

Alkenes: double bonds and addition reactions

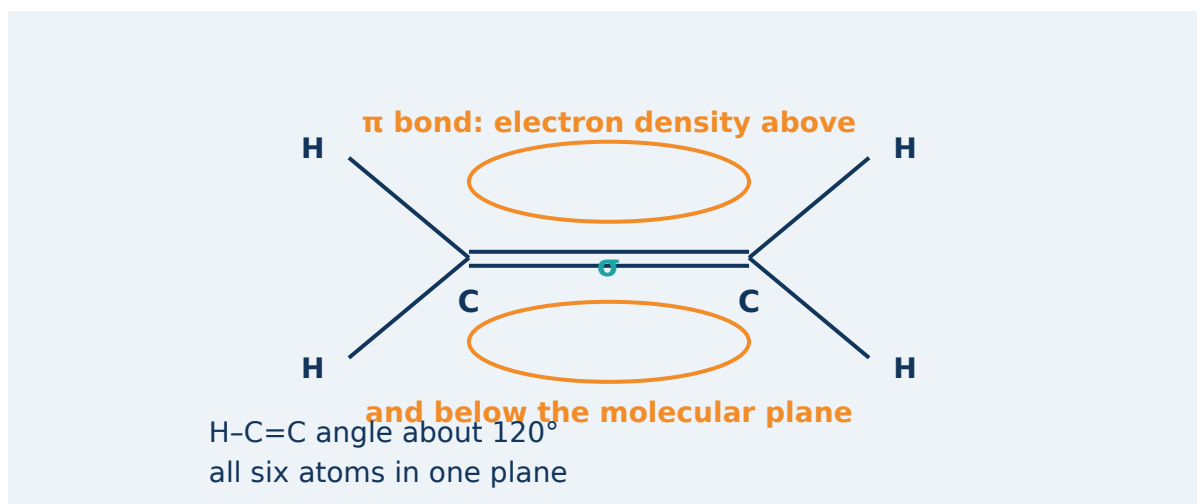
Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: Alkenes are hydrocarbons with a C=C double bond whose exposed π electrons attract electrophiles. They react by electrophilic addition: the π bond breaks and two new σ bonds form. Markovnikov's rule predicts the major product, because the more substituted carbocation is more stable. Alkenes also join into addition polymers.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** A Level 3.3.4

What makes an alkene reactive?

Alkenes are hydrocarbons with the general formula C_nH_{2n} that contain a carbon-carbon double bond. The double bond is made of a strong σ bond between the nuclei and a π bond formed by sideways overlap of p orbitals. The π electrons lie above and below the plane of the molecule, exposed and easy to reach, so alkenes are attacked by positive species called electrophiles. Each carbon of the double bond has three neighbours at about 120° , and rotation about the bond is restricted.



In ethene the sigma bond lies between the nuclei; the pi bond is a cloud above and below the plane, where electrophiles attack.

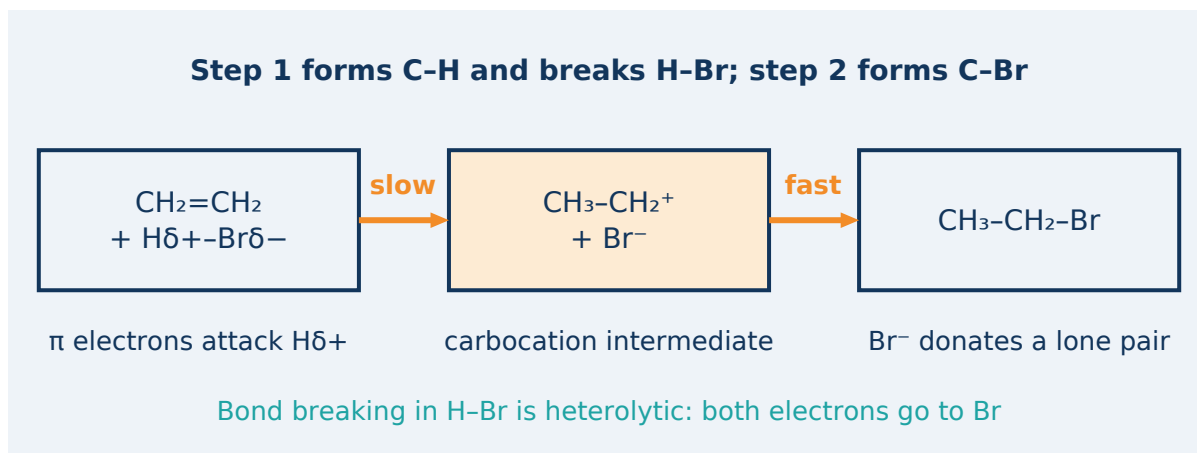
Definition

An **electrophile** is an electron-pair acceptor: a positive ion or the positive end of a polar molecule that is attracted to a region of high electron density.

How does electrophilic addition work?

When HBr meets ethene, the H-Br bond is polar ($H\delta^+$, $Br\delta^-$). The π electrons attack the hydrogen, the H-Br bond breaks heterolytically and a carbocation forms. The bromide ion then donates a lone pair to the positive carbon. Two σ bonds replace one π bond, so the product is

saturated: this is an addition reaction.



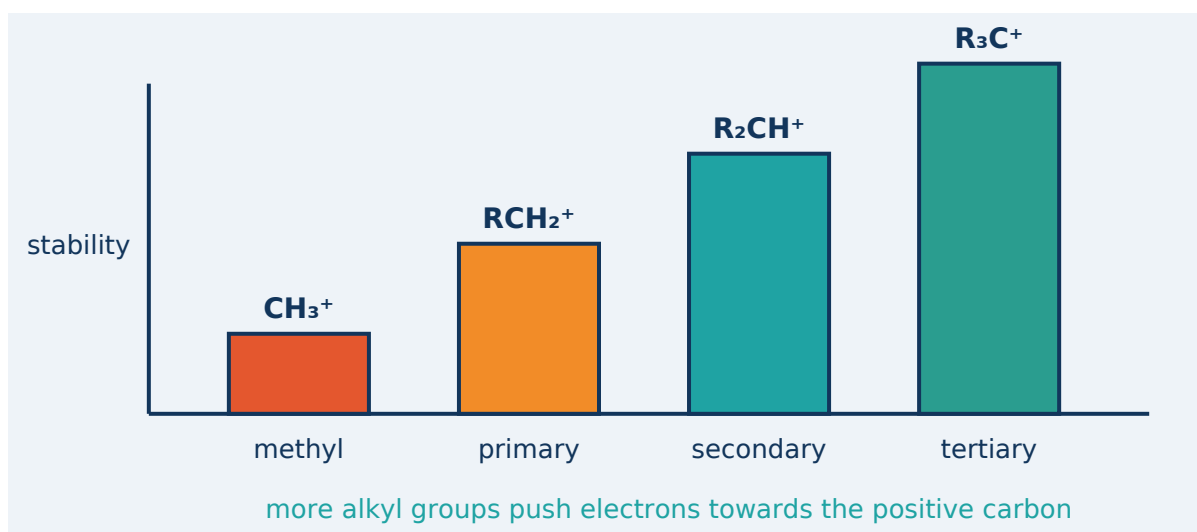
Electrophilic addition of HBr to ethene: a slow first step makes a carbocation, a fast second step makes bromoethane.

Non-polar bromine reacts too, because the approaching π electrons induce a dipole in Br_2 . Common reagents and products are summarised below.

Reagent	Conditions	Product from propene
H_2	nickel catalyst, 150 °C	propane
Br_2	room temperature	1,2-dibromopropane
HBr	room temperature	2-bromopropane (major)
$\text{H}_2\text{O}(\text{g})$	H_3PO_4 catalyst, 300 °C, 65 atm	propan-2-ol (major)

What does Markovnikov's rule predict?

With an unsymmetrical alkene such as propene, the hydrogen can add to either carbon. If H adds to the CH_2 end, a secondary carbocation forms; if it adds to the CH end, a primary one forms. Alkyl groups push electron density towards the positive carbon, so more alkyl groups mean a more stable ion.



Carbocation stability rises with the number of alkyl groups; Markovnikov addition follows the most stable ion.

Key law

Markovnikov's rule: in the addition of HX to an unsymmetrical alkene, the hydrogen bonds to the carbon that already has more hydrogens, because this gives the more stable carbocation and so the major product.

Worked example

Predict the major product of but-1-ene and HBr.

$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$: H goes to the terminal CH_2 , giving the secondary ion $\text{CH}_3\text{CH}_2\text{CH}^+\text{CH}_3$. Br^- then attacks it. Major product: **2-bromobutane**; the minor product is 1-bromobutane.

Worked example

Predict the product of 2-methylpropene with steam and an acid catalyst.

$(\text{CH}_3)_2\text{C}=\text{CH}_2$: H adds to CH_2 , giving the tertiary ion $(\text{CH}_3)_3\text{C}^+$. Water then adds and loses H^+ . Product: **2-methylpropan-2-ol**, $(\text{CH}_3)_3\text{COH}$.

How do you test for a double bond?

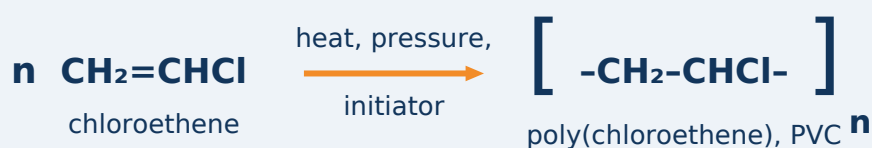
Shake the sample with bromine water. An alkene decolourises it from orange-brown to colourless because Br_2 adds across the double bond, giving a dibromoalkane. An alkane leaves the orange colour in the dark.

Common mistake

Do not write that the bromine water goes "clear". Clear means transparent; the correct word is **colourless**. Also draw the first curly arrow from the $\text{C}=\text{C}$ bond to the hydrogen, never from the hydrogen to the bond.

How do alkenes form addition polymers?

Under heat and pressure with an initiator, many alkene molecules join as the double bond opens. The polymer chain has a repeat unit containing the same atoms as the monomer, and no other product forms. To find the repeat unit, draw the monomer with its two double-bond carbons in the main chain, open the bond and add a bond at each end.



The $\text{C}=\text{C}$ opens: each carbon bonds to a neighbouring monomer.

The repeat unit has the same atoms as the monomer.

In addition polymerisation the double bond opens and the repeat unit contains exactly the atoms of the monomer.

Monomer	Polymer	Repeat unit	Use
ethene	poly(ethene)	$-\text{CH}_2-\text{CH}_2-$	bags, bottles
propene	poly(propene)	$-\text{CH}_2-\text{CH}(\text{CH}_3)-$	crates, ropes
chloroethene	PVC	$-\text{CH}_2-\text{CHCl}-$	pipes, cable cover
tetrafluoroethene	PTFE	$-\text{CF}_2-\text{CF}_2-$	non-stick pans

Worked example

Find the molar mass of a PVC chain with 1 200 repeat units.

Repeat unit $\text{C}_2\text{H}_3\text{Cl}$: $2(12.0) + 3(1.0) + 35.5 = 62.5 \text{ g/mol}$. Chain: $1\,200 \times 62.5 = \mathbf{75\,000 \text{ g/mol}}$.

Lina's tip

To name a polymer's monomer, cover one repeat unit with your finger: the two chain carbons are the old double bond, and everything hanging off them stays on the monomer.

Key points to remember

- Alkenes: general formula C_nH_{2n} ; one σ bond plus one π bond; bond angle about 120°
- Electrophilic addition: π electrons attack $\text{H}\delta+$, a carbocation forms, then Br^- adds
- Markovnikov: H adds to the carbon with more hydrogens; the tertiary carbocation beats secondary, which beats primary
- Test: bromine water goes from orange-brown to colourless
- Addition polymer: repeat unit has the same atoms as the monomer

Alkenes: double bonds and addition reactions: frequently asked questions

Why do alkenes undergo addition rather than substitution?

Breaking the π bond costs less energy than breaking a σ bond, and two stronger σ bonds form in its place. The product is saturated and more stable, so addition is favourable.

What is a carbocation?

A carbocation is an ion with a positively charged carbon atom that has only three bonds. Tertiary ones are the most stable because three alkyl groups push electron density towards the charge.

Why does bromine react with alkenes although Br_2 is non-polar?

The π electrons of the alkene repel the electrons in the approaching Br_2 molecule. This induces a temporary dipole, so one bromine atom becomes electrophilic and is attacked.

How is ethanol made from ethene?

Ethene and steam react at 300 °C and about 65 atm over a phosphoric acid catalyst on silica. The reaction is reversible and exothermic, so unreacted gas is recycled.

Why are addition polymers hard to break down?

Their chains contain only strong, non-polar C-C and C-H bonds. Water and microorganisms cannot attack them easily, so they are not biodegradable.