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ANSWER BOOK

The Arrhenius equation and the rate-determining step

Rate equations · Unit C09

AQA 3.1.9.1, 3.1.9.2 · OCR A 5.1.1 (i) to (k)

18 questions · 60 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 AE-Q2

B1 k = Ae^(-Ea/RT), where A is the pre-exponential factor. **B1** Ea must be in J mol^{-1} and T in kelvin. [2]

A2 AE-Q8

B1 the catalyst provides an alternative route with a lower activation energy. **B1** a smaller Ea makes e^(-Ea/RT) larger at the same temperature, so k increases. [2]

A3 AE-Q10

B1 an intermediate is made and used up during the reaction, so its concentration cannot be set independently; it depends on the concentrations of the reactants that formed it. **B1** the reactants that formed it in the earlier step appear in the rate equation in its place. [2]

A4 AE-Q18

B1 Cl is the catalyst: it is used in the first step and regenerated in the second. **B1** ClO is the intermediate: it is made in the first step and used up in the second. [2]

SECTION B · Standard, 3 to 5 marks

B1 AE-Q5

M1 rearrange: A = k ÷ e^(-Ea/RT) = k × e^(Ea/RT). **M1** Ea/RT = 75 000 ÷ (8.31 × 300) = 30.08. **M1** e^30.08 = 1.16 × 10^{13}, so A = 3.2 × 10^{-4} × 1.16 × 10^{13}. **A1** A = 3.7 × 10^{9} s^{-1}, to two significant figures, with the units of a first-order k. [4]

B2 AE-Q11

B1 run the clock reaction with the same concentrations at five or six temperatures, measuring each temperature in the mixture. **B1** record the time t at each, and use 1/t as a measure of the rate, which is proportional to k at fixed concentrations. **B1** plot ln(1/t) against 1/T with T in kelvin and draw the best-fit straight line. **B1** the gradient equals -Ea/R, so Ea = -gradient × 8.31 J K^{-1} mol^{-1}. [4]

B3 AE-Q15

B1 SN2 takes place in one step, whereas SN1 takes place in two steps. **B1** SN2 passes through a transition state only, whereas SN1 forms a carbocation intermediate. **B1** SN2 has rate = k[RX][OH^-], second order, whereas SN1 has rate = k[RX], first order. **B1** SN2 is typical of primary halogenoalkanes, whereas SN1 is typical of tertiary ones. [4]

B4 AE-Q16

B1 the steps add up to the overall equation, so the mechanism passes that test. **B1** its slow step involves two X and no Y, so it predicts rate = k$[X]^2$, which is not the rate equation measured. **B1** the mechanism is therefore rejected. **B1** a consistent mechanism is X + Y → XY (slow), then XY + X → X_2Y (fast). [4]

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B5 AE-Q1 — **B1** the slowest step in the reaction mechanism, which limits the overall rate; reject 'the first step'. **B1** rate = k[A][B][C], since the intermediate AB is replaced by the A and B that formed it. **B1** the reaction is third order overall; error carried forward from the rate equation given. [3]

B6 AE-Q7 — **B1** e^(-Ea/RT) is the fraction of collisions with energy equal to or greater than the activation energy. **B1** raising T makes -Ea/RT less negative, and because the dependence is exponential this fraction rises steeply. **B1** so a much larger proportion of collisions succeed and k, and the rate, rise by far more than the temperature does. [3]

B7 AE-Q9 — **B1** a tertiary carbocation is stabilised by the three alkyl groups, which push electron density towards the positive carbon. **B1** the three alkyl groups also crowd the carbon atom and hinder attack by the hydroxide ion from the side opposite the halogen. **B1** a primary carbocation is unstable and a primary carbon is open to attack, so the one-step SN2 route has the lower activation energy. [3]

B8 AE-Q12 — **B1** step 1, fast: two NO molecules combine, $2NO \rightarrow N_2O_2$. **B1** step 2, slow: $N_2O_2 + O_2 \rightarrow 2NO_2$. **B1** the steps add to the overall equation, and the slow step uses O_2 and an intermediate made from two NO, giving $[NO]^2[O_2]$. [3]

B9 AE-Q13 — **B1** one H_2O_2 molecule and one I^- ion react in the rate-determining step. **B1** the H^+ ions and the second I^- ion react only in fast steps after the slow step. **B1** species that react only after the rate-determining step do not affect the rate, so H^+ is zero order. [3]

B10 AE-Q19 — **M1** k(catalysed) ÷ k(uncatalysed) = e^(-80 000/RT) ÷ e^(-95 000/RT) = e^(15 000/RT). **M1** 15 000 ÷ (8.31 × 300) = 6.02. **A1** factor = e^6.02 = 4.1×10^2, to two significant figures, with no units as it is a ratio. [3]

B11 AE-Q21 — **B1** the cross disappears when a fixed amount of sulfur has formed, so 1/t is proportional to the rate. **B1** the starting concentrations are the same in every run, so the rate, and therefore 1/t, is a constant multiple of k. **B1** ln(1/t) = ln k + a constant, so the constant moves the line up or down without changing its gradient, -Ea/R. [3]

B12 AE-Q22 — **M1** from $k = Ae^{(-Ea/RT)}$, $\ln(k_2 \div k_1) = (Ea \div R)(1/T_1 - 1/T_2)$, with Ea in J mol^{-1}. **M1** = (60 000 ÷ 8.31) × (1/310 - 1/320) = 7220 × 1.008 × 10^{-4} = 0.728. **A1** $k_2 \div k_1 = e^{0.728}$ = 2.07, so the rate constant roughly doubles; allow 2.1. [3]

SECTION C · Long, 6 marks or more

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C1 AE-Q17

Indicative content [6]

B1 1-bromobutane has rate = $k[C_4H_9Br][OH^-]$, so both the halogenoalkane and hydroxide are in the rate-determining step. **B1** 2-bromo-2-methylpropane has rate = $k[(CH_3)_3CBr]$, so only the halogenoalkane is in the rate-determining step. **B1** SN2: the hydroxide lone pair attacks the δ+ carbon from the side opposite the bromine. **B1** SN2: the C–Br bond breaks as the C–O bond forms, in one step through a single transition state. **B1** SN1: the C–Br bond breaks heterolytically in a slow first step to give a tertiary carbocation and Br^-. **B1** SN1: the hydroxide ion bonds to the carbocation in a fast second step, so hydroxide is zero order.

Levels

Level 3 (5–6 marks) both rate equations are read correctly to say which species are in the rate-determining step, and both mechanisms are described in full, the one-step SN2 attack from the side opposite the bromine with a single transition state, and the two-step SN1 with the slow heterolysis to a tertiary carbocation and the fast attack by hydroxide; the answer links each mechanism back to its rate equation.

Level 2 (3–4 marks) the rate equations are matched to the two mechanisms and both are outlined; the answer does not say which species are in the rate-determining step, or one mechanism lacks its key step.

Level 1 (1–2 marks) one mechanism is named or the rate equations are said to differ; the overall order is commonly taken as the number of steps in the mechanism.

C2 AE-Q20

Indicative content [6]

B1 in the first, fast step a lone pair on the oxygen of propanone accepts H^+, giving protonated propanone, $(CH_3)_2C{=}OH^+$. **B1** the second step, loss of H^+ from a carbon atom of the protonated propanone to give the enol, is slow and rate-determining. **B1** the protonated propanone is an intermediate, so it cannot appear in the rate equation; the one propanone and one H^+ that made it take its place. **B1** iodine reacts with the C=C bond of the enol only in the fast third step, after the rate-determining step, so it is zero order. **B1** the protonated propanone and the enol are both intermediates: each is made in one step and used up in a later one. **B1** H^+ is the catalyst: it is used in step 1 and given back in step 2, so it is in the rate equation but not in the overall equation.

Levels

Level 3 (5–6 marks) all three steps are described with their relative speeds, the rate equation is derived from the slow step with the intermediate replaced by the species that formed it, the zero order in iodine is explained from its place after the rate-determining step, and both intermediates and the catalyst are identified with the reasons.

Level 2 (3–4 marks) the slow step is identified and the rate equation explained from it, with the intermediates or the catalyst named; why iodine is zero order, or why an intermediate cannot appear in the rate equation, is not explained.

Level 1 (1–2 marks) H^+ is called the catalyst or the slow step said to set the rate; iodine is usually put in the rate equation because it is a reactant in the overall equation.

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