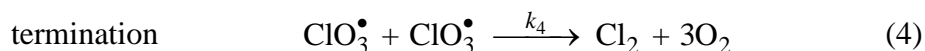
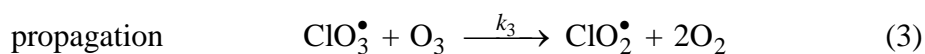
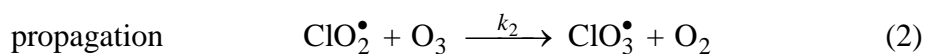
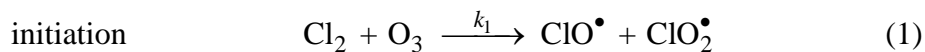


University of Alberta
Department of Chemical Engineering
Ch E 145 - Chemical Reactor Analysis
Seminar #5

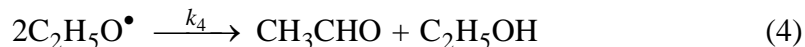
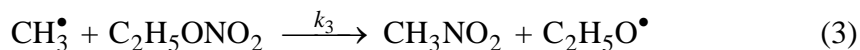
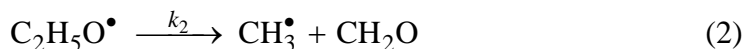
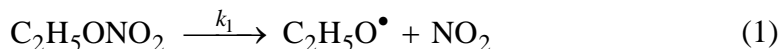
February 17, 2017

1. Consider the catalytic decomposition of ozone by chlorine. The following mechanism is proposed:



Find the rate of disappearance of O_3 .

2. The pyrolysis of ethyl nitrate has the following proposed mechanism:



The reaction rate at different concentrations of ethyl nitrate are:

| | | | | | |
|--|--------|--------|--------|--------|--------|
| $\text{C}_{\text{C}_2\text{H}_5\text{ONO}_2} \frac{\text{mol}}{\text{m}^3}$ | 0.0975 | 0.0759 | 0.0713 | 0.2714 | 0.2436 |
| $\left(-r_{\text{C}_2\text{H}_5\text{ONO}_2}\right) \frac{\text{mol}}{\text{m}^3\text{s}}$ | 0.0134 | 0.0122 | 0.0121 | 0.023 | 0.0209 |

Use the PSSH to deduce a rate equation and test it for consistency against the experimental data.

Solution to problem 1

Apply the PSSH to the intermediates ClO_2^\bullet and ClO_3^\bullet . The net rate of disappearance of O_3 is given by:

$$(-r_{\text{O}_3}) = k_1[\text{Cl}_2][\text{O}_3] + k_2[\text{ClO}_2^\bullet][\text{O}_3] + k_3[\text{ClO}_3^\bullet][\text{O}_2] \quad (5)$$

The net rate of formation of ClO_2^\bullet is set to zero:

$$r_{\text{ClO}_2} = k_1[\text{Cl}_2][\text{O}_3] - k_2[\text{ClO}_2^\bullet][\text{O}_3] + k_3[\text{ClO}_3^\bullet][\text{O}_2] = 0 \quad (6)$$

The net rate of formation of ClO_3^\bullet is set to zero:

$$r_{\text{ClO}_3} = k_2[\text{ClO}_2^\bullet][\text{O}_3] - k_3[\text{ClO}_3^\bullet][\text{O}_3] - k_4[\text{ClO}_3^\bullet]^2 = 0 \quad (7)$$

Equations (6) and (7) can be combined to give an expression for ClO_3^\bullet :

$$[\text{ClO}_3^\bullet] = \sqrt{\frac{k_1}{k_4}} [\text{Cl}_2]^{1/2} [\text{O}_3]^{1/2} \quad (8)$$

Substitution of Equation (8) into Equation (7) gives:

$$[\text{ClO}_2^\bullet] = \frac{k_3}{k_2} \sqrt{\frac{k_1}{k_4}} [\text{Cl}_2]^{1/2} [\text{O}_3] + \frac{k_1}{k_2} [\text{Cl}_2] \quad (9)$$

Substitution of Equation (9) into Equation (5) gives:

$$(-r_{\text{O}_3}) = 2k_3 \sqrt{\frac{k_1}{k_4}} [\text{Cl}_2]^{1/2} [\text{O}_3]^{3/2} + 2k_1 [\text{Cl}_2][\text{O}_3] \quad (10)$$

If the rate of the initiation reaction is slow compared to the rate of propagation, then the second term on the right hand side is small and, in this case, the rate of reaction is:

$$(-r_{\text{O}_3}) = k' [\text{Cl}_2]^{1/2} [\text{O}_3]^{3/2}$$

Solution to problem 2

Let A refer to $\text{C}_2\text{H}_5\text{ONO}_2$, B to $\text{C}_2\text{H}_5\text{O}^\bullet$ and C to CH_3^\bullet . Then apply the PSSH to B and C .

$$r_{\text{B}} = k_1[\text{A}] - k_2[\text{B}] + k_3[\text{A}][\text{C}] - k_4[\text{B}]^2 = 0$$

$$r_{\text{C}} = k_2[\text{B}] - k_3[\text{A}][\text{C}] = 0$$

These equations can be rearranged. By adding the two equations, we deduce:

$$[\text{B}] = \left(\frac{k_1}{k_4} \right)^{0.5} [\text{A}]^{0.5}$$

Substituting $[\text{B}]$ into the expression for r_{C} gives:

$$[\text{C}] = \frac{k_2[\text{B}]}{k_3[\text{A}]} = \frac{k_2}{k_3} \left(\frac{k_1}{k_4} \right)^{0.5} [\text{A}]^{-0.5}$$

The rate of disappearance of A is given by:

$$(-r_{\text{A}}) = k_1[\text{A}] + k_3[\text{A}][\text{C}]$$

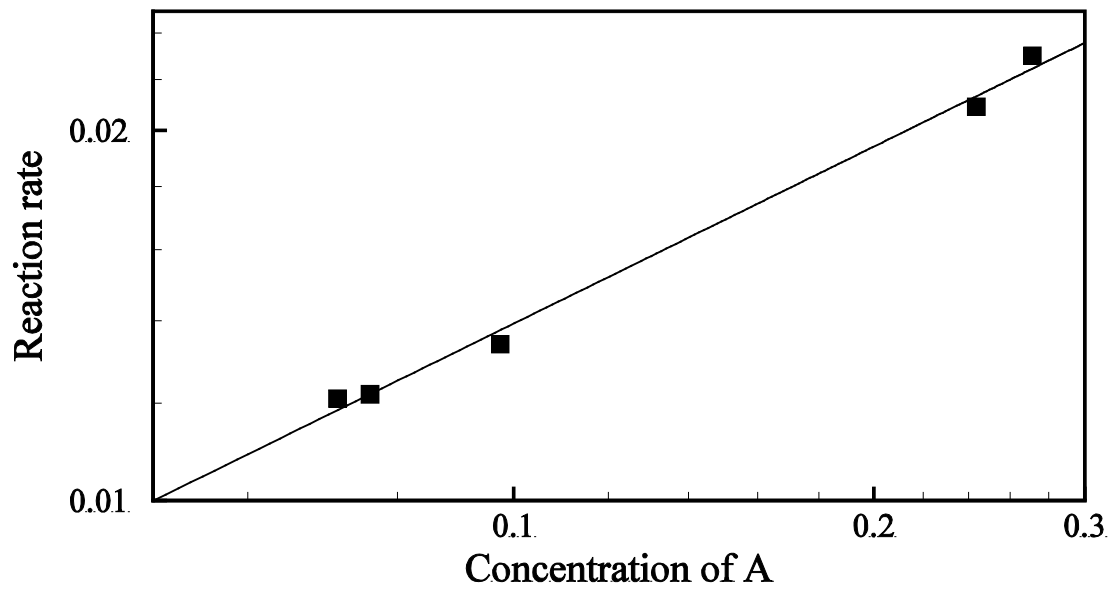
Substitute for $[\text{C}]$:

$$(-r_{\text{A}}) = k_1[\text{A}] + k_2 \left(\frac{k_1}{k_4} \right)^{0.5} [\text{A}]^{0.5}$$

Normally k_1 and k_4 are small compared with k_2 , because the propagation steps are much faster than initiation and termination. In this case, the second term dominates and we write:

$$(-r_{\text{A}}) \approx k'[\text{A}]^{0.5}$$

To test the validity of the assumptions, a plot of reaction rate vs. concentration can be made. This plot should give a straight line correlation when log scales are used with a slope of 0.5 if the model is valid. The plot is shown in the following figure.



The equation of the line is:

$$(-r_A) = 42.69 [A]^{0.4858}$$

The data appear to be closely correlated by the proposed model.