1.5.2 Electron arrows and addition mechanisms

Name: _____ Class: _____ Date: _____ **Total: 30 marks**

KEY WORDS homolytic fission • electrophile • carbocation

Objective

Use the correct electron arrows in radical initiation and electrophilic addition. Show complete drawing answers, then explain evidence and limitations.

1 Key knowledge and worked examples

■ Match the arrow to the electrons moved

Homolytic breaking divides a bond pair: each curly half-arrow moves one electron. Heterolytic breaking transfers both electrons to one fragment: use an electron-pair curly arrow. An electrophile accepts an electron pair; a radical has an unpaired electron.

In HBr addition, draw a pair arrow from the alkene π bond to H and another from H–Br to Br. Br^- then donates a lone pair to the carbocation. For propene, the major route forms a secondary rather than primary carbocation before bromide attacks.

2 Practice

2.1 Draw the UV initiation step for chlorine substitution, including curly half-arrows and radical dots. [3]

2.2 Write both propagation equations for substitution of methane by chlorine and one termination equation producing ethane. Explain why the propagation steps can continue a chain. [4]

2.3 Draw the simple electrophilic-addition mechanism of bromine to ethene. Include induced bond polarity, electron-pair arrows, the intermediate and final product. [5]

3 Exam-style questions

3.1 Explain why HBr addition to propene mainly gives 2-bromopropane rather than 1-bromopropane. Give the structural formula and class of each possible carbocation. [4]

3.2 A methane/chlorine reaction gives chloromethane, dichloromethane and small amounts of ethane. Explain the origin of the latter two products and why the process is unsuitable for obtaining only pure chloromethane directly. [3]

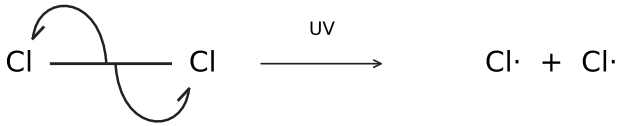
3.3 Draw the addition-polymerisation equation for propene, showing a complete repeat unit, continuation bonds, brackets and n. Explain why its empirical formula alone cannot distinguish the polymer from its monomer. [5]

3.4 Draw the electron-pair mechanism for hydrogen bromide adding to ethene. Show H–Br polarity, both arrows in the first step, the carbocation and bromide ion, the attack arrow and final organic product. Explain why ethene gives no choice between two different constitutional products. [6]

Solutions

Original authored guidance. Arrow starts must identify the actual bond or electron pair, not a positive charge.

2.1

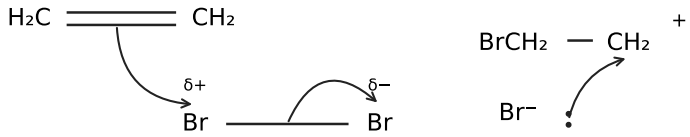


Homolysis: one electron from the bond goes to each chlorine atom.
Each curly half-arrow tracks one electron.

Award for $Cl_2 \rightarrow 2Cl\cdot$ and UV, two half-arrows starting at the bond and ending at different Cl atoms.

2.2 $Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot$; $CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$; $2CH_3\cdot \rightarrow C_2H_6$. Propagation regenerates a radical, allowing further reaction with the remaining molecules. Termination consumes radicals without regenerating one.

2.3



Product: $BrCH_2–CH_2Br$

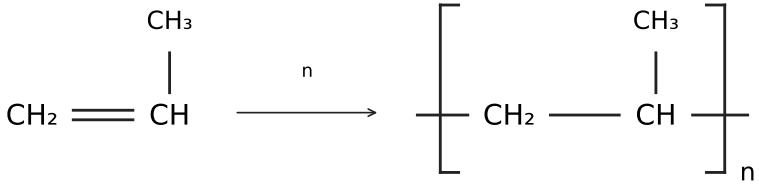
Simple electrophilic-addition model: π pair → Brδ⁺; Br–Br pair → Brδ⁻.
A bromide lone pair supplies the second C–Br bond.

Award induced $Br\delta^+–Br\delta^-$ polarity, π-bond pair arrow to $Br\delta^+$ and Br–Br pair arrow to $Br\delta^-$, $BrCH_2CH_2^+$ plus Br^- with a lone-pair arrow to the positive carbon, and 1,2-dibromoethane product. This syllabus-level model makes no claim about a unique stereochemical product from every substituted alkene.

3.1 $CH_3–CH^+–CH_3$ is secondary; $CH_3–CH_2–CH_2^+$ is primary. The secondary carbocation is more stable, so its route is favoured; Br^- attack gives 2-bromopropane as the major product. Product ratio is not explained by a carbon atom simply wanting more bonds.

3.2 Chloromethane can undergo further radical substitution to form dichloromethane. Two methyl radicals can combine in termination to form ethane. Further substitution and competing termination products create a mixture requiring separation rather than one directly pure product.

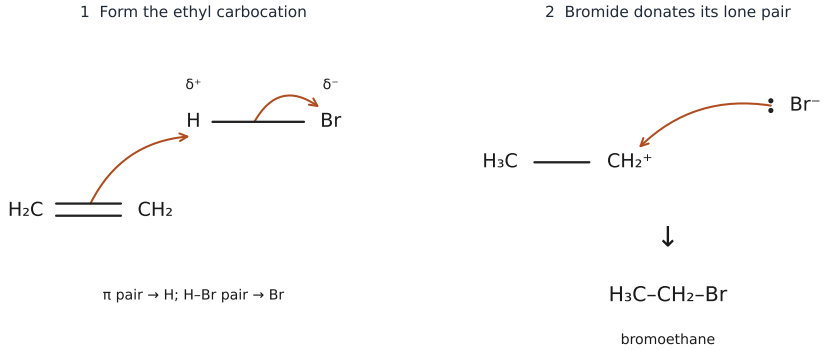
3.3



Propene → poly(propene); continuation bonds cross the brackets.
Side groups stay attached; no small molecule is eliminated.

Award correct monomer and methyl side group, single-bond backbone, continuation bonds/brackets/n and balanced n monomers. Both monomer C_3H_6 and repeat-unit composition have empirical ratio CH_2, so empirical formula does not reveal molecular size or connectivity.

3.4



$H\delta^+–Br\delta^-$ polarity; pair arrow from C=C to H and pair arrow from H–Br to Br; $CH_3CH_2^+$ plus Br^- and bromide lone-pair arrow to the positive carbon; bromoethane CH_3CH_2Br. The two ethene carbons are equivalent, so either direction of proton addition leads to the same connectivity.