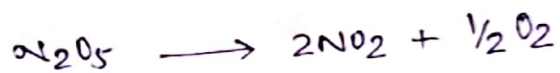


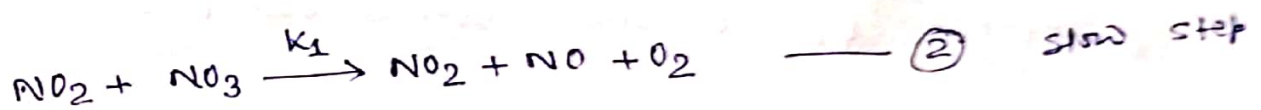
For example: -

① decomposition of  $N_2O_5$

$N_2O_5$  decomposes as:



The proposed mechanism are -



from eqs --- ①  
rate constant ---

$$K = \frac{[NO_2][NO_3]}{[N_2O_5]} \quad \text{--- ④}$$

$$\text{or } [NO_2][NO_3] = K [N_2O_5] \quad \text{--- ⑤}$$

Since, the slowest step is the rate determining step. Hence,

from eqs --- ②

$$r = k_1 [NO_2][NO_3] \quad \text{--- ⑥}$$

from eqs --- ⑤ and eqs --- ⑥ we have,

$$r = k_1 \cdot K [N_2O_5]$$

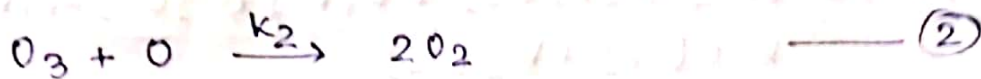
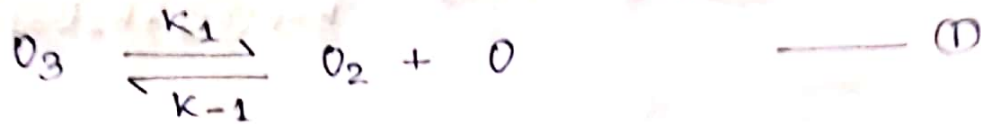
$$\text{or } \boxed{r = k' [N_2O_5]}$$

where,

$$k' = k_1 \cdot K$$

## Q (5) Thermal decomposition of $O_3$

For the thermal decomposition of  $O_3$ , the following proposed mechanisms are:



Ozone decomposes in the step --- (1) and --- (2) and is formed in the reverse step --- (1) hence, overall rate of formation of  $O_3$  is -

$$r = \frac{d(O_3)}{dt} = -k_1 [O_3] + k_{-1} [O_2] [O] - k_2 [O_3] [O] \quad \text{--- (3)}$$

$$\therefore = -k_1 [O_3] + \{k_{-1} [O_2] - k_2 [O_3]\} [O]$$

The rate of formation of very short lived species  $[O]$  is given as:

$$\frac{d[O]}{dt} = k_1 [O_3] - k_{-1} [O_2] [O] - k_2 [O_3] [O]$$

on using steady-state approximation (SSA) -

$$0 = k_1 [O_3] - k_{-1} [O_2] [O] - k_2 [O_3] [O]$$

$$k_1 [O_3] = \{k_{-1} [O_2] + k_2 [O_3]\} [O]$$

$$\therefore [O] = \frac{k_1 [O_3]}{k_{-1} [O_2] + k_2 [O_3]} \quad \text{--- (4)}$$

Now putting the value of  $[O]$  from eq<sup>n</sup> - (4) in eq<sup>n</sup> - (3)

We get -

$$\begin{aligned} \gamma &= \frac{-k_1 [O_3] + k_1 k_{-1} [O_2] [O_3]}{1 + k_{-1} [O_2] + k_2 [O_3]} - \frac{k_1 k_2 [O_3]^2}{k_{-1} [O_2] + k_2 [O_3]} \\ &= \frac{-k_1 k_{-1} [O_2] [O_3] - k_1 k_2 [O_3]^2 + k_1 k_{-1} [O_2] [O_3] - k_1 k_2 [O_3]^2}{k_{-1} [O_2] + k_2 [O_3]} \end{aligned}$$

$$\therefore \gamma = \frac{-2 k_1 k_2 [O_3]^2}{k_{-1} [O_2] + k_2 [O_3]}$$

On using further approximation that in the above equation -  $k_{-1} [O_2] \gg k_2 [O_3]$ , then the second term in the denominator is neglected, so,

$$\gamma = \frac{-2 k_1 k_2 [O_3]^2}{k_{-1} [O_2]}$$

$$\therefore \boxed{\gamma = -K' \frac{[O_3]^2}{[O_2]}}$$

Where,  $K' = \frac{2 k_1 k_2}{k_{-1}}$