Problem 3-05 Reaction mechanisms, apparent activation energy

Certain reaction proceeds as the sequence of the following elementary steps:

$$\mathrm{A + B} \xrightarrow{k_1} \mathrm{C + B}$$

$$\mathrm{C + B} \xrightarrow{k_2} \mathrm{A + B}$$

$$\mathrm{C} \xrightarrow{k_3} \mathrm{D}$$

(a) Assuming that C is an unstable intermediate, which cannot be detected in the reaction mixture, write the rate law expressing the rate of product D formation.

(b) What change in this rate law will occur in case that the second elementary step is much faster than the third one? Calculate the apparent activation energy under these conditions, if you know the values activation energies: $E_1^* = 15$ kJ mol^{-1}, $E_2^* = 40$ kJ mol^{-1}, and $E_3^* = 10$ kJ mol^{-1}.

$$\left[\text{(a) } \frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}\tau} = \frac{k_1 \cdot k_3 \cdot c_\mathrm{A} \cdot c_\mathrm{B}}{k_3 + k_2 \cdot c_\mathrm{B}}\ ;\text{(b) } \frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}\tau} = \frac{k_1 \cdot k_3}{k_2} \cdot c_\mathrm{A}\ \ (k_2 \cdot c_\mathrm{B} >> k_3),\ E^* = -15\ \mathrm{kJ\ mol^{-1}}]\right]$$

Solution:

Reaction rate = rate of D formation: $\dfrac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}\tau} = k_3 \cdot c_\mathrm{C}$

C – unstable intermediate

$$\frac{\mathrm{d}c_\mathrm{C}}{\mathrm{d}\tau} = 0 = k_1 \cdot c_\mathrm{A} \cdot c_\mathrm{B} - k_2 \cdot c_\mathrm{B} \cdot c_\mathrm{C} - k_3 \cdot c_\mathrm{C} \qquad \Rightarrow \qquad c_\mathrm{C} = \frac{k_1 \cdot c_\mathrm{A} \cdot c_\mathrm{B}}{k_3 + k_2 \cdot c_\mathrm{B}}$$

(a) $$\frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}\tau} = k_3 \cdot \frac{k_1 \cdot c_\mathrm{A} \cdot c_\mathrm{B}}{k_3 + k_2 \cdot c_\mathrm{B}}$$

(b)

$$\frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}\tau} = k_3 \cdot \frac{k_1 \cdot c_\mathrm{A} \cdot c_\mathrm{B}}{\cancel{k_3} + k_2 \cdot c_\mathrm{B}} = \frac{k_1 \cdot k_3}{k_2} \cdot c_\mathrm{A}$$

$k_3 << k_2 \cdot c_\mathrm{B}$

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E^*}{\boldsymbol{R}T}$$

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{\mathrm{d}\ln k_1}{\mathrm{d}T} + \frac{\mathrm{d}\ln k_3}{\mathrm{d}T} - \frac{\mathrm{d}\ln k_2}{\mathrm{d}T} = \frac{E_1^*}{\boldsymbol{R}T} + \frac{E_3^*}{\boldsymbol{R}T} - \frac{E_2^*}{\boldsymbol{R}T}$$

$E^* = E_1^* + E_3^* - E_2^*$ = 15 + 10 – 40 = –15 kJ mol^{-1}