For example :-

① decomposition of N_2O_5

N_2O_5 decomposes as:

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2$$

The proposed mechanism are-

$$N_2O_5 \underset{}{\overset{K}{\rightleftharpoons}} NO_2 + NO_3 \quad \text{——— ①} \quad \text{fast equilibrium step}$$

$$NO_2 + NO_3 \xrightarrow{K_1} NO_2 + NO + O_2 \quad \text{——— ②} \quad \text{slow step}$$

$$NO + NO_3 \xrightarrow{K_2} 2NO_2 \quad \text{——— ③} \quad \text{fast-step}$$

from eqs —①
rate constant —

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

or $[NO_2][NO_3] = K [N_2O_5]$ ——— 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,

$$r = K_1 \cdot K [N_2O_5]$$

or $\boxed{r = k' [N_2O_5]}$ where, $k' = K_1 \cdot K$

(8) Thermal decomposition of O_3

For the thermal decomposition of O_3, the following proposed mechanism are:

$$O_3 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} O_2 + O \quad \text{--- (1)}$$

$$O_3 + O \xrightarrow{K_2} 2O_2 \quad \text{--- (2)}$$

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 —

$$r = \frac{d[O_3]}{dt} = -K_1[O_3] + K_{-1}[O_2][O] - K_2[O_3][O] \quad \text{--- (3)}$$

or

$$= -K_1[O_3] + \{K_{-1}[O_2] - K_2[O_3]\}[O]$$

The rate of formation of very short lived speises $[O]$ 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) —

$$0 = K_1[O_3] - K_{-1}[O_2][O] - K_2[O_3][O]$$

$$K_1[O_3] = \{K_{-1}[O_2] + K_2[O_3]\}[O]$$

$$\text{or} \quad [O] = \frac{K_1[O_3]}{K_{-1}[O_2] + K_2[O_3]} \quad \text{--- (4)}$$

Now putting the value of [O] from eqⁿ – (7) in eqⁿ – (3)

we get -

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

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

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

On ussing further approximation that in the above equation – $k_{-1} [O_2] >> k_2 [O_3]$, then the second term in the denominator is neglected. so,

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

or $$\boxed{r = -k' \frac{[O_3]^2}{[O_2]}}$$

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