

# Chemistry 2710 Spring 2001 Assignment 3 Solutions

1. (a)  $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$   
(b) We apply the EA to the first reaction, giving us the equation

$$k_1[\text{N}_2\text{O}_5] \approx k_{-1}[\text{NO}_2][\text{NO}_3]. \quad (1)$$

We must also apply the SSA to the nitrogen trioxide concentration:

$$\frac{d[\text{NO}_3]}{dt} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] + k_3[\text{NO}_2][\text{O}_3] - 2k_4[\text{NO}_3]^2 \approx 0.$$

Note that equation 1 implies that the first two terms of this last equation cancel out.

$$\begin{aligned} \therefore k_3[\text{NO}_2][\text{O}_3] &\approx 2k_4[\text{NO}_3]^2. \\ \therefore [\text{NO}_2] &\approx \frac{2k_4[\text{NO}_3]^2}{k_3[\text{O}_3]}. \end{aligned} \quad (2)$$

If we substitute this last equation into equation 1, we get

$$\begin{aligned} k_1[\text{N}_2\text{O}_5] &\approx \frac{2k_{-1}k_4[\text{NO}_3]^3}{k_3[\text{O}_3]}. \\ \therefore [\text{NO}_3] &\approx \left( \frac{k_1k_3}{2k_{-1}k_4} [\text{N}_2\text{O}_5][\text{O}_3] \right)^{1/3}. \end{aligned} \quad (3)$$

Substituting equation 3 into equation 2 and simplifying, we get

$$[\text{NO}_2] \approx \left( \frac{2k_1^2k_4}{k_{-1}^2k_3} \frac{[\text{N}_2\text{O}_5]^2}{[\text{O}_3]} \right)^{1/3}.$$

We now have the concentrations of  $\text{NO}_2$  and of  $\text{NO}_3$  expressed exclusively in terms of the concentrations of dinitrogen pentoxide and of ozone. We should be able to get the rate in terms of the latter two concentrations now:

$$\begin{aligned} \frac{d[\text{O}_3]}{dt} &= -k_3[\text{NO}_2][\text{O}_3] \\ &\approx - \left( \frac{2k_1^2k_3^2k_4}{k_{-1}^2} [\text{N}_2\text{O}_5]^2[\text{O}_3]^2 \right)^{1/3}. \\ v &= -\frac{1}{2} \frac{d[\text{O}_3]}{dt} \\ &\approx \left( \frac{k_1^2k_3^2k_4}{4k_{-1}^2} [\text{N}_2\text{O}_5]^2[\text{O}_3]^2 \right)^{1/3}. \end{aligned}$$

(c) The rate law we obtained above is in a simple form with orders of reaction of  $\frac{2}{3}$  with respect to each of  $\text{N}_2\text{O}_5$  and  $\text{O}_3$ .

(d) If we used the SSA for both intermediates, we would solve the pair of equations

$$\begin{aligned}\frac{d[\text{NO}_3]}{dt} &= k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] + k_3[\text{NO}_2][\text{O}_3] - 2k_4[\text{NO}_3]^2 \approx 0, \\ \frac{d[\text{NO}_2]}{dt} &= k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}_2][\text{O}_3] + 2k_4[\text{NO}_3]^2 \approx 0.\end{aligned}$$

If we add these two equations, we get

$$2k_1[\text{N}_2\text{O}_5] - 2k_{-1}[\text{NO}_2][\text{NO}_3] \approx 0$$

which is equivalent to equation 1. Solving this equation along with  $d[\text{NO}_3]/dt \approx 0$  is exactly what we did in question 1b so applying the SSA to both catalytic intermediates would give exactly the same rate law in this case.

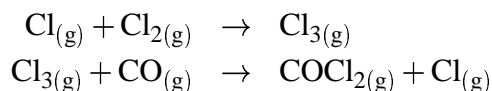
2. (a) **Mechanism 1:**  $\text{Cl}, \text{Cl}_3$

**Mechanism 2:**  $\text{Cl}, \text{COCl}$

(b) **Mechanism 1:**

**Initiation:**  $\text{Cl}_{2(g)} \rightarrow 2\text{Cl}_{(g)}$

**Chain propagation:**



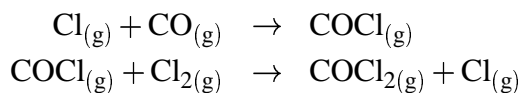
**Termination:**  $2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)}$

**None of the above:**  $\text{Cl}_{3(g)} \rightarrow \text{Cl}_{(g)} + \text{Cl}_{2(g)}$

**Mechanism 2:**

**Initiation:**  $\text{Cl}_{2(g)} \rightarrow 2\text{Cl}_{(g)}$

**Chain propagation:**



**Termination:**  $2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)}$

**None of the above:**  $\text{COCl}_{(g)} \rightarrow \text{Cl}_{(g)} + \text{CO}_{(g)}$

(c) **Mechanism 1:** We will use the SSA for both radicals:

$$\begin{aligned}\frac{d[\text{Cl}]}{dt} &= 2k_1[\text{Cl}_2] - 2k_{-1}[\text{Cl}]^2 - k_2[\text{Cl}][\text{Cl}_2] + k_{-2}[\text{Cl}_3] + k_3[\text{Cl}_3][\text{CO}] \approx 0, \\ \frac{d[\text{Cl}_3]}{dt} &= k_2[\text{Cl}][\text{Cl}_2] - k_{-2}[\text{Cl}_3] - k_3[\text{Cl}_3][\text{CO}] \approx 0.\end{aligned}\tag{4}$$

If we add these equations, we get

$$\begin{aligned} k_1[\text{Cl}_2] &\approx k_{-1}[\text{Cl}]^2. \\ \therefore [\text{Cl}] &\approx \sqrt{\frac{k_1[\text{Cl}_2]}{k_{-1}}}. \end{aligned} \quad (5)$$

From equation 4, we have

$$[\text{Cl}_3] \approx \frac{k_2[\text{Cl}][\text{Cl}_2]}{k_{-2} + k_3[\text{CO}]}.$$

If we now substitute in equation 5, we get

$$[\text{Cl}_3] \approx \frac{k_2}{k_{-2} + k_3[\text{CO}]} \sqrt{\frac{k_1[\text{Cl}_2]^3}{k_{-1}}}.$$

The rate of the reaction is therefore

$$v_1 = \frac{d[\text{COCl}_2]}{dt} = k_3[\text{Cl}_3][\text{CO}] \approx \frac{k_2 k_3 [\text{CO}]}{k_{-2} + k_3 [\text{CO}]} \sqrt{\frac{k_1 [\text{Cl}_2]^3}{k_{-1}}}.$$

**Mechanism 2:** In this case, we want to apply the SSA to Cl and to COCl:

$$\begin{aligned} \frac{d[\text{Cl}]}{dt} &= 2k_1[\text{Cl}_2] - 2k_{-1}[\text{Cl}]^2 - k_2[\text{Cl}][\text{CO}] + k_{-2}[\text{COCl}] \\ &\quad + k_3[\text{COCl}][\text{Cl}_2] \approx 0, \\ \frac{d[\text{COCl}]}{dt} &= k_2[\text{Cl}][\text{CO}] - k_{-2}[\text{COCl}] - k_3[\text{COCl}][\text{Cl}_2] \approx 0. \end{aligned} \quad (6)$$

The solution proceeds exactly as before. If we add the two equations and rearrange, we get

$$[\text{Cl}] \approx \sqrt{\frac{k_1[\text{Cl}_2]}{k_{-1}}}.$$

Equation 6 can be rearranged to

$$\begin{aligned} [\text{COCl}] &\approx \frac{k_2[\text{Cl}][\text{CO}]}{k_{-2} + k_3[\text{Cl}_2]} \approx \frac{k_2[\text{CO}]}{k_{-2} + k_3[\text{Cl}_2]} \sqrt{\frac{k_1[\text{Cl}_2]}{k_{-1}}}. \\ \therefore v_2 &= \frac{d[\text{COCl}_2]}{dt} = k_3[\text{COCl}][\text{Cl}_2] \approx \frac{k_2 k_3 [\text{CO}]}{k_{-2} + k_3 [\text{Cl}_2]} \sqrt{\frac{k_1 [\text{Cl}_2]^3}{k_{-1}}}. \end{aligned}$$

**Comparison:** It is perhaps easiest to see how the two could be distinguished by comparing the predictions made by the two mechanisms at high and low pressures of the two reactants.

low [Cl <sub>2</sub> ]	high [Cl <sub>2</sub> ]	low [CO]	high [CO]
$v_1 \propto [\text{Cl}_2]^{3/2}$	$v_1 \propto [\text{Cl}_2]^{3/2}$	$v_1 \propto [\text{CO}]$	$v_1 \propto [\text{CO}]^0$
$v_2 \propto [\text{Cl}_2]^{3/2}$	$v_2 \propto [\text{Cl}_2]^{1/2}$	$v_2 \propto [\text{CO}]$	$v_2 \propto [\text{CO}]$

The two mechanisms therefore predict different dependences on the Cl<sub>2</sub> and CO pressures. In mechanism 1, the order of the reaction with respect to Cl<sub>2</sub> is always  $\frac{3}{2}$ . However, the order changes from  $\frac{3}{2}$  to  $\frac{1}{2}$  in mechanism 2 going from very low to very high pressures of Cl<sub>2</sub>. Furthermore, in mechanism 1, the order with respect to CO changes from 1 to 0 as the CO pressure is increased while mechanism 2 predicts a constant order of reaction of 1 with respect to this reactant. The two mechanisms therefore can be distinguished experimentally by carrying out experiments over a range of pressures of the two reactants.