InkChemistry

ANSWER BOOK

Alkenes: structure, electrophilic addition and Markovnikov's rule

Alkenes and alcohols · Unit C18

AQA 3.3.4.1, 3.3.4.2 · OCR A 4.1.3

20 questions · 64 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 ASE-Q1

B1 the general formula is C_nH_{2n}, for alkenes with one double bond and no ring. **B1** unsaturated means the molecule contains at least one carbon–carbon double bond, so more atoms can be added to it. [2]

A2 ASE-Q15

B1 alkyl groups release electron density along their σ bonds towards the positive carbon, the inductive effect. **B1** a tertiary carbocation has three alkyl groups and a primary one has one, so the positive charge is spread more in the tertiary ion and it is more stable. [2]

A3 ASE-Q18

B1 the solution changes from purple to colourless; accept 'decolourised'. **B1** the product is ethane-1,2-diol, $HOCH_2CH_2OH$, with an OH group on each carbon of the old double bond. [2]

A4 ASE-Q19

B1 propanone, CH_3COCH_3, comes from a carbon of the double bond carrying two CH_3 groups, and ethanoic acid from a carbon carrying one CH_3 group and one hydrogen. **B1** joining those two carbons by the double bond gives $(CH_3)_2C{=}CHCH_3$, 2-methylbut-2-ene. [2]

SECTION B · Standard, 3 to 5 marks

B1 ASE-Q4

B1 a curly arrow from the C=C double bond to the H atom of H–Br; allow the arrow to the δ+ H if dipoles are shown. **B1** a curly arrow from the H–Br bond to the Br atom, the bond breaking heterolytically to give Br^-. **B1** the structure of the secondary carbocation, $CH_3C^+HCH_3$, with the positive charge on the middle carbon. **B1** a curly arrow from a lone pair on the bromide ion to the positively charged carbon; reject an arrow starting at the minus sign rather than a lone pair. [4]

B2 ASE-Q6

B1 the induced dipole on Br_2, δ+ on the bromine nearer the double bond, with a curly arrow from the C=C double bond to that bromine atom. **B1** a curly arrow from the Br–Br bond to the further bromine atom. **B1** the structure of the carbocation, $CH_2BrC^+H_2$, with a bromine on one carbon and the positive charge on the other. **B1** a curly arrow from a lone pair on Br^- to the positively charged carbon. [4]

B3 ASE-Q8

B1 pent-1-ene gives 2-bromopentane, $CH_3CHBrCH_2CH_2CH_3$, as the major product. **B1** it forms through the secondary carbocation $CH_3C^+HCH_2CH_2CH_3$, the hydrogen having bonded to the CH_2 end. **B1** 2-methylpent-2-ene gives 2-bromo-2-methylpentane, $(CH_3)_2CBrCH_2CH_2CH_3$, as the major product. **B1** it forms through the tertiary carbocation $(CH_3)_2C^+CH_2CH_2CH_3$, more stable than the secondary alternative; ignore the name of the minor product. [4]

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B4 ASE-Q9

B1 shake the liquid with bromine water at room temperature; accept bromine dissolved in an organic solvent. **B1** an unsaturated hydrocarbon turns the bromine water from orange to colourless; accept 'decolourised', reject 'clear'. **B1** a saturated hydrocarbon, with no C=C bond, leaves the bromine water orange. **B1** water molecules, in large excess, compete with bromide ions to bond to the carbocation, so the main product is 2-bromocyclohexan-1-ol. [4]

B5 ASE-Q16

B1 a curly arrow from the C=C double bond to the H atom of an O–H group in H_2SO_4. **B1** a curly arrow from that O–H bond to the O atom. **B1** the structure of the carbocation $CH_3C^+H_2$, and the hydrogensulfate ion with its negative charge on an oxygen. **B1** a curly arrow from a lone pair on the negatively charged oxygen of HSO_4^- to the positively charged carbon. [4]

B6 ASE-Q2

B1 one σ bond, formed by the direct overlap of orbitals, with its electron density between the two carbon nuclei. **B1** one π bond, formed by the sideways overlap of a p orbital on each carbon, with its electron density above and below the plane of the molecule. **B1** each carbon has three regions of electron density, so the arrangement is trigonal planar with bond angles of about 120°. [3]

B7 ASE-Q3

B1 the π bond of an alkene is a region of high electron density, above and below the plane of the molecule. **B1** an electrophile is an electron pair acceptor, so it is attracted to that region, and the π bond is weaker than a σ bond so it breaks readily. **B1** alkanes have only σ bonds, with their electron density held between the nuclei, so there is no exposed electron-rich region to attract an electrophile. [3]

B8 ASE-Q5

B1 as a Br_2 molecule approaches the double bond, the high electron density of the π bond repels the electron pair in the Br–Br bond. **B1** the electrons move towards the far bromine atom, so a dipole is induced, with the nearer bromine δ+ and the far bromine δ-. **B1** the δ+ bromine atom can then accept a pair of electrons from the π bond, so it acts as an electrophile. [3]

B9 ASE-Q7

B1 2-bromopropane forms via a secondary carbocation, $CH_3C^+HCH_3$, and 1-bromopropane via a primary carbocation, $CH_3CH_2C^+H_2$. **B1** alkyl groups release electron density towards the positive carbon, and the secondary carbocation has two alkyl groups against one, so it is more stable; ignore any reference to the stability of the products. **B1** the more stable carbocation forms faster, by a route with a lower activation energy, so more product comes by that route. [3]

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B10 ASE-Q10 [3]

B1 the first step gives the same carbocation, $CH_2BrC^+H_2$, whatever then attacks it. **B1** in the second step any species with a lone pair can bond to the positive carbon: a bromide ion, a chloride ion or a water molecule. **B1** the products are 1,2-dibromoethane, 1-bromo-2-chloroethane and 2-bromoethanol, the last after the added water molecule loses H^+.

B11 ASE-Q12 [3]

M1 amount of propene = 2.10 ÷ 42.0 = 0.0500 mol. **M1** propene and bromine react in a 1 : 1 ratio, so 0.0500 mol of Br_2 reacts. **A1** mass of bromine = 0.0500 × 159.8 = 7.99 g, to three significant figures.

B12 ASE-Q14 [3]

B1 but-2-ene is symmetrical, so either carbon of the double bond gives the same secondary carbocation and the only product is 2-bromobutane. **B1** but-1-ene is unsymmetrical, so a secondary and a primary carbocation can both form, and there are two products. **B1** from but-1-ene the major product is 2-bromobutane, via the more stable secondary carbocation, and 1-bromobutane is the minor product.

B13 ASE-Q17 [3]

B1 a phosphoric acid catalyst, H_3PO_4, on a silica support. **B1** a temperature of about 300 °C. **B1** a pressure of about 60 to 70 atm.

B14 ASE-Q20 [3]

B1 the hot concentrated reagent breaks the C=C bond, and each carbon of the double bond becomes part of a C=O group. **B1** pent-2-ene, $CH_3CH{=}CHCH_2CH_3$, gives two carboxylic acids, ethanoic acid and propanoic acid. **B1** pent-1-ene, $CH_2{=}CHCH_2CH_2CH_3$, gives butanoic acid, and its terminal CH_2 is oxidised to carbon dioxide, which turns limewater milky.

B15 ASE-Q21 [3]

B1 each carbon mixes its 2s orbital with two 2p orbitals to form three sp^2 hybrid orbitals. **B1** the sp^2 orbitals lie in one plane at 120° and overlap end on to form the σ bonds, to the other carbon and to two hydrogens. **B1** the unhybridised 2p orbital on each carbon, at right angles to that plane, overlaps sideways with the other to form the π bond.

SECTION C · Long, 6 marks or more

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C1 [6]
ASE-Q11

Indicative content

B1 H–Br drawn with δ+ on H and δ- on Br, and a curly arrow from the C=C double bond to the H atom; allow the dipole to be omitted if the arrow is correct. **B1** a curly arrow from the middle of the H–Br bond to the Br atom, showing heterolytic fission and the formation of the bromide ion. **B1** the tertiary carbocation $(CH_3)_2C^+CH_2CH_3$, drawn with the positive charge on the carbon carrying the methyl and ethyl groups. **B1** a curly arrow from a lone pair on Br^- to the positive carbon, giving 2-bromo-2-methylbutane, $(CH_3)_2CBrCH_2CH_3$, as the major product. **B1** if the hydrogen bonds to the other carbon of the double bond, a primary carbocation forms instead, leading to 1-bromo-2-methylbutane as the minor product. **B1** the tertiary carbocation is more stable because three alkyl groups release electron density towards the positive carbon, so it forms faster by the route of lower activation energy.

Levels

Level 3 (5–6 marks) every curly arrow, charge and intermediate of the mechanism is correct, the major product is drawn and named, the alternative primary carbocation is identified, and the preference is explained through carbocation stability from the inductive effect of alkyl groups.

Level 2 (3–4 marks) the dipole, the first two arrows and the tertiary carbocation are right and the major product is given; the bromide arrow is absent or starts from the wrong place, or the two carbocations are not compared.

Level 1 (1–2 marks) one correct arrow or the correct product, typically with the primary carbocation drawn as the intermediate or the positive charge on the CH_2 carbon, and no reason for the major product.

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