Enhanced Reactivity of Superoxide in Water-Solid Matrices

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Supporting Information

The Eley-Rideal kinetic model was used to examine the generation of superoxide and its reactivity with HCO in the H$_2$O$_2$-birnessite system. Reactions 1-4 serve as the basis for the model.

$$
\begin{align*}
\text{MnO}_2 & \quad \text{H}_2\text{O}_2 \quad \xleftrightarrow[k_1]{k} \quad \text{H}_2\text{O}_2\text{sorbed} \quad K_1 \\
\text{H}_2\text{O}_2\text{sorbed} & \quad \xleftrightarrow[k_2]{k_{-2}} \quad \text{O}_2^-\text{sorbed} \quad K_2 \\
\text{O}_2^-\text{sorbed} & \quad \text{HCA} \quad \xleftrightarrow[k_3]{	ext{Products}} \\
\text{O}_2^- & \quad \xleftrightarrow[k'_{1}]{k'_{-1}} \quad \text{O}_2^-\text{sorbed} \quad K'_1
\end{align*}
$$

where $K_1$ = the adsorption coefficient for H$_2$O$_2$,

$k_1$ = sorption rate for H$_2$O$_2$,

$k_{-1}$ = desorption rate for H$_2$O$_2$,

$k_2$ = decomposition of hydrogen peroxide with the formation of superoxide on the surface,

$k_{-2}$ = dismutation rate for superoxide on the surface,

$K_2$ = equilibrium constant for the reaction (2),

$k_3$ = reaction rate for the reaction between superoxide and HCA,

$K'_1$ = the adsorption coefficient for superoxide,

$k'_{1}$ = sorption rate for O$_2^-$. 


\[ k'_{-1} = \text{desorption rate for } O_2^- \]

The assumptions of the model are as follows: Reactions 1 through 4 take place at the catalyst surface, the initial rate of superoxide formation is proportional to the concentration of \( H_2O_2 \), and the concentration of superoxide is at steady-state.

Assuming steady-state conditions for superoxide:

\[ k_2 \cdot [H_2O_2]_{\text{sorbed}} - k_{-2} \cdot [O_2^-]_{\text{sorbed}} - k_3 \cdot [O_2^-]_{\text{sorbed}} = 0 \]  \hspace{1cm} (5)

\[ k_{-1} [H_2O_2]_{\text{sorbed}} = k_1 [H_2O_2] \]  \hspace{1cm} (6)

\[ k'_{-1} [O_2^-]_{\text{sorbed}} = k'_1 [O_2^-] \]  \hspace{1cm} (7)

\[ k_2 \cdot k_1 \cdot [H_2O_2] - k_{-2} \cdot k'_1 [O_2^-] - k_3 \cdot k'_1 [O_2^-] = 0 \]  \hspace{1cm} (8)

\[ [O_2^-] = \frac{k_2 \cdot k_1 \cdot [H_2O_2]}{K'_1 (k_{-2} + k_3)} \]  \hspace{1cm} (9)

The Eley-Rideal mechanism for the reaction between sorbed superoxide and aqueous HCA may be expressed as:

\[ \text{rate} = \frac{k_3 K'_1 [HCA] \cdot [O_2^-]}{1 + K'_1 [O_2^-]} \]  \hspace{1cm} (10)

\[ \text{rate} = k_3 \cdot [HCA] \cdot \theta_{O_2^-} \]  \hspace{1cm} (11)

where \( \theta_{O_2^-} \) is the surface coverage by superoxide,

\[ k_{\text{obs}} = \frac{\text{rate}}{[HCA]} \]  \hspace{1cm} (12)

\[ k_{\text{obs}} = \frac{k_3 K'_1 [O_2^-]}{1 + K'_1 [O_2^-]} \]  \hspace{1cm} (13)

Substituting equation (9) into equation (13):
\[
\frac{k_{\text{obs}}}{k_3} = \frac{k_2 \cdot K_1 \cdot [H_2O_2]}{K_1' (k_2 + k_3)} + \frac{1}{k_3}
\]

or

\[
\frac{1}{k_{\text{obs}}} \cdot \frac{1}{k_3} \cdot \frac{k_2 \cdot K_1 \cdot [H_2O_2]}{(k_2 + k_3)} = \frac{1}{k_3}
\]

A Lineweaver-Burk type plot of \( \frac{1}{k_{\text{obs}}} \) (min) vs. \( \frac{1}{[H_2O_2]} \) (mM\(^{-1}\)) yielded a y-intercept \( \left( \frac{1}{k_3} \right) \) of 11.4 min; therefore, \( k_3 = 0.0015 \) s\(^{-1}\). The slope was 294 min·mM (\( R^2 = 0.99 \)). Therefore,

\[
\frac{1}{k_3} \cdot \frac{k_2 \cdot K_1}{(k_2 + k_3)} = 294 \text{ min·mM}
\]

Assuming that \( K_1 = K_{H_2O_2} \approx 1 \) M\(^{-1}\); \( k_{-2} < k_2 \); and \( k_{-2} < k_3 \), \( k_2 \) is approximately 0.057 M\(^{-1}\) s\(^{-1}\).