ChemE 2200 - Physical Chemistry II for Engineers

Quiz 12 - April 23, 2025

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.

$$\mathrm{NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO}$$

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

$$\mathrm{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}$$

Use the second reaction to write a rate equation for $[CO_2]$.

$$\frac{d[\mathrm{CO_2}]}{dt} = k_2[\mathrm{NO_3}][\mathrm{CO}] \qquad (1)$$

Assume the first reaction is rate-limiting and the second reaction is fast. Apply the steady-state approximation to $[NO_3]$.

$$\frac{d[\mathrm{NO_3}]}{dt} = 0 = k_1[\mathrm{NO_2}]^2 - k_2[\mathrm{NO_3}][\mathrm{CO}]$$

$$k_1[\mathrm{NO_2}]^2 = k_2[\mathrm{NO_3}][\mathrm{CO}] \qquad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[\mathrm{CO_2}]}{dt} = k_1[\mathrm{NO_2}]^2$$

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. $H\cdot + H\cdot \rightarrow H_2$

+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:

$$\mathrm{NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO} \qquad \frac{d[\mathrm{CO_2}]}{dt} = k_2[\mathrm{NO_3}][\mathrm{CO}] \ (1)$$

$$\mathrm{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}$$

Assume Steady State on NO_3

$$\frac{d[\mathrm{NO_3}]}{dt} = k_1[\mathrm{NO_2}]^2 - k_2[\mathrm{NO_3}][\mathrm{CO}] = 0$$

$$k_2[\mathrm{NO_3}][\mathrm{CO}] = k_1[\mathrm{NO_2}]^2 \ (2)$$

Substitute (2) into (1)

$$\frac{d[\mathrm{CO_2}]}{dt} = k_1[\mathrm{NO_2}]^2$$