In class activity: Reaction mechanisms and catalysis
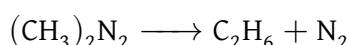
Lecture notes for chemical reaction engineering

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Gas phase decomposition of azomethane

Consider the gas-phase decomposition of azomethane, AZO, to give ethane and nitrogen

$$(CH_3)_2N_2 \longrightarrow C_2H_6 + N_2$$

Experimental observations show that the rate of formation of ethane is first order with respect to AZO at pressures greater than 1 atm (relatively high concentrations)

$$r_{C_2H_6} \propto C_{AZO}$$

and second order at pressures below 50 mmHg (low concentrations):

$$r_{C_2H_6} \propto C_{AZO}^2$$

We could combine these two observations to postulate a rate law of the form

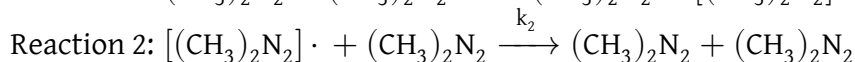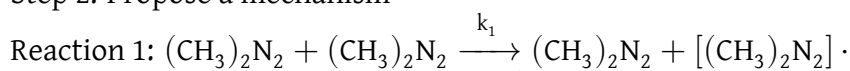$$r_{C_2H_6} = \frac{k_1 C_{AZO}^2}{1 + k_2 C_{AZO}}$$

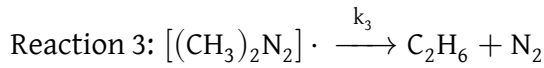find a mechanism that is consistent with the experimental observations

> 💡 Solution
>
> Step 1: Propose an active intermediate.
> We will choose as an active intermediate an azomethane molecule that has been excited through molecular collisions, to form AZO $\cdot$, that is, $[(CH_3)_2N_2] \cdot$.
> Step 2: Propose a mechanism
>
> Reaction 1: $(CH_3)_2N_2 + (CH_3)_2N_2 \xrightarrow{k_1} (CH_3)_2N_2 + [(CH_3)_2N_2] \cdot$
>
> Reaction 2: $[(CH_3)_2N_2] \cdot + (CH_3)_2N_2 \xrightarrow{k_2} (CH_3)_2N_2 + (CH_3)_2N_2$

Reaction 3: $[(CH_3)_2N_2] \cdot \xrightarrow{k_3} C_2H_6 + N_2$

Step 3: Write rate laws

Reaction 1: $r_1 = k_1 C_{AZO}^2$

Reaction 2: $r_2 = -k_2 C_{AZO} \cdot C_{AZO}$

Reaction 3: $r_3 = -k_3 C_{AZO} \cdot$

Step 4: Write rate of formation of product.

$r_{C_2H_6} = k_3 C_{AZO} \cdot$

Step 5: Write net rate of formation of the active intermediate and use the PSSH

$r_{AZO \cdot} = r_1 + r_2 + r_3$

$r_{AZO \cdot} = k_1 C_{AZO}^2 - k_2 C_{AZO} \cdot C_{AZO} - k_3 C_{AZO} \cdot = 0$

Solving for $C_{AZO} \cdot$

$$C_{AZO \cdot} = \frac{k_1 C_{AZO}^2}{k_2 C_{AZO} + k_3}$$

Step 6: Eliminate the concentration of the active intermediate species in the rate laws by solving the simultaneous equations developed in Steps 4 and 5.

$$r_{C_2H_6} = \frac{k_1 k_3 C_{AZO}^2}{k_2 C_{AZO} + k_3}$$

Step 7: Compare with experimental data.

At low AZO concentrations, $k_2 C_{AZO} \ll k_3$

for which case we obtain the following second-order rate law:

$$r_{C_2H_6} = k_1 C_{AZO}^2$$
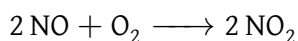
At high concentrations $k_2 C_{AZO} \gg k_3$

in which case the rate expression follows first-order kinetics

$$r_{C_2H_6} = k C_{AZO}$$

Nitric oxide combustion

Find the reaction rate law of the following reaction
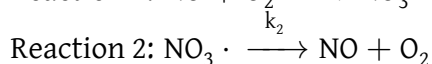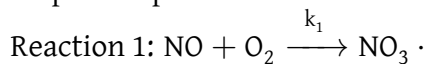
$2\,NO + O_2 \longrightarrow 2\,NO_2$

Experimental result: At low NO concentration, the reaction rate decreases with increasing temperature.
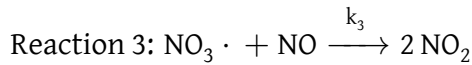
> ### 💡 Solution
>
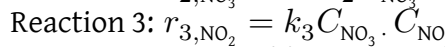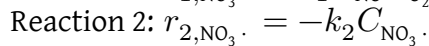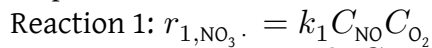> Step 1: Propose an active intermediate.
> We will choose as an active intermediate $NO_3 \cdot \cdot$.
> Step 2: Propose a mechanism
>
> Reaction 1: $NO + O_2 \xrightarrow{k_1} NO_3 \cdot$
>
> Reaction 2: $NO_3 \cdot \xrightarrow{k_2} NO + O_2$

Reaction 3: $NO_3 \cdot + NO \xrightarrow{k_3} 2 NO_2$

Step 3: Write rate laws

Reaction 1: $r_{1,NO_3 \cdot} = k_1 C_{NO} C_{O_2}$

Reaction 2: $r_{2,NO_3 \cdot} = -k_2 C_{NO_3 \cdot}$

Reaction 3: $r_{3,NO_2} = k_3 C_{NO_3 \cdot} C_{NO}$

Step 4: Write rate of formation of product.

$r_{NO_2} = k_3 C_{NO_3 \cdot} C_{NO}$

Step 5: Write net rate of formation of the active intermediate and use the PSSH

$r_{NO_3 \cdot} = r_1 - r_2 - r_3/2$

$r_{NO_3 \cdot} = k_1 C_{NO} C_{O_2} - k_2 C_{NO_3 \cdot} - \frac{k_3}{2} C_{NO_3 \cdot} C_{NO} = 0$

Solving for $C_{NO_3 \cdot}$.

$$C_{NO_3 \cdot} = \frac{k_1 C_{NO} C_{O_2}}{k_2 + \frac{k_3}{2} C_{NO}}$$

Step 6: Eliminate the concentration of the active intermediate species in the rate laws by solving the simultaneous equations developed in Steps 4 and 5.

At low NO concentrations, $k_2 \gg \frac{k_3}{2} C_{NO}$

$$C_{NO_3 \cdot} = \frac{k_1}{k_2} C_{NO} C_{O_2}$$

$$r_{NO_2} = \frac{k_1 k_3}{k_2} C_{NO}^2 C_{O_2}$$

Step 7: Compare with experimental data.

Experimental result: At low NO concentration, the reaction rate decreases with increasing temperature.

$$r_{NO_2} = \frac{A_1 A_3}{A_2} \exp\left[\frac{E_2 - (E_1 + E_3)}{RT}\right] C_{NO}^2 C_{O_2}$$

For reaction rate to decrease with temperature, $E_2 > E_1 + E_3$

Decomposition of cumene to form benzene and propylene

Develop rate laws for catalytic decomposition of cumene to form benzene and propylene.

$$C_6H_5CH(CH_3)_2 \longrightarrow C_6H_6 + C_3H_6$$
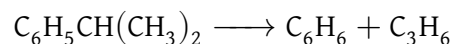
💡 Solution

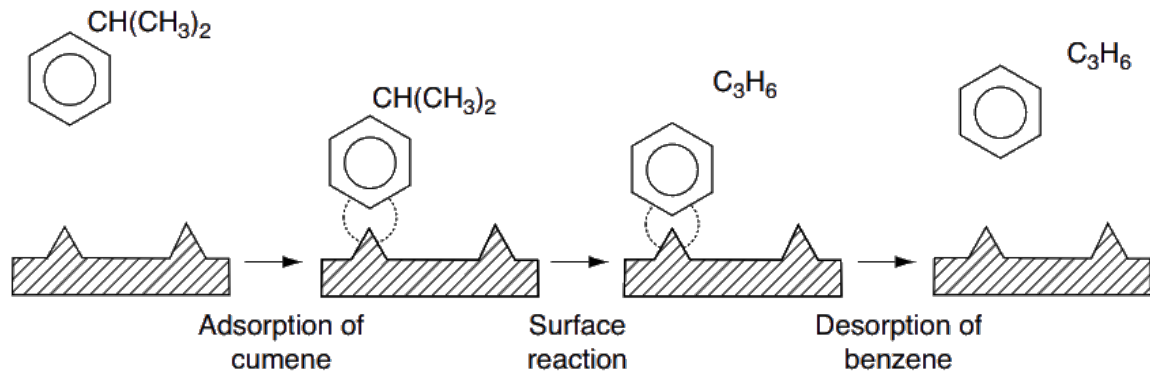Reaction: Cumene (C) $\longrightarrow$ Benzene (B) + Propylene (P)

Steps:

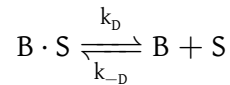Figure 1: Sequence of steps in a reaction-limited catalytic reaction.

Adsorption:

$$C + S \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} C \cdot S$$

Surface reaction:

$$C \cdot S \underset{k_{-S}}{\overset{k_S}{\rightleftharpoons}} B \cdot S + P$$

Desorption:

$$B \cdot S \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} B + S$$
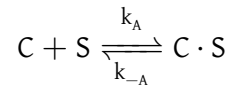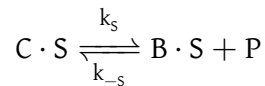
Reaction rates:
Adsorption:

$$r_{AD} = k_A P_C C_V - k_{-A} C_{C \cdot S}; \qquad r_{AD} = k_A \left(P_C C_V - \frac{C_{C \cdot S}}{K_A} \right)$$

Surface reaction:

$$r_S = k_S C_{C \cdot S} - k_{-S} P_P C_{B \cdot S} -; \qquad r_S = k_S \left(C_{C \cdot S} - \frac{P_P C_{B \cdot S}}{K_S} \right)$$

Desorption:

$$r_D = k_D C_{B \cdot S} - k_{-D} P_B C_V; \qquad r_D = k_D \left(C_{B \cdot S} - \frac{P_B C_V}{K_{DB}} \right);$$

$$K_B = \frac{1}{K_{DB}}; \Rightarrow r_D = k_D \left(C_{B \cdot S} - K_B P_B C_V \right)$$

For steady state operations the reaction rates of these three steps are equal.

$$-r'_C = r_{AD} = r_S = r_D$$

Case 1: Adsorption of Cumene Rate-Limiting

$$-r'_C = r_{AD} = k_A \left(P_C C_V - \frac{C_{C \cdot S}}{K_A} \right)$$

Because we cannot measure either C_V or $C_{C \cdot S}$, we must replace these variables in the rate law with measurable quantities in order for the equation to be meaningful.

For adsorption-limited reactions, the surface-specific reaction rate k_S, and desorption-specific reaction rate k_D are large by comparison, and we can set

$$\frac{r_S}{k_S} \approx 0; \text{ and } \frac{r_D}{k_D} \approx 0$$

Therefore,

$$C_{C \cdot S} = \frac{C_{B \cdot S} P_P}{K_S}$$

And,

$$C_{B \cdot S} = K_B P_B C_V$$

Combining,

$$C_{C \cdot S} = K_B \frac{P_B P_P}{K_S} C_V$$

and

$$-r'_C = k_A \left(P_C C_V - \frac{K_B P_B P_P C_V}{K_S K_C} \right)$$

The concentration of vacant sites, C_V, can now be eliminated by utilizing the site balance to give the total concentration of sites, C_t which is assumed constant.

$$C_t = C_V + C_{C \cdot S} + C_{B \cdot S}$$

$$C_t = C_V + \frac{K_B P_B P_P C_V}{K_S} + K_B P_B C_V$$

Solving for C_V we have

$$C_V = \frac{C_t}{1 + \frac{K_B P_P P_B}{K_S} + K_B P_B}$$

and the rate equation

$$r'_C = \frac{C_t k_A \left(P_C - \frac{P_B P_P}{K_P} \right)}{1 + \frac{K_B P_P P_B}{K_S} + K_P P_B}$$

At t = 0 min we have $P_C = P_{C,0}$, $P_P = 0$ (no product) and $P_B = 0$ (no product)

$$-r'_{CO} = r_{AD} = C_t k_A P_{CO} = k P_{CO}$$

Plot initial rate $-r'_{C,0}$ vs. $P_{C,0}$ is linear.

Case 2: Surface Reaction Rate-Limiting

$$-r'_C = r_S = k_S \left(C_{C \cdot S} - \frac{P_P C_{B \cdot S}}{K_S} \right)$$

- k_S : small
- k_A : large or $r_{AD}/k_A \approx 0$
- k_D : large or $r_D/k_D \approx 0$

From Adsorption reaction

$$\text{C} \cdot \text{S} = K_C P_C C_V$$

From Desorption reaction

$$\text{B} \cdot \text{S} = K_B P_B C_V$$

From site balance

$$C_V = \frac{C_t}{1 + K_B P_B + K_C P_C}$$

Therefore,

$$r_S = \frac{k_S K_C C_t \left(P_C - \frac{P_B P_P}{K_B}\right)}{1 + K_B P_B + K_C P_C}$$

At t = 0

$$-r'_{C,0} = r_S = \frac{k P_{C,0}}{1 + K_C P_{C,0}}; \qquad k = k_S K_C C_t$$

At low partial pressure of C we have $1 \gg K_C P_{C,0}$

$$-r'_{C,0} = k P_{C,0}$$

Initial rate increases linearly with the partial pressure of C
At high initial partial pressure of C we have $K_C P_{C,0} \gg 1$

$$-r'_{C,0} = k/k_C$$

Initial rate is constant.
Case 3: Desorption of Benzene the Rate-Limiting

$$-r'_C = r_D = k_D \left(C_{\text{B} \cdot \text{S}} - K_B P_B C_V\right)$$

- k_D : small
- k_A : large or $r_{AD}/k_A \approx 0$
- k_S : large or $r_S/k_S \approx 0$

From adsorption reaction

$$C_{\text{C} \cdot \text{S}} = K_C P_C C_V$$

From surface reaction

$$C_{B,S} = K_S \left(\frac{C_{C,S}}{P_P}\right)$$

From site balance

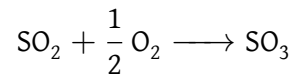$$C_V = \frac{C_t}{1 + K_C K_S \frac{P_C}{P_P} + K_C P_C}$$

Therefore reaction rate:

$$-r'_{C,0} = r_D = k_D K_C K_S C_t \left(\frac{P_C - \frac{P_B P_P}{K_P}}{P_P + K_C K_S P_C + K_C P_P P_C} \right)$$

At t = 0; $-r'_{C,0} = k_D C_t = constant$
Initial rate is constant.

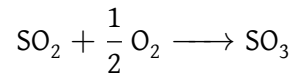# Rate law for catalytic reaction
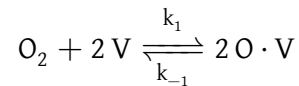
Find the reaction rate law of the reaction

$$SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3$$
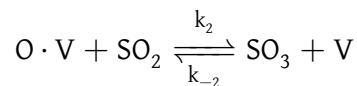
> 💡 Solution
>
> Reaction:
> $$SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3$$
>
> Mechanism:
> Oxygen adsorption (V is vacant site):
>
> $$O_2 + 2\,V \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,O \cdot V$$
>
> Surface reaction:
>
> $$O \cdot V + SO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} SO_3 + V$$
>
> Reaction rates:
> Reaction 1:
> $$r_1 = k_1 P_{O_2} C_V^2 - k_{-1} C_{O \cdot V}^2$$
>
> Reaction 2:
>
> $$r_2 = k_2 C_{O \cdot V} P_{SO_2} - k_{-2} P_{SO_3} C_V$$
>
> Assume reaction 2 is slow (rate limiting step)
> Therefore, $r_1/k_1 \approx 0$
>
> $$\therefore C_{O \cdot V}^2 = K_1 P_{O_2} C_V^2$$
>
> Rate for reaction 2 then becomes:
>
> $$r_2 = k_2 \left(K_1 P_{O_2} \right)^{1/2} C_V P_{SO_2} - k_{-2} P_{SO_3} C_V$$

Site balance:

$$C_t = C_V + C_{S,O} = C_V + K_1^{1/2} P_{O_2}^{1/2} C_V$$

$$C_V = \frac{C_t}{1 + (K_1 P_{O_2})^{1/2}}$$

Substituting in equation for r_2

$$r_2 = \frac{k_2 \left(K_1 P_{O_2}\right)^{1/2} P_{SO_2} C_t}{1 + \left(K_1 P_{O_2}\right)^{1/2}} - \frac{k_{-2} P_{SO_3} C_t}{1 + \left(K_1 P_{O_2}\right)^{1/2}}$$

$$r_2 = \frac{k_2 C_t P_{SO_2} \left(K_1 P_{O_2}\right)^{1/2} - k_{-2} C_t P_{SO_3}}{1 + \left(K_1 P_{O_2}\right)^{1/2}}$$
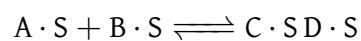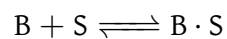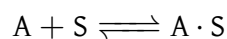
at t = 0

$$r_{2,0} = \frac{k_2 C_t P_{SO_2} \left(K_1 P_{O_2}\right)^{1/2}}{1 + \left(K_1 P_{O_2}\right)^{1/2}}$$

Compare with the experimental data

- Differential reactor
- Measureable data
- Keep P_{SO_2} constant, change P_{O_2}
- Keep P_{O_2} constant, change P_{SO_2}
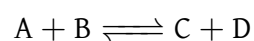
Surface reaction limiting reaction

The reaction $A + B \rightleftharpoons C + D$ is carried out over a solid catalyst, the reaction mechanism is believed to be

$$A + S \rightleftharpoons A \cdot S$$
$$B + S \rightleftharpoons B \cdot S$$
$$A \cdot S + B \cdot S \rightleftharpoons C \cdot S D \cdot S$$
$$C \cdot S \rightleftharpoons C + S$$
$$D \cdot S \rightleftharpoons D + S$$
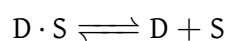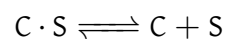
Assuming step 3 is the slowest step, derive the rate law for the reaction.

💡 Solution

Reaction:

$$A + B \rightleftharpoons C + D$$

Mechanism:

Adsorption:

$$A + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A \cdot S$$

$$B + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B \cdot S$$

Surface reaction:

$$A \cdot S + B \cdot S \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C \cdot S + D \cdot S$$

Desorption:

$$C \cdot S \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C + S$$

$$D \cdot S \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} D + S$$
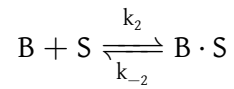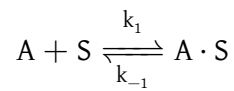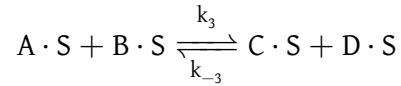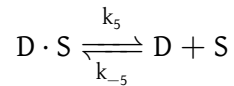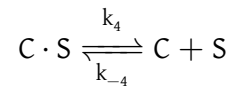
Reaction rates:

$$r_1 = k_1 P_A C_V - k_{-1} C_{A \cdot S}$$
$$r_2 = k_2 P_B C_V - k_{-2} C_{B \cdot S}$$
$$r_3 = k_3 C_{A \cdot S} C_B \cdot S - k_{-3} C_{C \cdot S} C_{D \cdot S}$$
$$r_4 = k_4 C_{C \cdot S} - k_{-4} P_C C_V$$
$$r_5 = k_5 C_{D \cdot S} - k_{-5} P_D C_V$$

and

$$K_1 = \frac{k_1}{k_{-1}}$$

$$K_2 = \frac{k_2}{k_{-2}}$$

$$K_3 = \frac{k_3}{k_{-3}}$$

$$K_4 = \frac{k_4}{k_{-4}}$$

$$K_5 = \frac{k_5}{k_{-5}}$$

Assume surface reaction is rate limiting

$$r_3 = k_3 C_{A \cdot S} C_{B \cdot S} - k_{-3} C_{C \cdot S} C_{D \cdot S}$$

We need to eliminate $C_{A \cdot S}, C_{B \cdot S}, C_{C \cdot S},$ and $C_{D \cdot S}$

$$C_{A \cdot S} = K_1 P_A C_V$$
$$C_{B \cdot S} = K_2 P_B C_V$$
$$C_{C \cdot S} = K_3 P_C C_V$$
$$C_{D \cdot S} = K_4 P_D C_V$$

and

$$r = k_3 K_1 K_2 P_A P_B C_V^2 - k_{-3} K_4 K_5 P_C P_D C_V^2$$

Write site balance to calculate C_V:

$$C_t = C_V + C_{A \cdot S} + C_{B \cdot S} + C_{C \cdot S} + C_{D \cdot S}$$

$$C_V = \frac{C_t}{1 + K_1 P_A + K_2 P_B + K_3 P_C + K_4 P_D}$$

Substituting

$$r = r_3 = \frac{k_3 K_1 K_2 P_A P_B C_t^2 - k_{-3} K_4 K_5 P_C P_D C_t^2}{(1 + K_1 P_A + K_2 P_B + K_3 P_C + K_4 P_D)^2}$$

Initial rates in differential reactor
at t = 0 $P_C, P_D = 0$

$$r_0 = \frac{k_3 K_1 K_2 P_A P_B C_t}{1 + K_1 P_A + K_2 P_B}$$