

In class activity: Reaction mechanisms and catalysis

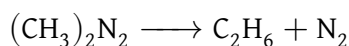
Lecture notes for chemical reaction engineering

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Gas phase decomposition of azomethane

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



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)

$$r_{\text{C}_2\text{H}_6} \propto C_{\text{AZO}}$$

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

$$r_{\text{C}_2\text{H}_6} \propto C_{\text{AZO}}^2$$

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

$$r_{\text{C}_2\text{H}_6} = \frac{k_1 C_{\text{AZO}}^2}{1 + k_2 C_{\text{AZO}}}$$

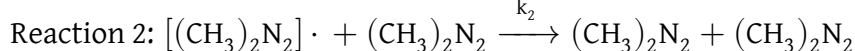
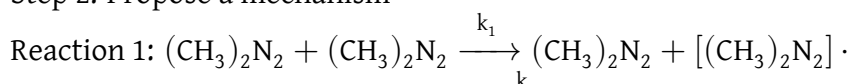
find a mechanism that is consistent with the experimental observations

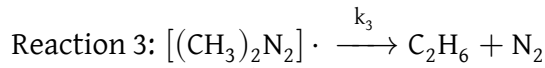
Solution

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 $\text{AZO} \cdot$, that is, $[(\text{CH}_3)_2\text{N}_2] \cdot$.

Step 2: Propose a mechanism





Step 3: Write rate laws

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

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

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

Step 4: Write rate of formation of product.

$r_{\text{C}_2\text{H}_6} = k_3 C_{\text{AZO}} \cdot$

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

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

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

Solving for $C_{\text{AZO}} \cdot$

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

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.

$$r_{\text{C}_2\text{H}_6} = \frac{k_1 k_3 C_{\text{AZO}}^2}{k_2 C_{\text{AZO}} + k_3}$$

Step 7: Compare with experimental data.

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

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

$$r_{\text{C}_2\text{H}_6} = k_1 C_{\text{AZO}}^2$$

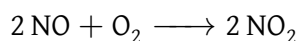
At high concentrations $k_2 C_{\text{AZO}} \gg k_3$

in which case the rate expression follows first-order kinetics

$$r_{\text{C}_2\text{H}_6} = k C_{\text{AZO}}$$

Nitric oxide combustion

Find the reaction rate law of the following reaction



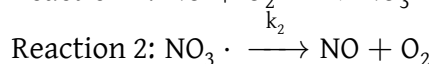
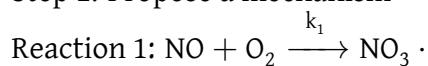
Experimental result: At low NO concentration, the reaction rate decreases with increasing temperature.

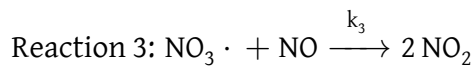
Solution

Step 1: Propose an active intermediate.

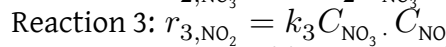
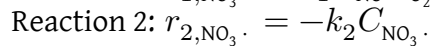
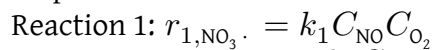
We will choose as an active intermediate $\text{NO}_3 \cdot$.

Step 2: Propose a mechanism

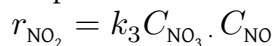




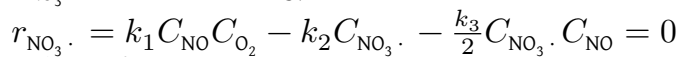
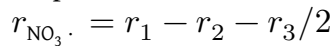
Step 3: Write rate laws



Step 4: Write rate of formation of product.



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



Solving for $C_{\text{NO}_3 \cdot}$

$$C_{\text{NO}_3 \cdot} = \frac{k_1 C_{\text{NO}} C_{\text{O}_2}}{k_2 + \frac{k_3}{2} C_{\text{NO}}}$$

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, $k_2 \gg \frac{k_3}{2} C_{\text{NO}}$

$$C_{\text{NO}_3 \cdot} = \frac{k_1}{k_2} C_{\text{NO}} C_{\text{O}_2}$$

$$r_{\text{NO}_2} = \frac{k_1 k_3}{k_2} C_{\text{NO}}^2 C_{\text{O}_2}$$

Step 7: Compare with experimental data.

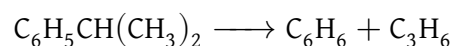
Experimental result: At low NO concentration, the reaction rate decreases with increasing temperature.

$$r_{\text{NO}_2} = \frac{A_1 A_3}{A_2} \exp \left[\frac{E_2 - (E_1 + E_3)}{RT} \right] C_{\text{NO}}^2 C_{\text{O}_2}$$

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.



Solution

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

Steps:

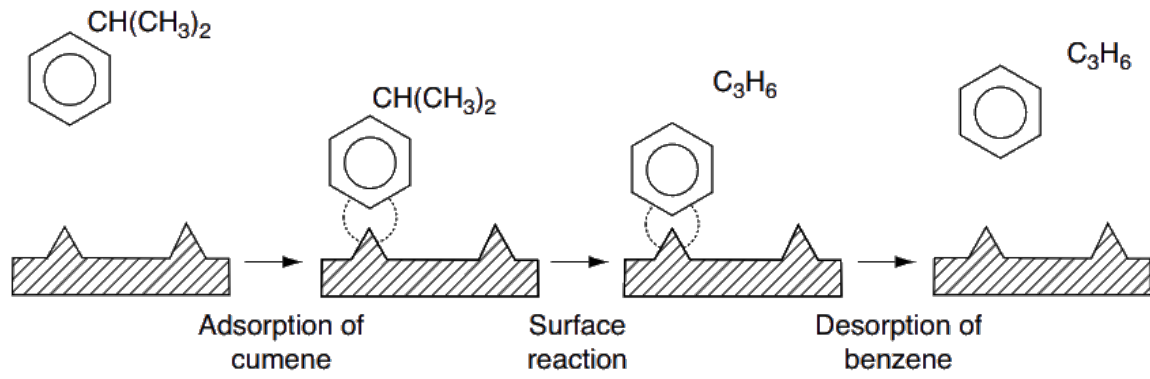
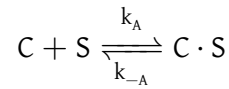
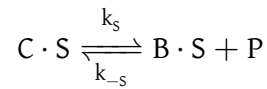


Figure 1: Sequence of steps in a reaction-limited catalytic reaction.

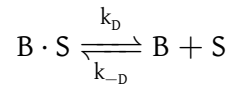
Adsorption:



Surface reaction:



Desorption:



Reaction rates:

Adsorption:

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

Surface reaction:

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

Desorption:

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

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

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

$$C \cdot S = K_C P_C C_V$$

From Desorption reaction

$$B \cdot S = K_B P_B C_V$$

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 $t = 0$

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

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

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

- 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

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

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:

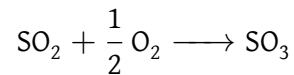
$$-r'_{C,0} = r_D = k_D K_C K_S C_t \left(\frac{P_C - \frac{P_B P_P}{K_P}}{P_P + K_C K_S P_C + K_C P_P P_C} \right)$$

At $t = 0$; $-r'_{C,0} = k_D C_t = \text{constant}$

Initial rate is constant.

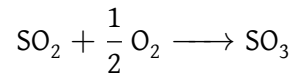
Rate law for catalytic reaction

Find the reaction rate law of the reaction



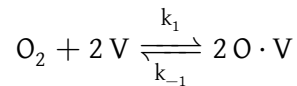
Solution

Reaction:

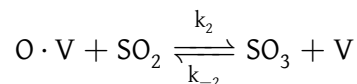


Mechanism:

Oxygen adsorption (V is vacant site):



Surface reaction:



Reaction rates:

Reaction 1:

$$r_1 = k_1 P_{\text{O}_2} C_V^2 - k_{-1} C_{\text{O} \cdot \text{V}}^2$$

Reaction 2:

$$r_2 = k_2 C_{\text{O} \cdot \text{V}} P_{\text{SO}_2} - k_{-2} P_{\text{SO}_3} C_V$$

Assume reaction 2 is slow (rate limiting step)

Therefore, $r_1/k_1 \approx 0$

$$\therefore C_{\text{O} \cdot \text{V}}^2 = K_1 P_{\text{O}_2} C_V^2$$

Rate for reaction 2 then becomes:

$$r_2 = k_2 \left(K_1 P_{\text{O}_2} \right)^{1/2} C_V P_{\text{SO}_2} - k_{-2} P_{\text{SO}_3} C_V$$

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

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

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

at $t = 0$

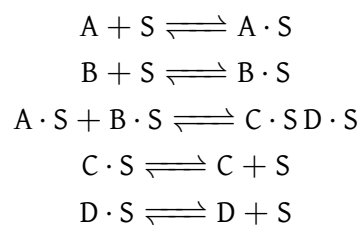
$$r_{2,0} = \frac{k_2 C_t P_{SO_2} (K_1 P_{O_2})^{1/2}}{1 + (K_1 P_{O_2})^{1/2}}$$

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

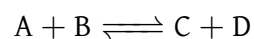
The reaction $A + B \rightleftharpoons C + D$ is carried out over a solid catalyst, the reaction mechanism is believed to be



Assuming step 3 is the slowest step, derive the rate law for the reaction.

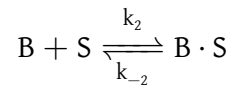
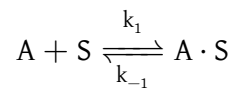
 Solution

Reaction:

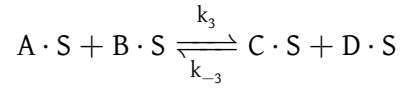


Mechanism:

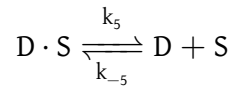
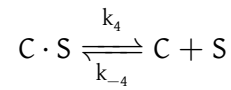
Adsorption:



Surface reaction:



Desorption:



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 :

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

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

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 $t = 0$ $P_C, P_D = 0$

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