

## 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<sub>N</sub>1. For a primary halogenoalkane,  $r = k[RX][OH^-]$  supports one concerted attack/departure step: S<sub>N</sub>2. The nucleophile appears in the overall S<sub>N</sub>1 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<sup>−</sup>. State the simple substitution mechanism supported and the slow-step event. [2]

---



---



---

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

---

---

---

---

---