

4.1.2 Kinetic mechanisms and activation energy

Name: _____ Class: _____ Date: _____ Total: 15 marks

KEY WORDS rate-determining step

Objective

Use rate evidence to evaluate a mechanism without claiming a unique proof. Questions and marking guidance are original.

1 Key knowledge and worked examples

A mechanism is a sequence of elementary steps. The slow step controls rate in the simple model used here; prior equilibria may supply species involved in that step. A proposed mechanism must sum to the overall reaction and agree with kinetic evidence. Agreement does not prove uniqueness.

■ Worked explanation

For a tertiary halogenoalkane, $r = k[RX]$ supports slow C–X cleavage followed by nucleophile attack: S_N1. For a primary halogenoalkane, $r = k[RX][OH^-]$ supports one concerted attack/departure step: S_N2. The nucleophile appears in the overall S_N1 reaction even though its concentration does not appear in this simple rate law.

Temperature changes k . With the supplied Arrhenius form, $\ln k = \ln A - E_a/(RT)$, a plot of $\ln k$ against $1/T$ has gradient $-E_a/R$. Use kelvin and consistent J/kJ. A catalyst changes the pathway and increases rate; it does not change the reaction's net enthalpy or equilibrium constant. A heterogeneous catalyst can adsorb reactants at its surface; surface-site availability matters.

2 Practice

2.1 A reaction is first order in RX and zero order in OH^- . State the simple substitution mechanism supported and the slow-step event. [2]

2.2 A plot of $\ln k$ against $1/T$ has gradient -6000 K . Given $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, calculate E_a in kJ mol^{-1} . [3]

2.3 Explain why doubling nucleophile concentration can double the rate of S_N2 but leave the simple S_N1 rate unchanged. [2]

3 Exam-style questions

3.1 For $A + B \rightarrow C$, measured $r = k[A]$. A proposed sequence is slow $A \rightarrow I$, then fast $I + B \rightarrow C$. Check its overall equation and rate consistency. Explain the limit of the conclusion. [4]

3.2 A solid catalyst loses activity when a strongly adsorbed impurity enters the feed. Explain using surface sites, then distinguish the effects of removing the impurity and raising temperature on an equilibrium yield at fixed pressure. [4]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 S_N1; slow heterolytic C–X cleavage forming a carbocation and halide ion.

2.2 $E_a = -R \times \text{gradient} = 49860 \text{ J mol}^{-1} = 49.9 \text{ kJ mol}^{-1}$.

2.3 Nucleophile participates in the S_N2 rate-determining collision; it attacks after the slow ionisation in the simple S_N1 sequence.

3.1 Adding the steps cancels intermediate I and gives $A + B \rightarrow C$. Slow unimolecular A step gives rate proportional to [A], and B reacts afterwards. Consistency supports this mechanism but other mechanisms may give the same law.

3.2 Impurity blocks active sites, reducing available adsorption/reaction sites. Removing it restores rate but does not change the equilibrium constant at fixed temperature. Raising temperature changes K and yield according to the reaction enthalpy.