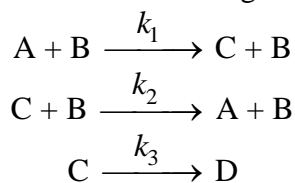


Problem 3-05 Reaction mechanisms, apparent activation energy

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



- (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: $E_1^* = 15 \text{ kJ mol}^{-1}$, $E_2^* = 40 \text{ kJ mol}^{-1}$, and $E_3^* = 10 \text{ kJ mol}^{-1}$.

$$\left[\text{(a)} \frac{dc_D}{d\tau} = \frac{k_1 \cdot k_3 \cdot c_A \cdot c_B}{k_3 + k_2 \cdot c_B} ; \text{(b)} \frac{dc_D}{d\tau} = \frac{k_1 \cdot k_3}{k_2} \cdot c_A \quad (k_2 \cdot c_B \gg k_3), E^* = -15 \text{ kJ mol}^{-1} \right]$$

Solution:

Reaction rate = rate of D formation: $\frac{dc_D}{d\tau} = k_3 \cdot c_C$

C – unstable intermediate

$$\frac{dc_C}{d\tau} = 0 = k_1 \cdot c_A \cdot c_B - k_2 \cdot c_B \cdot c_C - k_3 \cdot c_C \quad \Rightarrow \quad c_C = \frac{k_1 \cdot c_A \cdot c_B}{k_3 + k_2 \cdot c_B}$$

$$\text{(a)} \quad \frac{dc_D}{d\tau} = k_3 \cdot \frac{k_1 \cdot c_A \cdot c_B}{k_3 + k_2 \cdot c_B}$$

(b)

$$\frac{dc_D}{d\tau} = k_3 \cdot \frac{k_1 \cdot c_A \cdot c_B}{k_3 + k_2 \cdot c_B} = \frac{k_1 \cdot k_3}{k_2} \cdot c_A$$

$k_3 \ll k_2 \cdot c_B$

$$\frac{d \ln k}{dT} = \frac{E^*}{RT}$$

$$\frac{d \ln k}{dT} = \frac{d \ln k_1}{dT} + \frac{d \ln k_3}{dT} - \frac{d \ln k_2}{dT} = \frac{E_1^*}{RT} + \frac{E_3^*}{RT} - \frac{E_2^*}{RT}$$

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