Kinetics 3 • Chem 220

Consider the catalyzed reaction and proposed mechanism below:

Overall: \[ 2 \text{SO}_2 + \text{O}_2 \xrightarrow{\text{catalyst}} 2 \text{SO}_3 \]

Step 1: \[ \text{NO} + \text{O}_2 \leftrightarrow \text{NO}_2 \] fast, equilibrium

Step 2: \[ \text{NO}_2 + \text{NO} \rightarrow 2 \text{NO}_2 \] slow

Step 3: \[ \text{NO}_2 + \text{SO}_2 \rightarrow \text{SO}_3 + \text{NO} \] fast

Note: Step 3 must occur twice for each step 1,2 combination. This does NOT affect the rate law.

A) Write the differential rate law expression in terms of overall reactant and/or catalyst concentrations only.

\[
\text{rate} = k_2 \left[ \text{NO}_2 \right]^2 \left[ \text{NO} \right] \quad \text{(must replace NO}_3 \text{)}
\]

Step 1:
\[
\frac{k_1 \left[ \text{NO}_2 \right]^2 \left[ \text{O}_2 \right]}{k_7} = \frac{k_2 \left[ \text{NO}_3 \right]}{k_3}
\]

\[
\text{rate} = k_2 \left( \frac{k_1}{k_7} \right) \left[ \text{NO}_2 \right]^2 \left[ \text{O}_2 \right]
\]

B) What is the role of NO\textsubscript{3} in this process?

Intermediate

C) Consider the initial rates experiment data below:

<table>
<thead>
<tr>
<th>Trial</th>
<th>[SO\textsubscript{2}] (M)</th>
<th>[O\textsubscript{2}] (M)</th>
<th>[NO\textsubscript{2}] (M)</th>
<th>(-\Delta[\text{SO}_2]/\Delta t) (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.150</td>
<td>0.0100</td>
<td>0.0800</td>
<td>6.48 x 10\textsuperscript{-5}</td>
</tr>
<tr>
<td>2</td>
<td>0.450</td>
<td>0.0100</td>
<td>0.0800</td>
<td>5.81 x 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>3</td>
<td>0.150</td>
<td>0.0100</td>
<td>0.1600</td>
<td>1.30 x 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>4</td>
<td>0.150</td>
<td>0.0500</td>
<td>0.0800</td>
<td>6.51 x 10\textsuperscript{-5}</td>
</tr>
</tbody>
</table>

Write the differential rate law expression for this reaction based on the experimental data.

\[
\text{rate} = k_2 \left[ \text{SO}_2 \right]^2 \left[ \text{NO}_2 \right]
\]

D) Does the experimentally determined rate law support the mechanism? Which is likely correct? Explain briefly.

NO\textsubscript{3}, it does NOT match the rate law derived from the mechanism.

The experimental rate laws should be correct, our rate laws must be determined experimentally. The reaction likely proceeds by a different mechanism.

E) What is the necessary concentration of SO\textsubscript{2} to achieve an initial rate \((-\Delta[O_2]/\Delta t)\) equal to 2.30 x 10\textsuperscript{-4} M/s when [NO\textsubscript{3}] = [O\textsubscript{2}] = 0.200 M?

\[
\frac{-\Delta[\text{SO}_2]}{\Delta t} = k \left[ \text{SO}_2 \right]^2 \left[ \text{NO} \right]
\]

\[
(6.48 \times 10^{-5} \text{M/s}) = k \left( 0.150 \text{M} \right)^2 \left( 0.0800 \text{M} \right)
\]

\[
k = \frac{1}{0.150^2 \times 0.0800} = 3.60 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}
\]

\[
\frac{(-\Delta[\text{O}_2])}{\Delta t} = \frac{-\Delta[\text{SO}_2]}{\Delta t}
\]

\[
\frac{1}{\text{M/s}} \left( \frac{-\Delta[\text{SO}_2]}{\Delta t} \right) = 2 \left( \frac{-\Delta[\text{O}_2]}{\Delta t} \right) = 2 \left( 2.30 \times 10^{-4} \text{ s}^{-1} \right)
\]

\[
\text{rate} = 4.60 \times 10^{-4} \text{ M/s}
\]

Note: This different than the rate defined in the table.
\[ \text{rate} = k [SO_2]^2 [NO] \]

\[
[SO_2] = \sqrt{\frac{\text{rate}}{k [NO]}} = \sqrt{\frac{4.60 \times 10^{-4} \text{ M/s}}{3.60 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1} (0.200 \text{ M})}}
\]

\[ [SO_2] = 0.253 \text{ M} \]