

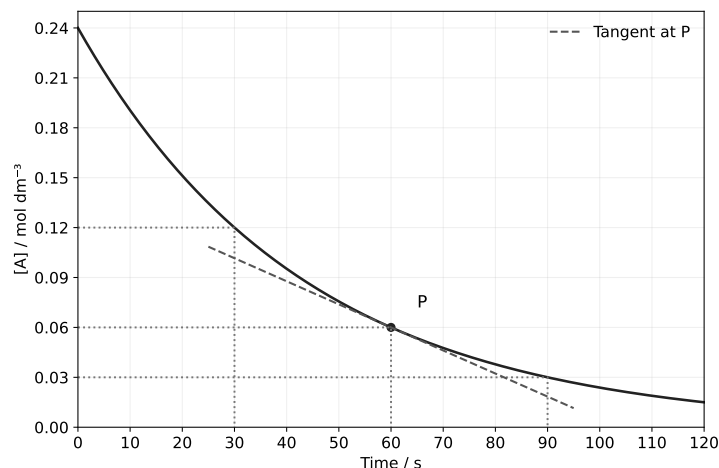
Solutions

Original marking guidance: M1 method, A1 accuracy, B1 reasoning. Accept suitably drawn graphical estimates within reading precision.

2.1 I is second order: doubling $[A]$ from 0.100 to 0.200 multiplies rate from 0.0040 to 0.0160 by four. II is zero order: rate remains 0.0080 over the displayed measured range, 0.025–0.300 mol dm⁻³, not after A is exhausted. III is first order: doubling $[A]$ doubles rate from 0.0040 to 0.0080.

2.2 Times 30, 60 and 90 s, within graph-reading precision. Successive half-lives 60–30 = 30 s and 90–60 = 30 s. Constant successive half-lives support first order under the stated fixed conditions; one interval alone cannot establish their constancy or exclude every competing model.

2.3 Draw a tangent touching P and following its local direction, not an origin-to-P chord. For example, approximate tangent points (40 s, 0.0877 mol dm⁻³) and (80 s, 0.0323 mol dm⁻³) give gradient $(0.0323 - 0.0877)/(80 - 40) = -0.001385$ mol dm⁻³ s⁻¹. Disappearance rate is the negative of this gradient, positive, approximately 1.4×10^{-3} mol dm⁻³ s⁻¹.



3.1 For example (2.9, -3.1) and (3.3, -5.5) give plotted gradient $(-5.5 + 3.1)/(3.3 - 2.9) = -6.0$. Since $x = 1000/T$, this gradient is $-E_a/(1000R)$. Thus $E_a = 6.0 \times 1000 \times 8.31 = 49860$ J mol⁻¹, or 49.9 kJ mol⁻¹. Omitting the factor 1000 underestimates E_a one thousandfold.

3.2 One compatible sequence is rapid $P + H^+ \rightleftharpoons PH^+$, slow $PH^+ \rightarrow E + H^+$, then fast $E + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$. Atoms and net charge are conserved in each; accept a chemically equivalent balanced sequence consistent with the stated conditions. Slow-step rate $r = k_2[PH^+]$ and substitution give $r = k_2K[P][H^+] = k[P][H^+]$. This is first order in propanone and H^+ , zero order in iodine. Cancel PH^+ and E, and one consumed/regenerated H^+ : $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$. The H^+ used in protonation is regenerated during enol formation; iodination creates another H^+ overall, so catalytic regeneration and net acid production both occur. Rate/stoichiometric agree-

ment supports a possible mechanism but does not prove it unique; early-rate comparisons require acid concentration and other kinetic factors controlled.

3.3 Replacing high-mobility OH^- by lower-mobility ethanoate changes conductivity as reaction progresses. Maintain/calibrate temperature and the same probe/cell geometry; calibrate conductivity against known compositions and control mixing/starting concentrations and relevant solvent background. No gas is formed or lost from the closed apparatus, so gas volume or mass loss supplies no reaction-progress signal.