

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]

2.3 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]