Figure S1. Kinetic trace showing the absence of MV$^{3+}$ oxidation by H$_2$O$_2$ in alkaline solution.

Conditions – 0.48 mM MV$^{2+}$, 18 µM H$_2$O$_2$, 1.3 M (CH$_3$)$_2$CHOH, 32 mM NaOH, Ar-saturated solution.
Note 1. Kinetics of MV⁺⁺ Decay According to Reaction Mechanism in Scheme 2

Reactions:

\[
\begin{align*}
\text{ONOO}^- & \xrightleftharpoons[k_h]{k_{h}} \text{NO}^- + \text{O}_2^- \\
\text{MV}^+ + \text{O}_2^- & \xrightarrow[k_{s0}]{k_{so}} \text{MV}^{2+} + \text{HO}_2^- \\
\end{align*}
\]

Initial concentrations: \([\text{ONOO}^-]_0; [\text{MV}^+]_0; [\text{O}_2^-]_0 = [\text{NO}^-]_0 \approx 0\)

Stoichiometric balance: \([\text{NO}^-] = [\text{MV}^++]_0 - [\text{MV}^+]\)

Rate law: (at \([\text{ONOO}^-]_0 >> [\text{MV}^++]_0\) and with steady-state approximation for \([\text{O}_2^-]\))

\[
\begin{align*}
\frac{d[\text{MV}^++]}{dt} &= - k_{s0}[\text{MV}^++][\text{O}_2^-]_{st} \\
\frac{d[\text{O}_2^-]_{st}}{dt} &= 0 = k_h[\text{ONOO}^-] - k_h[\text{NO}^-][\text{O}_2^-]_{st} - k_{s0}[\text{MV}^++][][\text{O}_2^-]_{st} \\
\text{or} \quad [\text{O}_2^-]_{st} &= k_h[\text{ONOO}^-]/(k_h[\text{MV}^++]_0 + (k_{s0} - k_h)[\text{MV}^++])
\end{align*}
\]

Integral form of rate law:

\[
\ln \frac{[\text{MV}^++]_0}{[\text{MV}^++]_0} + (1 - \frac{k_{s0}}{k_{h}})(1 - \frac{[\text{MV}^++]}{[\text{MV}^++]_0}) = -k_h \frac{k_{s0}}{k_{h}} \frac{[\text{ONOO}^-]_0}{[\text{MV}^++]_0} t
\]
**Note 2. Determination of $k_{so}$ for the MV$^{\cdot\cdot}$ + O$_2$$^-\cdot$ Reaction**

**Solution composition:** 0.1 mM MV$^{2+}$, 1 mM H$_2$O$_2$, 10 mM NaOH, Ar-saturated.

Under these conditions, the ratios $[\text{H}_2\text{O}_2]/[\text{HO}_2^-]$ and $[\text{OH}^-]/[\text{O}^-]$ are both approximately 1.

The MV$^{\cdot\cdot}$ radical was produced through the following reactions:

$$\text{e}^-_{\text{aq}} + \text{MV}^{2+} \rightarrow \text{MV}^{\cdot\cdot}$$

$$\text{H}^+ + \text{MV}^{2+} \rightarrow \text{H}^+ + \text{MV}^{\cdot\cdot}$$

The O$_2$$^-\cdot$ radical was generated through oxidation of H$_2$O$_2$/HO$_2^-$$:\n
$$\text{e}^-_{\text{aq}} + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{OH}^\cdot$$

$$\text{H}^+ + \text{OH}^- \rightarrow \text{e}^-_{\text{aq}} + \text{H}_2\text{O}$$

$$\text{OH}^\cdot + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2$$

$$\text{OH}^\cdot + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{H}^+ + \text{O}_2$$

From the tabulated rate constants for these reactions [1], the estimated lifetimes for $\text{e}^-_{\text{aq}}$, H$^\cdot$, and OH$^\cdot$/O$^-$$\cdot$ are about 0.07, 3, and 0.3 µs, respectively, under our conditions. Alkaline pH has been chosen because it matches the conditions of Figures 1 and 2. More importantly, the high pH allows to use low H$_2$O$_2$ concentration and still efficiently compete with MV$^{2+}$ for OH$^\cdot$; while the ratio $k(\text{OH}^- + \text{H}_2\text{O}_2)/k(\text{OH}^- + \text{MV}^{2+}) \approx 0.1$, the ratio $k(\text{OH}^- + \text{HO}_2^-)/k(\text{OH}^- + \text{MV}^{2+}) \approx 30$. The radiation yield $G(\text{MV}^{\cdot\cdot}) = 1.4$ radicals per 100 eV has been experimentally determined from its absorption at 600 nm. The total radiation yield $G(\text{MV}^{\cdot\cdot}) + G(\text{O}_2$$^-\cdot$) = $G(\text{e}^-_{\text{aq}}) + G(\text{OH}^-) + G(\text{H}^\cdot) = 6.2$, from which $G(\text{O}_2$$^-\cdot$) = 4.2 and the ratio $[\text{O}_2$$^-\cdot$]$_0/[\text{MV}^{\cdot\cdot}]_0 = 3.4$ corresponds reasonably well to the pseudo-first-order conditions. To ensure even better pseudo-first-order situation, the kinetics of MV$^{\cdot\cdot}$ decay have been fitted by the exponential functions to approximately half-lives and plotted against the mean $[\text{O}_2$$^-\cdot$] over the fitting range. The exponential fits were of excellent quality.
Figure S2. Dependence of the apparent first-order rate constant for MV$$^{++}$$ decay, $$k_{\text{app}}$$, upon [O$_2^-$•]. The rate constant $$k_{so} = (2.85 \pm 0.06) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$ for MV$$^{++}$$ + O$_2^-$• reaction at $$\mu = 10 \text{ mM}$$ was calculated from the slope of this dependence. The concentration of O$_2^-$• was varied by changing the radiation dose.

Discussion:

The appreciable intercept of in Figure S2 indicates an additional channel for MV$$^{++}$$ decay. Good linearity of the dose dependence suggests that this channel is not due to the radiation-produced species. We conjecture that the intercept is due to the trace amounts (about 3 µM) of oxygen in the peroxide solution. The solution pH around the pK$_a$ of H$_2$O$_2$ and the design of the pulse radiolysis cell, which has a large glass frit, create favorable conditions for H$_2$O$_2$ decomposition, both uncatalyzed and catalyzed by adventitious metal ions and glass surfaces [2]. Even with extreme measures taken to minimize catalysis the decomposition proceeds with appreciable rate in alkali [3]. Since the only variable parameter involved in the $$k_{so}$$ determination is the radiation dose, the presence of intercept should not affect these measurements. Applying standard corrections for ionic strength to $$k_{so} = 2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$ measured at $$\mu = 10 \text{ mM}$$, one obtains 3.5 $$\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$ at $$\mu = 0$$ and 2.6 $$\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$ at $$\mu = 20 \text{ mM}$$; the latter corresponds to the reaction conditions in Figures 1 and 2. Considering the method for estimating [O$_2^-$•], it would also be prudent to increase the uncertainty in $$k_{so}$$ to $$\pm 0.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$.
Our result is close to \( k_{so} = (2.8 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) obtained by Levey and Ebbesen [4] in the similar experiments at unspecified, but presumably low (\( \leq 6 \text{ mM} \)), ionic strength and at pH 7. At this pH, a very large \( \text{H}_2\text{O}_2 \) concentration (up to 160 mM) had to be used because of the slowness of \( \text{OH}^- + \text{H}_2\text{O}_2 \) compared to \( \text{OH}^- + \text{MV}^{2+} \) reaction; consequently, significant model-dependent corrections to \( G(e_{aq}) + G(\text{OH}^+) + G(\text{H}^+) \) had to be applied. Considering uncertainties associated with this procedure, the agreement with our measurement is excellent. As no primary data have been presented in that paper, it is not known whether an intercept was present in the dose dependence.

Farrington and co-workers reported \( k_{so} = 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \) at \( \mu = 100 \text{ mM} \) [5] based on the \( \text{MV}^{++} \) decay in the presence of oxygen. This value corresponds to \( 1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) at \( \mu = 10 \text{ mM} \), which is by about a factor of 2 lower than our value. However, this determination is indirect and relies on the numerical simulation of the simultaneous reactions of \( \text{MV}^{++} \) with both \( \text{O}_2 \) and \( \text{O}_2^- \). As the former reaction is some 3 times slower and precedes the latter, these simulations are not expected to be sufficiently sensitive to the \( k_{so} \) value.

References:
Note 3. Rate Constants and Other Parameters Used in Simulations for Figure 3

<table>
<thead>
<tr>
<th>No.</th>
<th>reaction</th>
<th>$k, \text{M}^{-1}\text{s}^{-1}$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{OH}^+ + \text{HCO}_2^- \rightarrow \text{H}_2\text{O} + \text{CO}_2^{2-}$</td>
<td>$4.3 \times 10^9$</td>
<td>[1]</td>
</tr>
<tr>
<td>2</td>
<td>$\text{e}_\text{aq}^- + \text{NO}_2^- \rightarrow \text{NO}_2^{2-}$</td>
<td>$3.5 \times 10^9$</td>
<td>[1]</td>
</tr>
<tr>
<td>3</td>
<td>$\text{e}_\text{aq}^- + \text{O}_2 \rightarrow \text{O}_2^{2-}$</td>
<td>$1.9 \times 10^{10}$</td>
<td>[1]</td>
</tr>
<tr>
<td>4</td>
<td>$\text{H}^+ + \text{HCO}_2^- \rightarrow \text{H}_2 + \text{CO}_2^{2-}$</td>
<td>$2.1 \times 10^8$</td>
<td>[2]</td>
</tr>
<tr>
<td>5</td>
<td>$\text{H}^+ + \text{NO}_2^- \rightarrow \text{HNO}_2^{2-}$</td>
<td>$1.6 \times 10^9$</td>
<td>[3], [4]</td>
</tr>
<tr>
<td>6</td>
<td>$\text{HNO}_2^{2-} + \text{OH}^- \rightarrow \text{NO}_2^{2-} + \text{H}_2\text{O}$</td>
<td>$1.6 \times 10^9$</td>
<td>[4]</td>
</tr>
<tr>
<td>7</td>
<td>$\text{NO}_2^{2-} (+\text{H}_2\text{O}) \rightarrow \text{NO}^+ + 2\text{OH}^-$</td>
<td>$1.6 \times 10^9$</td>
<td>[4]</td>
</tr>
<tr>
<td>8</td>
<td>$\text{CO}_2^{2-} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2^{2-}$</td>
<td>$4.3 \times 10^9$</td>
<td>[5]</td>
</tr>
<tr>
<td>9</td>
<td>$\text{NO}^+ + \text{O}_2^{2-} \rightarrow \text{ONOO}^-$</td>
<td>$4.8 \times 10^9$</td>
<td>this work</td>
</tr>
</tbody>
</table>

Concentrations: \([\text{O}_2] = 0.18 \text{ mM}\) (air saturated in 1 M 1:1 electrolyte [6]); \([\text{NaHCO}_2] = 1 \text{ M}\); \([\text{NaNO}_2] = 10 \text{ mM}\); \([\text{NaOH}] = 1 \text{ mM}\).

Molar absorptivities: \(\varepsilon_{300}(\text{ONOO}^-) = 1650 \text{ M}^{-1}\text{cm}^{-1}\) [7]; \(\varepsilon_{300}(\text{CO}_2^{2-}) = 600 \text{ M}^{-1}\text{cm}^{-1}\) [8]; \(\varepsilon_{300}(\text{O}_2^{2-}) = 320 \text{ M}^{-1}\text{cm}^{-1}\) [8]; optical path 2 cm.

References: