Competition Between $\text{O}_2$ and $\text{H}_2\text{O}_2$ in the Oxidation of Fe(II) in Natural Waters

Melchor González-Dávila, J. Magdalena Santana-Casiano, and Frank J. Millero

Received January 31, 2005; accepted August 1, 2005

The oxidation rates of nanomolar levels of Fe(II) in seawater (salinity $S = 36.2$) by mixtures of $\text{O}_2$ and $\text{H}_2\text{O}_2$ has been measured as a function of pH (5.8–8.4) and temperature (3–35 °C). A competition exists for the oxidation of Fe(II) in the presence of both $\text{O}_2$ ($\mu$ mol·L$^{-1}$ levels) and $\text{H}_2\text{O}_2$ (nmol·L$^{-1}$ levels). A kinetic model has been applied to explain the experimental results that considers the interactions of Fe(II) with the major ions in seawater. In the presence of both oxidants, the hydrolyzed Fe(II) species dominate the Fe(II) oxidation process between pH 6 and 8.5. Over pH range 6.2–7.9, the FeOH$^+$ species are the most active, whereas above pH 7.9, the Fe(OH)$_2^0$ species are the most active at the levels of $\text{CO}_3^{2-}$ concentration present in seawater. The predicted Fe(II) oxidation rate at $[\text{Fe(II)}]_0 = 30$ nmol·L$^{-1}$ and pH = 8.17 in the oxygen-saturated seawater with $[\text{H}_2\text{O}_2]_0 = 50$ nmol·L$^{-1}$ ($\log_{10} k = 2.24$ s$^{-1}$) is in excellent agreement with the experimental value of $\log_{10} k = 2.29$ s$^{-1}$ ($[\text{H}_2\text{O}_2]_0 = 55$ nmol·L$^{-1}$, pH = 8).

KEY WORDS: Kinetics; oxidation; iron; oxygen; hydrogen peroxide; model.

1. INTRODUCTION

Most natural surface waters are oxic and their redox chemistry is governed by the oxygen–water couple. However, oxidants other than $\text{O}_2$, such $\text{H}_2\text{O}_2$, can also play an important role in these systems. $\text{H}_2\text{O}_2$ is a product of the partial reduction of $\text{O}_2$ itself, but it is also generated photochemically from the oxidation of dissolved organic matter.$^{(1)}$ The concentration of $\text{H}_2\text{O}_2$ can vary from about 10 to 150 nmol·L$^{-1}$ in oligotrophic waters to concentrations exceeding 500 nmol·L$^{-1}$ in coastal waters.$^{(2,3)}$ Earlier studies have suggested that at nanomolar levels of

---

1Departamento de Química, Facultad de Ciencias del Mar, Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria; Spain; e-mail: mgonzalez@dqui.ulpgc.es, jmsantana@dqui.ulpgc.es.
2Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, Florida 33149; e-mail: fmillero@rsmas.miami.edu.
Fe(II), H₂O₂ and O₂ compete in the oxidation of Fe(II). In a recent study, the oxidation of Fe(II) by oxygen in the presence of trace amounts of H₂O₂ has been examined.

The mechanism used to describe the Fe(II) oxidation in seawater is expressed by Eqs. (1)–(8):

\[
\begin{align*}
\text{Fe(II)} + O_2 & \rightarrow \text{Fe(III)} + O_2^- \quad k_1 \\
\text{Fe(II)} + O_2^- & \rightarrow \text{Fe(III)} + H_2O_2 \quad k_2 \\
\text{Fe(II)} + H_2O_2 & \rightarrow \text{Fe(III)} + OH^* + OH^- \quad k_3 \\
\text{Fe(II)} + OH^* & \rightarrow \text{Fe(III)} + OH^- \quad k_4 \\
\text{Fe(III)} + O_2^- & \rightarrow \text{Fe(II)} + O_2 \quad k_5 \\
\text{Fe(III)} + 3OH^- & \rightarrow \text{Fe(OH)₃(s)} \quad k_6 \\
\text{Cu(II)} + O_2^- & \rightarrow \text{Cu(I)} + O_2 \quad k_7 \\
\text{Cu(I)} + O_2^- + 2H^+ & \rightarrow \text{Cu(II)} + H_2O_2 \quad k_8
\end{align*}
\]

The concentration of H₂O₂ present in the solutions is assumed to be that generated by Eq. (2). However, in the oceans H₂O₂ can also be generated by photochemical processes. Under these conditions, reaction (3) is not entirely dependent on reactions (1) and (2).

If the overall oxygen reduction reaction is described by:

\[
O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O \quad \log_{10} K = 83.1, \quad p\varepsilon^\circ = 20.78
\]

then the overall reaction can be subdivided into two two-electron sequences:

\[
\begin{align*}
O_2(g) + 2H^+ + 2e^- & \rightleftharpoons H_2O_2 \quad \log_{10} K = 23.5, \quad p\varepsilon^\circ = 11.75 \\
H_2O_2(g) + 2H^+ + 2e^- & \rightleftharpoons 2H_2O \quad \log_{10} K = 59.6, \quad p\varepsilon^\circ = 29.8
\end{align*}
\]

The acquisition of the first two electrons from O₂ to H₂O₂ is energetically less favorable than the acquisition of the next two electrons from H₂O₂ to H₂O. Under these conditions, from a purely energetic point of view, we would expect peroxide to be a more reactive oxidant than oxygen in oxic waters. This increases its importance in coastal areas where the photochemical production of H₂O₂ from dissolved organic matter is more important.

Previous work in oxygen-saturated seawater at low Fe(II) concentrations (50 nmol·L⁻¹), with H₂O₂ concentration in the range 20–90 nmol·L⁻¹ and at a pH of 8.0, suggested that oxidation of Fe(II) is affected by the competition between both of these oxidants. In this paper, we present further evidence for this competitive effect. The conditions that control the competition of the two oxidants...