Alkenes

The C=C bond, E-Z isomerism, addition reactions and tests, the electrophilic addition mechanism and carbocations, addition polymers and their disposal.

Structure of alkenes

Alkenes are **unsaturated hydrocarbons** with the general formula C_nH_{2n}. They have one or more carbon–carbon double bonds. The double bond is made of:

- a **σ (sigma) bond**, formed by head-on overlap of orbitals along the line between the nuclei, and
- a **π (pi) bond**, formed by sideways overlap of p orbitals, with electron density above and below the plane of the molecule.

The π bond is weaker than the σ bond and has high electron density exposed, so alkenes are attacked by **electrophiles**.

Geometric (E–Z) isomerism

There is no rotation about a C=C double bond, because rotation would break the π bond. If each carbon of the double bond has two **different** groups, two stereoisomers exist. They have the same structural formula but different arrangements in space.

- **Cis** (Z) has the two identical or higher-priority groups on the same side.
- **Trans** (E) has them on opposite sides.

For compounds with three or four different groups, the cis/trans names are ambiguous, so the **E–Z system** is used. On each carbon, give priority to the substituent with the higher atomic number (use the first point of difference for longer groups). If the two higher-priority groups are on the **same side**, it is **Z** (from the German *zusammen*); on **opposite sides** is **E** (*entgegen*).

> **TRY IT**
>
> Is $CH_3CH=CHCH_3$ able to show E–Z isomerism? Name the isomers.

Each carbon has H and CH_3 (different), so yes: (Z)-but-2-ene, with the methyls on the same side, and (E)-but-2-ene, on opposite sides.

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Reactions of alkenes

Reaction	Reagent and conditions	Product
Hydrogenation	H_2, nickel catalyst, about 150 °C	Alkane
Halogenation	Br_2 or Cl_2 at room temperature	Dihalogenoalkane
With hydrogen halide	HBr, HCl or HI (gas)	Halogenoalkane
Hydration	Steam, concentrated phosphoric acid catalyst, high temperature and pressure	Alcohol
Oxidation	Cold, dilute acidified potassium manganate(VII)	Diol (the purple solution goes colourless)

Test for a C=C bond

Shake the sample with **bromine water**, or bromine dissolved in a solvent. An alkene **decolourises** it, from orange-brown to colourless, whereas an alkane does not.

Unsymmetrical alkenes

When HBr adds to propene, two products are possible. The major product is 2-bromopropane, because it forms through the more stable carbocation.

The mechanism: electrophilic addition

An **electrophile** is an electron-pair acceptor. Alkenes react with electrophiles in the following steps (shown for bromine and ethene).

1. The π electrons in the double bond **polarise** the approaching Br_2 molecule. The Br nearer the alkene becomes $\delta+$ and the other $\delta-$.
2. A curly arrow goes from the double bond to the $\delta+$ bromine. The Br–Br bond breaks **heterolytically**, with a curly arrow from the bond to the second bromine, forming Br^-. A **carbocation** intermediate forms.
3. A curly arrow goes from a lone pair on Br^- to the positive carbon, forming 1,2-dibromoethane.

For HBr the H–Br bond is already polar ($H^{\delta+}$), so no polarisation is needed. The π electrons attack $H^{\delta+}$, and the Br^- then attacks the carbocation.

NOTE

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Curly arrows start from a bond or a lone pair and point to where the electron pair ends up. Do not start an arrow from an atom.

Evidence and stability of carbocations

Evidence for the carbocation mechanism comes from adding bromine in the presence of sodium chloride. The product mixture contains CH_2BrCH_2Cl as well as CH_2BrCH_2Br. The chloride ion has attacked the carbocation, so a carbocation intermediate must exist.

Carbocation stability: **tertiary > secondary > primary**, because alkyl groups push electrons towards the positive carbon and stabilise it.

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Explain why the main product from HBr and propene is 2-bromopropane.

The H^+ adds to give either a primary carbocation, $CH_3CH_2CH_2^+$, or a secondary one, $CH_3CH^+CH_3$. The secondary carbocation is more stable (two electron-donating alkyl groups), so it forms in greater amounts, and bromide attack on it gives 2-bromopropane as the major product.

Addition polymerisation

Many alkene molecules (**monomers**) join to form a long chain (**polymer**), with no other product. The repeat unit is found by opening the double bond.

$$n\,CH_2=CHCl \rightarrow [-CH_2-CHCl-]_n$$

To find the monomer, remove the brackets and the extension bonds and put the double bond back in.

Monomer	Polymer
Ethene	Poly(ethene)
Propene	Poly(propene)
Chloroethene	Poly(chloroethene), PVC
Tetrafluoroethene	PTFE
Methyl 2-methylpropenoate	Perspex

Polymer disposal

Addition polymers are mostly saturated chains with strong non-polar bonds, so they are **not biodegradable**. Problems are landfill, litter and harm to wildlife. Chemists reduce the problems by:

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- developing **biodegradable polymers** (such as ones made from starch or poly(lactic acid)) which microorganisms can break down,
- **recycling**, and
- **incineration** to release energy, with the **toxic gases** produced (such as hydrogen chloride from PVC) removed by passing through basic scrubbers.

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