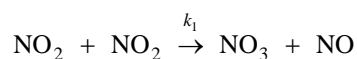
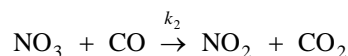


Solution:

The rate equation suggests the rate-limiting step involves the reaction of two NO_2 molecules. The product of this reaction is dictated by the fact that NO_3 is the only intermediate observed.



The intermediate NO_3 reacts with the other reactant, as follows.



Use the second reaction to write a rate equation for $[\text{CO}_2]$.

$$\frac{d[\text{CO}_2]}{dt} = k_2[\text{NO}_3][\text{CO}] \quad (1)$$

Assume the first reaction is rate-limiting and the second reaction is fast. Apply the steady-state approximation to $[\text{NO}_3]$.

$$\begin{aligned} \frac{d[\text{NO}_3]}{dt} &= 0 = k_1[\text{NO}_2]^2 - k_2[\text{NO}_3][\text{CO}] \\ k_1[\text{NO}_2]^2 &= k_2[\text{NO}_3][\text{CO}] \end{aligned} \quad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[\text{CO}_2]}{dt} = k_1[\text{NO}_2]^2$$

Thus $k = k_1$.

Grading Rubric:

+3 : mechanism agrees with the overall reaction

+3 : all steps are likely to be elementary

- Make 1 bond

- Break 1 bond

- Make 1 bond, break 1 bond

- No tri-molecular reactions

- No formation of a diatomic molecule by a collision of 2 atoms

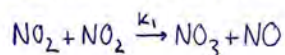
Ex. $\text{H} \cdot + \text{H} \cdot \rightarrow \text{H}_2$

+1 : NO_3 is the only intermediate

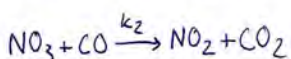
+2 : Used steady state approximation to derive a rate equation

+1 : Final rate equation matches the one given

Correct Mechanism:



$$\frac{d[\text{CO}_2]}{dt} = k_2[\text{NO}_3][\text{CO}] \quad (1)$$



Assume Steady State on NO_3

$$\frac{d[\text{NO}_3]}{dt} = k_1[\text{NO}_2]^2 - k_2[\text{NO}_3][\text{CO}] = 0$$

$$k_2[\text{NO}_3][\text{CO}] = k_1[\text{NO}_2]^2 \quad (2)$$

Substitute (2) into (1)

$$\frac{d[\text{CO}_2]}{dt} = k_1[\text{NO}_2]^2$$