

Reaction Mechanisms and Catalysis

Answer key with worked solutions

A. Elementary steps

1. Molecularity.

(a) unimolecular: $\text{rate} = k[\text{O}_3]$ (b) bimolecular: $\text{rate} = k[\text{NO}][\text{O}_3]$ (c) bimolecular: $\text{rate} = k[\text{NO}_2]^2$

2. Hydrogen peroxide and iodide.

(a) Adding the steps and cancelling I^- and IO^- : $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$. (b) I^- is the **catalyst** (used in step 1, regenerated in step 2); IO^- is the **intermediate** (made in step 1, used in step 2). (c) From the slow step: $\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$. (d) **Homogeneous**: the catalyst is in the same phase (aqueous solution) as the reactant.

B. Testing mechanisms

3. Two mechanisms for $\text{NO} + \text{O}_2$.

(a) A: one elementary step $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$, so $\text{rate} = k[\text{NO}]^2[\text{O}_2]$. B: slow step rate $= k_2[\text{N}_2\text{O}_2][\text{O}_2]$; the pre-equilibrium gives $[\text{N}_2\text{O}_2] = K_1[\text{NO}]^2$, so $\text{rate} = k_2K_1[\text{NO}]^2[\text{O}_2]$. Both match.

(b) B: it uses only bimolecular steps, whereas A needs three molecules to collide at once, which is very unlikely. The rate law alone can't decide between them: it can rule a mechanism out, but not prove one.

4. Ozone.

Slow step: $\text{rate} = k_2[\text{O}][\text{O}_3]$. From the fast equilibrium:

$$K_1 = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}, \quad [\text{O}] = \frac{K_1[\text{O}_3]}{[\text{O}_2]}$$
$$\text{rate} = \frac{k_2K_1[\text{O}_3]^2}{[\text{O}_2]} = \frac{k[\text{O}_3]^2}{[\text{O}_2]}$$

Adding O_2 shifts the fast equilibrium to the left, lowering $[\text{O}]$, the intermediate needed in the slow step: the reaction is order -1 in O_2 .

C. Catalysts and enzymes

5. Hydrogenation on nickel.

(1) **Adsorption:** H₂ and ethene bond to active sites on the nickel surface. (2) **Weakening:** the H-H bond (and the C=C π bond) weakens or breaks. (3) **Reaction:** H atoms add to the adsorbed ethene, forming ethane. (4) **Desorption:** ethane leaves the surface, freeing the sites. A fine powder has a much larger **surface area**, so there are more active sites and the reaction is faster.

6. Michaelis-Menten.

(a) $[S] = K_m$, so $v = \frac{1}{2} V_{\max} = 75 \mu\text{mol L}^{-1} \text{min}^{-1}$

(b)

$$\begin{aligned} v &= \frac{(150 \mu\text{mol L}^{-1} \text{min}^{-1})(4.5 \text{ mmol/L})}{0.50 \text{ mmol/L} + 4.5 \text{ mmol/L}} \\ &= 135 \mu\text{mol L}^{-1} \text{min}^{-1} \end{aligned}$$

(c) $0.90 = \frac{[S]}{K_m + [S]}$ gives $[S] = 9K_m = 9 \times 0.50 \text{ mmol/L} = 4.5 \text{ mmol/L}$ (consistent with b).

(d) Exact:

$$\begin{aligned} v &= \frac{(150 \mu\text{mol L}^{-1} \text{min}^{-1})(0.050 \text{ mmol/L})}{0.55 \text{ mmol/L}} \\ &= 14 \mu\text{mol L}^{-1} \text{min}^{-1} \end{aligned}$$

Approximation:

$$\begin{aligned} v &\approx \frac{150 \mu\text{mol L}^{-1} \text{min}^{-1}}{0.50 \text{ mmol/L}} \times 0.050 \text{ mmol/L} \\ &= 15 \mu\text{mol L}^{-1} \text{min}^{-1} \end{aligned}$$

Close (within 10 %), because $[S]$ is well below K_m : the reaction is nearly first order in S.

D. Challenge

7. Inhibitors.

(a) No inhibitor:

$$v = \frac{(150 \mu\text{mol L}^{-1} \text{ min}^{-1})(1.0 \text{ mmol/L})}{1.5 \text{ mmol/L}} = 100 \mu\text{mol L}^{-1} \text{ min}^{-1}$$

$$\text{X: } \frac{(150 \mu\text{mol L}^{-1} \text{ min}^{-1})(1.0 \text{ mmol/L})}{2.5 \text{ mmol/L}} = 60 \mu\text{mol L}^{-1} \text{ min}^{-1}$$

$$\text{Y: } \frac{(90 \mu\text{mol L}^{-1} \text{ min}^{-1})(1.0 \text{ mmol/L})}{1.5 \text{ mmol/L}} = 60 \mu\text{mol L}^{-1} \text{ min}^{-1}$$

(b) At 10 mmol/L, X gives about $130 \mu\text{mol L}^{-1} \text{ min}^{-1}$ (excess substrate outcompetes it, so the rate approaches 150) but Y gives only about $86 \mu\text{mol L}^{-1} \text{ min}^{-1}$ (it can never exceed its lowered V_{max} of 90). The inhibitor whose effect shrinks at high [S] is the competitive one.

8. Turnover and temperature.

(a)

$$\begin{aligned} k_{\text{cat}} &= \frac{150 \mu\text{mol L}^{-1} \text{ min}^{-1}}{0.025 \mu\text{mol L}^{-1}} = 6.0 \times 10^3 \text{ min}^{-1} \\ &= \frac{6.0 \times 10^3 \text{ min}^{-1}}{60 \text{ s/min}} = 1.0 \times 10^2 \text{ s}^{-1} \end{aligned}$$

(b) At first, raising the temperature gives more collisions with enough energy to react, so the rate rises. Above the optimum (often about 37–45 °C for human enzymes), the protein **denatures**: the weak interactions holding its shape break, the active site no longer fits the substrate, and the rate falls sharply.