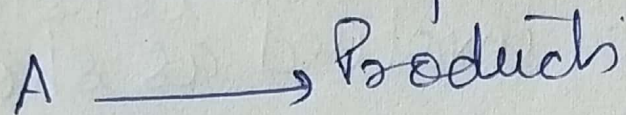


Lindemann mechanism: -

(1)

A unimolecular reaction, in general, means a reaction of the type



In such reactions, only one molecule of the reactant takes part in the reaction.

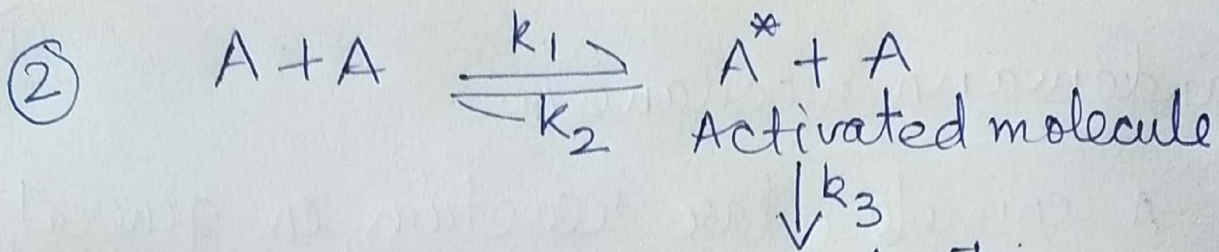
Consequently, the question arises:

How do molecules in a unimolecular reaction attain their energy of activation?

The answer to this question was first suggested by Lindemann in 1922. He pointed out that the behaviour of unimolecular

reactions can be explained on the basis of bimolecular collisions provided we suppose that a time lag exists between activation and reaction. During this time, the activated molecules may either react or deactivated to ordinary molecules.

Consequently, the rate of reaction will not be proportional to all the molecules activated but only to those which remain active. This concept may be given as:



where k_1, k_2, k_3 are the rate constants of the different processes involved as shown above.

∴ Rate of disappearance of A to form products = Rate of disappearance of A^* (i.e. rate at which A^* changes into products)

L.H.S of the above eq = $-\frac{d[A]}{dt}$

R.H.S of the above eq $\propto [A^*] = k_3[A^*]$

$$-\frac{d[A]}{dt} = k_3[A^*] \quad \text{--- (i)}$$

Hence

since $[A^*]$ is not known, it is necessary to obtain a relation for the concentration of A^* in terms of A.

To do so, we make use of steady state principle, it is obvious that

Rate of formation of $A^* = k_1[A]^2$

Rate of disappearance of $A^* =$ Rate of disappearance of A^* back into ordinary molecules + Rate of disappearance of A^* into product

$$= k_2[A^*][A] + k_3[A^*]$$

Hence $k_1[A]^2 = k_2[A^*][A] + k_3[A^*]$

$$k_1[A]^2 = [A^*] \{ k_2[A] + k_3 \} \quad (3)$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} \quad (2)$$

Substituting this value in eq. (1) above, we get

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2[A] + k_3} \quad (3)$$

Two possibilities are

(i) If the concentration of A is very high

$$k_2[A] \gg k_3$$

Eq. (3) becomes

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2[A]} = \frac{k_1 k_3 [A]}{k_2} = k[A] \quad (4)$$

where $k = \frac{k_1 k_3}{k_2}$

Thus under these conditions, eq. (4) predicts the reaction to be of first order.

ii) If the concentration of A is very low

$$k_2[A] \ll k_3 \text{ or } k_3 \gg k_2[A]$$

Eq. (3) becomes

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_3} = k_1 [A]^2$$

i.e. the reaction should be of second order.