to the O atom regenerating the  $\text{H}^+$  in the first step.



Acid-catalyzed hydration of 2-methyl-2-butene. (Figure credits to Mark Xavier Bailon)

## Addition of halogens to alkenes

Halogens spontaneously react with alkenes by electrophilic addition producing a dihalogenated alkane. **Products of these reactions are called vicinal dihalides** because of having the halides attached to adjacent carbon atoms.



Addition reaction of Br<sub>2</sub> and 2,3-dimethyl-2-butene. (Figure credits to Mark Xavier Bailon)

## References

McMurry, J. (2012). *Organic chemistry* (8th ed.). Belmont, CA: Cengage Learning Brooks/Cole.

Carey, F. A., & Giuliano, R. M. (2010). *Organic chemistry* (4th ed.). New York, NY: McGraw-Hill.

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