Supporting Information for

Kinetics and Mechanistic Studies of Anticarcinogenic Bisperoxovanadium(V) Compounds: Ligand Susbtitution Reactions at Physiological pH and Relevance to DNA Interactions

J. H. Hwang, R. K. Larson, and Mahdi M. Abu-Omar
Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569

Table S1. IR stretches, UV-Vis extinction coefficients, and $^{51}$V-NMR chemical shifts for the ammonium bisperoxovanadium compounds.

<table>
<thead>
<tr>
<th></th>
<th>IR, cm$^{-1}$</th>
<th>UV-Vis</th>
<th>$^{51}$V NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v$ (V=O)</td>
<td>$v_1$ (O-O)</td>
<td>$v_3$ (MO$_2$)</td>
</tr>
<tr>
<td>BpVBpy</td>
<td>928</td>
<td>878, 857</td>
<td>623</td>
</tr>
<tr>
<td>BpVphen</td>
<td>926</td>
<td>860, 846</td>
<td>649, 624</td>
</tr>
</tbody>
</table>

Figure S1. UV-Vis spectra of 0.9 mM bpVBpy and 0.9 mM bpVphen in 0.1 M, pH 6.8 sodium phosphate buffer.
Figure S2. Plot of [bpVphen] vs. time with 0.9 mM bpVphen and 50 mM picolinic acid in the absence (●) and presence (○) of light.
<table>
<thead>
<tr>
<th>[pic]_T, M</th>
<th>k_{obs}, s^{-1}</th>
<th>[dipic]_T, M</th>
<th>k_{obs}, s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>(4.81 ± 0.05) × 10^{-5}</td>
<td>0.005</td>
<td>(6.44 ± 0.03) × 10^{-5}</td>
</tr>
<tr>
<td>0.02</td>
<td>(9.48 ± 0.06) × 10^{-5}</td>
<td>0.01</td>
<td>(1.44 ± 0.02) × 10^{-4}</td>
</tr>
<tr>
<td>0.03</td>
<td>(1.33 ± 0.02) × 10^{-4}</td>
<td>0.02</td>
<td>(2.99 ± 0.02) × 10^{-4}</td>
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<tr>
<td>0.04</td>
<td>(1.76 ± 0.03) × 10^{-4}</td>
<td>0.03</td>
<td>(4.39 ± 0.03) × 10^{-4}</td>
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<tr>
<td>0.05</td>
<td>(2.18 ± 0.02) × 10^{-4}</td>
<td>0.035</td>
<td>(5.10 ± 0.02) × 10^{-4}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[pic]_T, M</th>
<th>k_{obs}, s^{-1}</th>
<th>[dipic]_T, M</th>
<th>k_{obs}, s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>(7.58 ± 0.04) × 10^{-6}</td>
<td>0.0025</td>
<td>(1.00 ± 0.07) × 10^{-5}</td>
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<tr>
<td>0.02</td>
<td>(1.66 ± 0.02) × 10^{-5}</td>
<td>0.005</td>
<td>(1.77 ± 0.02) × 10^{-5}</td>
</tr>
<tr>
<td>0.03</td>
<td>(2.19 ± 0.02) × 10^{-5}</td>
<td>0.01</td>
<td>(2.68 ± 0.04) × 10^{-5}</td>
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<tr>
<td>0.04</td>
<td>(3.28 ± 0.02) × 10^{-5}</td>
<td>0.015</td>
<td>(3.20 ± 0.02) × 10^{-5}</td>
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<tr>
<td>0.05</td>
<td>(3.88 ± 0.02) × 10^{-5}</td>
<td>0.02</td>
<td>(3.44 ± 0.02) × 10^{-5}</td>
</tr>
<tr>
<td>0.06</td>
<td>(4.65 ± 0.03) × 10^{-5}</td>
<td>0.03</td>
<td>(3.65 ± 0.02) × 10^{-5}</td>
</tr>
</tbody>
</table>

^{a} k_{obs} = v_i/[bpV(L-L)]_i. \(^{b}\) Reaction conditions: [bpV(L-L)]_i = 0.9 mM; Ionic strength (µ) = 1.00 M; in 0.1 M pH 6.8 sodium phosphate buffer at 20 °C.
Figure S3. Plot of absorbance vs. time for reactions of 0.9 mM bpVphen with 50 mM picolinic acid in the absence (□) and presence of 20 mM (△) and 50 mM (○) H₂O₂.
Figure S4. (A) $^{51}$V NMR spectrum of the bisperoxo species that resulted from mpVpic$_2$. (B) $^{51}$V NMR spectrum of the bisperoxo species that resulted from mpVdipic (10 mM dipicolinic acid). (C) $^{51}$V NMR spectrum of the bisperoxo species that resulted from mpVdipic (30 mM dipicolinic acid).
Figure S5. Plot of $\ln(k/T)$ vs. $1/T$ for the reaction of 0.9 mM bpVbpy with 50 mM picolinic acid (●, − − − − −) and 30 mM dipic (○, − − − − −) and for the reactions of 0.9 mM bpVphen with 50 mM picolinic acid (▲, - - - - -), 10 mM dipicolinic acid (□, — - — -), and 30 mM dipicolinic acid (◇, — --- — ---). Reaction conditions: $[\text{bpV}(L-L)]_i = 0.9$ mM; ionic strength ($\mu$) = 1.00 M; in 0.1 M pH 6.8 sodium phosphate buffer; temperature range: 10 – 40 °C.
Derivations of the Rate Laws

(A) Dipic Mechanism

Scheme S1

\[
\begin{align*}
\text{bpV(L-L)} & \quad + \quad 2\text{H}_2\text{O} \quad \xrightleftharpoons[k_{-1}\k_1]{k_1} \quad \text{bpV(H}_2\text{O}_2) \quad + \quad \text{L-L} \\
\text{bpV(H}_2\text{O}_2) & \quad + \quad \text{H}_2\text{dipic} \quad \xrightleftharpoons[k_{-2}\k_2]{k_2} \quad \text{mpVdipic} \quad + \quad \text{H}_2\text{O}_2 \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

The net rate of disappearance of bpV(L-L) ( = 'A') is given by the equation

\[
- \frac{d[A]}{dt} = v = \kappa_1[A]_r - \kappa_{-1}[I][L-L]
\] (S1.1)

The steady-state approximation, applied to the concentration of bpV(H2O)2 ( = 'I'), gives

\[
\frac{d[I]}{dt} = 0 = \kappa_1[A]_r - \kappa_{-1}[I][L-L] - \kappa_2[I][\text{H}_2\text{dipic}] + \kappa_{-2}[P][\text{H}_2\text{O}_2]
\] (S1.2)

\[
[I]_r = \frac{\kappa_1[A]_r + \kappa_{-2}[P][\text{H}_2\text{O}_2]}{\kappa_2[\text{H}_2\text{dipic}] + \kappa_{-1}[L-L]} \] (S1.3)

Substituting eq S1.3 into S1.1 and rearrangement gives

\[
v = \frac{\kappa_1[A]_r[\text{H}_2\text{dipic}] - \kappa_{-1}[I][\text{H}_2\text{O}_2][L-L]}{\kappa_2[\text{H}_2\text{dipic}] + \kappa_{-1}[L-L]}
\] (S1.4)

In order to express the rate law in terms of [A] as the only concentration variable, eqs S1.5, S1.6, and S1.7 must be incorporated, which express the stoichiometry of the reaction and the thermodynamic equilibrium condition (subscripted e).

\[
[A]_r + [I]_r + [P]_r = [A]_e + [I]_e + [P]_e
\] (S1.5)

\[
\frac{\kappa_1}{\kappa_{-1}} = K_1 = \frac{[I]_e[L-L]}{[A]_e}
\] (S1.6)

\[
\frac{\kappa_2}{\kappa_{-2}} = K_2 = \frac{[P]_e[\text{H}_2\text{O}_2]}{[I]_e[\text{H}_2\text{dipic}]}
\] (S1.7)
Eqs S1.5, S1.6, and S1.7 can be rearranged to

\[ [P]_r = [A]_r + [I]_r + [P]_e - [A]_r - [I]_r \]  

\[ K_1 K_2 = \frac{[P]_r [H_2O][L-L]}{[A]_r [H_dipic]} \]  

\[ [P]_r = \frac{K_1 K_2 [A]_r [H_dipic]}{[H_2O][L-L]} \]  

\[ [I]_r = \frac{K_1 [A]_r}{[L-L]} \]  

If eqs S1.3, S1.10, and S1.11 are substituted into eq S1.8, the result is

\[ [P]_r = [A]_r + \frac{K_1 [A]_r}{[L-L]} + \frac{K_1 K_2 [A]_r [H_dipic]}{[H_2O][L-L]} - \left\{ [A]_r + \left( \frac{k_1 [A]_r + k_2 [P]_r [H_2O]}{k_2 [H_dipic] + k_3 [L-L]} \right) \right\} \]  

which can be rearranged to

\[ [P]_r = \frac{\left( k_3 [H_2dipic] + k_4 [L-L] \right) \left( [H_2O][L-L] + K_1 [H_2O] + K_2 [H_dipic][A] \right) - \left( k_2 [H_dipic] + k_5 [L-L] + k_6 [H_2O][L-L][A] \right) - \left( k_3 [H_2dipic] + k_4 [L-L] \right) \left( [H_2O][L-L] \right)}{k_3 [H_2dipic] + k_5 [H_2O] + k_3 [L-L] \left( [H_2O][L-L] \right)} \]  

Substitution of eq S1.13 into eq S1.4 and algebraic rearrangements gives

\[ v = \frac{k_1 k_2 [H_2dipic] + k_3 k_4 [H_2O]}{k_3 [H_2dipic] + k_5 [H_2O] + k_3 [L-L]} \left( [A]_r - [A]_r \right) \]  

Dipic can exist in three different forms (namely, H_2dipic, Hdipic^−, and dipic^{2−}) in aqueous solutions. Thus, the acid-dissociation equilibrium of dipic (shown below) must be incorporated, and the rate law must be expressed in terms of [dipic]_T.

\[ \text{H}_2\text{dipic} \xleftrightarrow{K_{a1}^{\text{dipic}}} \text{Hdipic}^− + \text{H}^+ \]

\[ \text{Hdipic}^− \xleftrightarrow{K_{a2}^{\text{dipic}}} \text{dipic}^{2−} + \text{H}^+ \]
The acid-dissociation equilibrium constants for dipic are given by the equations

\[ K_{a_1}^{\text{dipic}} = \frac{[\text{Hdipic}^-][H^+]}{[\text{H}_2\text{dipic}]} \]  

(S1.15)

\[ K_{a_2}^{\text{dipic}} = \frac{[\text{dipic}^{2-}][H^+]}{[\text{Hdipic}^-]} \]  

(S1.16)

Also, the term \([\text{dipic}]_T\) is defined by the equation

\[ [\text{dipic}]_T = [\text{H}_2\text{dipic}] + [\text{Hdipic}^-] + [\text{dipic}^{2-}] \]  

(S1.17)

Multiplying eqs S1.15 by eq S1.16 and rearrangement gives the expression for \([\text{H}_2\text{dipic}]\)

\[ [\text{H}_2\text{dipic}] = \frac{[\text{dipic}^{2-}][H^+]^2}{K_{a_1}^{\text{dipic}} K_{a_2}^{\text{dipic}}} \]  

(S1.18)

Substituting eq S1.18 into eq S1.17 gives

\[ [\text{dipic}]_T = \frac{[\text{dipic}^{2-}][H^+]^2}{K_{a_1}^{\text{dipic}} K_{a_2}^{\text{dipic}}} + [\text{Hdipic}^-] + [\text{dipic}^{2-}] \]  

(S1.19)

The fraction of \(\text{Hdipic}^-\), designated \(f_{\text{Hdipic}^-}\), is given by

\[ f_{\text{Hdipic}^-} = \frac{[\text{Hdipic}^-]}{[\text{dipic}]_T} = \frac{[\text{Hdipic}^-]}{\left(\frac{[\text{dipic}^{2-}][H^+]^2}{K_{a_1}^{\text{dipic}} K_{a_2}^{\text{dipic}}} + [\text{Hdipic}^-] + [\text{dipic}^{2-}]\right)} \]  

(S1.20)

Dividing both the numerator and the denominator on the right side of eq S1.20 by \([\text{dipic}^{2-}][H^+]^2\)
and using eqs S1.15 and S1.16 gives

\[ [\text{Hdipic}^-] = \frac{K_{a_1}^{\text{dipic}}[H^+][\text{dipic}]_T}{K_{a_1}^{\text{dipic}} + K_{a_2}^{\text{dipic}}[H^+] + [H^+]^2} \]  

(S1.21)

If eq S1.21 is substituted into eq S1.19, \([\text{dipic}^{2-}]\) is expressed in terms of \([\text{dipic}]_T\), which is given by the equation

\[ [\text{dipic}^{2-}] = \frac{K_{a_1}^{\text{dipic}} K_{a_2}^{\text{dipic}}[\text{dipic}]_T}{K_{a_1}^{\text{dipic}} + K_{a_2}^{\text{dipic}}[H^+] + [H^+]^2} \]  

(S1.22)
Substitution of eq S1.22 into eq S1.18 gives

$$[H_{\text{dipic}}] = \frac{[\text{dipic}][H^+]^2}{K_{\text{a1}}^{\text{dipic}} + K_{\text{a2}}^{\text{dipic}} [H^+] + [H^+]^2} \quad (S1.23)$$

Substitution of eq S1.23 into eq S1.14 and rearrangement gives the full rate law

$$v = \left( \frac{k_1k_2[\text{dipic}][H^+]^2 + k_1k_2[\text{H}_2\text{O}_2][H^+]^2 + k_1k_2K_{\text{a1}}^{\text{dipic}} [\text{H}_2\text{O}_2][H^+]}{+ k_1k_2K_{\text{a1}}^{\text{dipic}} [\text{H}_2\text{O}_2][L-L][H^+]} + k_1k_2K_{\text{a2}}^{\text{dipic}} [\text{H}_2\text{O}_2][L-L]} \right) ([A] - [A]_c) \quad (S1.24)$$

Taking experimentally important terms in eq S1.24, the equation simplifies to eq 2.1

$$v = \left( \frac{k_1k_2[\text{dipic}][H^+]^2}{k_2[\text{dipic}][H^+]^2 + k_2[\text{H}_2\text{O}_2][H^+]^2} \right) ([A] - [A]_c) \quad (2.1)$$

which further simplifies to give the simplified, experimental rate law (eq 2.2)

$$v = \left( \frac{k_1k_2[\text{dipic}]}{k_2[\text{dipic}] + k_2[\text{H}_2\text{O}_2]} \right) ([A] - [A]_c) \quad (2.2)$$
(B) Pic Mechanism

Scheme S2

\[
\begin{align*}
\text{bpV(L-L)} & \quad + \quad \text{Hpic} \quad \xrightleftharpoons[k_{-3}]{k_3} \quad \text{mpV(pic)(L-L)} \quad + \quad \text{HO}_2^- \\
\text{'A'} & \quad \text{mpV(pic)(L-L)} & \quad + \quad \text{Hpic} \quad \xrightleftharpoons[k_{-4}]{k_4} \quad \text{mpV(pic)}_2 \quad + \quad \text{H}^+ \quad + \quad \text{L-L} \quad \text{'I'} \quad \text{who}' \quad + \quad \text{L-L} \quad \text{'P'} \quad \end{align*}
\]

\[
\text{H}_2\text{O}_2 \xrightleftharpoons[k_a]{K_a} \text{HO}_2^- \quad + \quad \text{H}^+
\]

The net rate of disappearance of \( \text{bpV(L-L)} (= \text{'}A\text{'} \) is given by the equation

\[
-\frac{d[A]}{dt} = \nu = k_3[A],[\text{Hpic}] - k_{-3}[I],[\text{HO}_2^-] \quad \text{(S2.1)}
\]

The steady-state approximation, applied to the concentration of \( \text{mpV(pic)(L-L)} (= \text{'}I\text{'} \), gives

\[
\frac{d[I]}{dt} = 0 = k_3[A],[\text{Hpic}] - k_{-3}[I],[\text{HO}_2^-] - k_4[I],[\text{Hpic}] + k_{-4}[P],[L-L][\text{H}^+] \quad \text{(S2.2)}
\]

\[
[I]_e = \frac{k_3[A],[\text{Hpic}] + k_{-4}[P],[L-L][\text{H}^+]}{k_4[\text{Hpic}] + k_{-3}[\text{HO}_2^-]} \quad \text{(S2.3)}
\]

Substituting eq S2.3 into S2.1 and rearrangement gives

\[
\nu = \frac{k_3k_4[A],[\text{Hpic}]^2 - k_{-3}k_4[P],[\text{HO}_2^-][L-L][\text{H}^+]}{k_4[\text{Hpic}] + k_{-3}[\text{HO}_2^-]} \quad \text{(S2.4)}
\]

In order to express the rate law in terms of \([A]\) as the only concentration variable, eqs S2.5, S2.6, and S2.7 must be incorporated, which express the stoichiometry of the reaction and the thermodynamic equilibrium condition (subscripted \(e\)).

\[
[A]_c + [I]_e + [P]_c = [A]_c + [I]_c + [P]_c \quad \text{(S2.5)}
\]

\[
\frac{k_3}{k_{-3}} = K_3 = \frac{[I]_c[\text{HO}_2^-]}{[A]_c[\text{Hpic}]} \quad \text{(S2.6)}
\]
\[
\frac{k_4}{k_4} = K_i = \frac{[P][L-L][H^+]}{[I],[Hpic]}
\]  \quad (S2.7)

Eqs S2.5, S2.6, and S2.7 can be rearranged to

\[
[P]_r = [A]_r + [I]_r + [P]_r - [A]_r - [I]_r
\]  \quad (S2.8)

\[
K_i K_4 = \frac{[P]_r [HO_2^-][L-L][H^+]}{[A]_r [Hpic]^2}
\]  \quad (S2.9)

\[
[P]_r = \frac{K_i K_4 [A]_r [Hpic]^2}{[HO_2^-][L-L][H^+]}
\]  \quad (S2.10)

\[
[I]_r = \frac{K_i K_4 [A]_r [Hpic]}{[HO_2^-]}
\]  \quad (S2.11)

If eqs S2.3, S2.10, and S2.11 are substituted into eq S2.8, the result is

\[
[P]_r = [A]_r + \frac{K_i [A]_r [Hpic]}{[HO_2^-]} + \frac{K_i K_4 [A]_r [Hpic]^2}{[HO_2^-][L-L][H^+]} - \left(\left[\frac{k_i [A]_r [Hpic] + k_4 [P]_r [L-L][H^+]}{k_4 [Hpic] + k_3 [HO_2^-]}\right]\right)
\]  \quad (S2.12)

which then rearranges to

\[
[P]_r = \frac{\left(\frac{\left(k_i [Hpic] + k_3 [HO_2^-]\right)[(HO_2^-)[L-L][H^+] + K_i [Hpic][L-L][H^+] + K_i K_4 [Hpic]^2}{[A]_r}\right)}{\left(k_i [Hpic] + k_3 [HO_2^-] + k_4 [L-L][H^+] [A]_r\right)}
\]  \quad (S2.13)

Substitution of eq S2.13 into eq S2.4 and algebraic rearrangements gives

\[
\nu = \left(\frac{K_i K_4 [Hpic]^2 + k_i k_4 [Hpic][L-L][H^+] + k_i k_4 [HO_2^-][L-L][H^+]}{k_i [Hpic] + k_3 [HO_2^-] + k_4 [L-L][H^+]}\right)\left([A]_r - [A]_r\right)
\]  \quad (S2.14)

Pic can exist in two different forms (namely, Hpic, and pic) in aqueous solutions. Thus, the acid-dissociation equilibrium of pic (shown below) must be incorporated, and the rate law must be expressed in terms of [pic]_T.

\[
\text{Hpic} \quad \xrightleftharpoons{K_{a}^{\text{pic}}} \quad \text{pic}^- + \text{H}^+
\]
The acid-dissociation equilibrium constant for pic is given by the equation

\[ K_{a\text{pic}} = \frac{[\text{pic}^-][H^+]}{[\text{Hpic}]} \]  
(S2.15)

Also, the term \([\text{dipic}]_T\) is defined by the equation

\[ [\text{pic}]_T = [\text{Hpic}] + [\text{pic}^-] \]  
(S2.16)

The fraction of Hpic, designated \(f_{\text{Hpic}}\), is given by

\[ f_{\text{Hpic}} = \frac{[\text{Hpic}]}{[\text{pic}]_T} = \frac{[\text{Hpic}]}{[\text{Hpic}] + [\text{pic}^-]} \]  
(S2.17)

Dividing both the numerator and the denominator on the right side of eq S2.17 by \([\text{pic}] - [\text{Hpic}]\) and using eq S2.15 gives

\[ [\text{Hpic}] = \frac{[\text{pic}]_T[H^+]}{K_{a\text{pic}} + [H^+]} \]  
(S2.18)

Since \(\text{HO}_2^-\) rapidly combines with \(H^+\) to form \(\text{H}_2\text{O}_2\), \([\text{HO}_2^-]\) can be expressed in terms of \([\text{H}_2\text{O}_2]\) by using the equations

\[ K_{a\text{HO}_2\text{O}_2} = \frac{[\text{HO}_2^-][H^+]}{[\text{H}_2\text{O}_2]} \]  
(S2.19)

\[ [\text{HO}_2^-] = \frac{K_{a\text{HO}_2\text{O}_2}[\text{H}_2\text{O}_2]}{[H^+]^2} \]  
(S2.20)

Substitution of eqs S2.18 and S2.20 into eq S2.14 and rearrangement yields the full rate law

\[ v = \left( \frac{k_3 k_4 [\text{pic}]_T^2 [H^+]^3}{k_3 k_{-4} K_{a\text{pic}} [\text{pic}]_T[L-L][H^+]} + \frac{k_3 k_{-4} K_{a\text{pic}} [\text{pic}]_T[L-L][H^+]}{k_3 k_{-4} K_{a\text{pic}} [\text{pic}]_T[L-L][H^+]^3} \right) \]

\[ + \frac{2 k_3 k_{-4} K_{a\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][L-L][H^+]^2}{2 k_3 k_{-4} K_{a\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][L-L][H^+]^2} \]

\[ + \frac{2 k_3 k_{-4} K_{a\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][L-L][H^+]^3}{k_3 k_{-4} K_{a\text{pic}} [\text{pic}]_T[L-L][H^+]^4} \]

\[ + \frac{k_4 [\text{pic}]_T[H^+]^2 + k_3 K_{a\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][H^+]^2 + k_4 [\text{pic}]_T[\text{pic}]_T[L-L][H^+]^2}{k_4 [\text{pic}]_T[H^+]^2 + k_3 K_{a\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][H^+]^2 + k_4 [L-L][H^+]^4} \]

\[ + \frac{2 k_3 K_{a\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][H^+] + 2 k_4 K_{a\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][H^+]^3}{2 k_3 K_{a\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][H^+] + 2 k_4 K_{a\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][H^+]^3} \]

(S2.21)
Taking experimentally important terms in eq S2.21, the equation simplifies to eq 3.1

\[
\nu = \left( \frac{k_3 k_4 [\text{pic}]_T [H^+]^3}{k_4 K_a^{\text{pic}} [\text{pic}]_T [H^+]^2 + k_{-3} K_a^{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2][H^+]^2} \right) ([A]_r - [A]_e) \tag{3.1}
\]

which further simplifies to give the simplified, experimental rate law (eq 3.2)

\[
\nu = \left( \frac{k_3 k_4 [\text{pic}]_T [H^+]^2}{k_4 K_a^{\text{pic}} [\text{pic}]_T + k_{-3} K_a^{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]} \right) ([A]_r - [A]_e) \tag{3.2}
\]