InkChemistry

ANSWER BOOK

Free-radical substitution

Alkanes and halogenoalkanes · Unit C17

AQA 3.3.2.4 · OCR A 4.1.2 (f), 4.1.2 (g)

18 questions · 58 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 FR-Q3

B1 the Cl–Cl bond is the weakest bond present, 243 kJ mol⁻¹ against 413 kJ mol⁻¹ for C–H. **B1** ultraviolet light provides enough energy to break it homolytically, giving two chlorine radicals. [2]

A2 FR-Q9

B1 use a large excess of methane. **B1** a chlorine radical is then much more likely to collide with a methane molecule than with a chloromethane molecule, so less further substitution occurs. [2]

A3 FR-Q14

M1 butane has six hydrogen atoms on its end carbons and four on its two middle carbons, ten in all. **A1** 6 ÷ 10 × 100 = 60%, to two significant figures. [2]

A4 FR-Q15

B1 each hydrogen on a middle carbon is replaced more readily than each hydrogen on an end carbon. **B1** the C–H bonds on a carbon joined to two other carbons are weaker, so a chlorine radical removes those hydrogens faster. [2]

A5 FR-Q17

B1 no more chlorine radicals are made by initiation once the light is off. **B1** the radicals already present are removed by termination, so no chains remain to carry the reaction. [2]

SECTION B · Standard, 3 to 5 marks

B1 FR-Q1

B1 ultraviolet light, or sunlight; reject 'heat' or a catalyst. **B1** the mechanism is free-radical substitution. **B1** a radical is a species with an unpaired electron; reject 'a charged atom'. **B1** in homolytic fission a covalent bond breaks with one electron of the bonding pair going to each atom. [4]

B2 FR-Q2

B1 initiation: $Cl_2 \rightarrow 2Cl\bullet$. **B1** first propagation step: $Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3$. **B1** second propagation step: $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$. **B1** a termination step, such as $\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$, or $2Cl\bullet \rightarrow Cl_2$, or $2\bullet CH_3 \rightarrow C_2H_6$. [4]

B3 FR-Q11

B1 $Cl\bullet + CH_3Cl \rightarrow HCl + \bullet CH_2Cl$. **B1** $\bullet CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$. **B1** $\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$, two methyl radicals combining; ignore the position of the dot in this equation. **B1** ethane shows that methyl radicals are present and that termination occurs by two radicals combining. [4]

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B4 FR-Q16 — **B1** the reagents are cheap and the reaction needs only ultraviolet light at room temperature. **B1** the first substitution gives both 1-chloropropane and 2-chloropropane, isomers with similar boiling points that are hard to separate. **B1** further substitution and termination add more products, and hydrogen chloride is a by-product, so the atom economy and yield of the wanted product are low. **B1** it is a poor method for one pure product; a route from propan-1-ol would be better. [4]

B5 FR-Q21 — **B1** two fishhook arrows start on the Cl–Cl bond, one ending on each chlorine atom; reject full-headed arrows. **B1** the products are two Cl• radicals, a dot on each Cl and no charge, with ultraviolet light over the reaction arrow. **B1** in propagation, one fishhook from the dot of Cl• and one from the C–H bond both end between Cl and H, forming H–Cl. **B1** a third fishhook from the C–H bond ends on the carbon, giving •CH_3 with the dot on carbon, and HCl. [4]

B6 FR-Q22 — **B1** one fishhook from the dot of •CH_3 and one from the Cl–Cl bond both end between C and the nearer Cl, forming C–Cl. **B1** a third fishhook from the Cl–Cl bond ends on the far Cl, giving CH_3Cl and Cl• with the dot on Cl. **B1** for termination, one fishhook runs from the dot of each methyl radical to the space between the two carbon atoms. **B1** the product is ethane, $CH_3–CH_3$, with the new C–C bond and no dots or charges remaining. [4]

B7 FR-Q5 — **B1** in each propagation step a radical reacts with a molecule and a new radical is formed. **B1** the chlorine radical used in the first propagation step is regenerated in the second, so the cycle repeats. **B1** one initiation step therefore leads to many molecules of product before termination removes the radicals. [3]

B8 FR-Q7 — **M1** Mr(CH_2Cl_2) = 12.0 + 2.0 + 71.0 = 85.0. **M1** total Mr of reactants = 16.0 + (2 × 71.0) = 158.0, and atom economy = 85.0 ÷ 158.0 × 100. **A1** atom economy = 53.8%, to three significant figures. [3]

B9 FR-Q8 — **B1** chloromethane still has C–H bonds, so a chlorine radical can take a hydrogen from it as well as from methane. **B1** further substitution gives dichloromethane, trichloromethane and tetrachloromethane. **B1** termination steps give other products, such as ethane from two methyl radicals, and its chlorinated derivatives. [3]

B10 FR-Q10 — **B1** this step breaks a C–H bond and makes a C–Br bond. **B1** ΔH = 413 - 290 = +123 kJ mol^{-1}, so the step is strongly endothermic. **B1** the step that does occur, Br• + CH_4 → HBr + •CH_3, is far less endothermic (+47 kJ mol^{-1} with H–Br 366), so it happens in preference; allow 'lower activation energy'. [3]

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B11 FR-Q13

B1 initiation by homolytic fission of bromine: $Br_2 \rightarrow 2Br\bullet$. **B1** $Br\bullet + CH_3CH_2CH_3 \rightarrow HBr + CH_3\dot{C}HCH_3$, the hydrogen taken from the middle carbon; accept $\bullet CH(CH_3)_2$. **B1** $CH_3\dot{C}HCH_3 + Br_2 \rightarrow CH_3CHBrCH_3 + Br\bullet$, the bromine radical regenerated. [3]

B12 FR-Q19

B1 the first propagation step, $I\bullet + CH_4 \rightarrow HI + \bullet CH_3$, breaks C–H and makes the weaker H–I bond. **B1** $\Delta H = 413 - 299 = +114$ kJ mol^{-1}, so the step is strongly endothermic with a very high activation energy. **B1** iodine radicals almost never complete it and recombine to I_2 first, so no chain is propagated. [3]

SECTION C · Long, 6 marks or more

C1 FR-Q23

Indicative content [6]

B1 initiation: ultraviolet light breaks the Cl–Cl bond homolytically, $Cl_2 \rightarrow 2Cl\bullet$, each atom taking one electron of the bonding pair. **B1** first propagation step: $Cl\bullet + CH_3CH_2CH_3 \rightarrow HCl + \bullet CH_2CH_2CH_3$, the chlorine radical taking a hydrogen from an end carbon. **B1** second propagation step: $\bullet CH_2CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CH_2Cl + Cl\bullet$, so the chlorine radical is regenerated and the chain continues. **B1** termination when two radicals combine, for example $\bullet CH_2CH_2CH_3 + Cl\bullet \rightarrow CH_3CH_2CH_2Cl$, or two propyl radicals giving hexane, C_6H_{14}. **B1** a chlorine radical can also take a hydrogen from the middle carbon, giving 2-chloropropane, a position isomer with a similar boiling point that is hard to separate. **B1** further substitution of the chloropropanes gives dichloropropanes and beyond, so the product is a mixture and the yield of 1-chloropropane is low.

Levels

Level 3 (5–6 marks) all three stages are named and each has a correct equation with radicals shown, the regeneration of the chlorine radical is pointed out, and both reasons for the mixture are given, substitution at the middle carbon and further substitution.

Level 2 (3–4 marks) initiation and both propagation steps are correct; termination is thin, a radical dot or a species is missing from one equation, or only one of the two reasons for the mixture of products is given.

Level 1 (1–2 marks) ultraviolet light is said to split chlorine, sometimes into ions rather than radicals, or one step is written; the chain is not followed and the other products are not accounted for.

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