A novel kinetic method for determination of HO$_2$/$O_2^-$ in ozone decomposition in water is described. In this study, potential interferences of O$_3$ and the hydroxyl radicals, 'OH(O3), are suppressed by HSO$_3$/$SO_2^-$. HO$_2$/$O_2^-$ formed in ozone decomposition reduces Fe$^{3+}$-EDTA into Fe$^{2+}$-EDTA and subsequently the well-known Fenton-like (FL) reaction of H$_2$O$_2$ and Fe$^{2+}$-EDTA produces the hydroxyl radicals, 'OH. Benzoic acid (BA) scavenges OH$_{1+}$ to produce OHBA, which are analyzed by fluorescence detection ($\lambda_{em}$ = 320 nm and $\lambda_{ex}$ = 400 nm). The concentration of HO$_2$/$O_2^-$ in ozone decomposition has been determined by the novel kinetic method using the experimentally determined half-life ($t_{1/2}$). The steady-state concentration of HO$_2$/$O_2^-$ is proportional to the O$_3$ concentration at a given pH. However, the steady-state concentration of HO$_2$/$O_2^-$ in ozone decomposition is inversely proportional to pH values. This pH dependence is due to significant loss of O$_2^-$ by O$_3$ at higher pH conditions. The steady-state concentrations of HO$_2$/$O_2^-$ are in the range of 2.49 ($\pm$ 0.10) x 10$^{-9}$ M (pH = 4.17) - 3.01 ($\pm$ 0.07) x 10$^{-10}$ M (pH = 7.59) at [O$_3$]$_o$ = 60 $\mu$M.

**Key Words**: Hydroperoxyl radical, Superoxide anion radical, Ozone, Fenton-like, Hydroxyl radical

### Introduction

The chemistry of ozone is of major interest in drinking water and wastewater treatment processes since ozone has been recognized as a potent oxidant to improve taste, color, and disinfection, and degradation of pollutants.$^1$ During ozone decomposition in water, however, the two major oxidants, ozone and the hydroxyl radicals (‘OH(O3)), govern the oxidative processes.$^{2,7}$ The reaction of transient hydroperoxyl/superoxide anion radical (HO$_2$/$O_2^-$) with ozone is one of the possible formation pathways for generating ‘OH(O3). This reaction has found comparable interest considering the production of the highly reactive ‘OH(O3) to eliminate ozone-refractory compounds in water treatment processes.$^8$

Numerous studies on the HO$_2$/$O_2^-$ reactions in the decomposition of aqueous ozone are now available in several studies.$^{2,7,8}$ So far, the best reaction model to explain the decomposition of ozone in water is the chain mechanism suggested by the elegant works of Hoigne and co-workers as follows:$^{8}$

\[
\begin{align*}
O_3 + OH^- &\rightarrow HO_2^- + O_2 \quad (1) \\
HO_2^- + H^+ &\leftrightarrow H_2O_2 \quad \text{pK}_a = 11.6 \quad (2) \\
HO_2^- + O_3 &\rightarrow O_2 + \text{OH}(O3) + O_2 \quad (3) \\
H_2O_2 + O_3 &\rightarrow HO_2^- + \text{OH}(O3) + O_2 \quad (4) \\
O_2^- + H^+ &\leftrightarrow HO_2^- \quad \text{pK}_a = 4.8 \quad (5) \\
O_2^- + O_3 &\rightarrow O_2 + O_2^- \quad (6) \\
HO_2^- + O_3 &\rightarrow 2O_2 + \text{OH}(O3) \quad (7) \\
O_2^- &\rightarrow O_2 + O^- \quad (8) \\
O^- + H^+ &\leftrightarrow \text{OH}(O3) \quad \text{pK}_a = 11.8 \quad (9) \\
\text{OH}(O3) + O_3 &\rightarrow HO_2^- + O_2 \quad (10)
\end{align*}
\]

$^8$Present address: Environmental & Whole Information System (E&WIS), Seoul 151-848, Korea.

In aqueous solution of ozone, the initiation of ozone decomposition can be accelerated with increasing the concentration of hydroxide ion, and ozone decomposition is propagated by hydrogen peroxide (H$_2$O$_2$/HO$_2^-$). The reaction between O$_3$ and H$_2$O$_2$/HO$_2^-$ leads to the formation of ‘OH(O3), HO$_2^-$, and O$_2$. Subsequently, O$_2^-$ reacts with O$_3$ to produce O$_3^-$, which is decomposed to O$_2$ and O$^-$. The additional hydroxyl radicals, ‘OH(O3), is generated in an acid-base equilibrium of O$^-$ (reactions 7-9). Then ‘OH(O3) reacts rapidly with O$_3$ producing HO$_2^-$. Thus, the decomposition of O$_3$ is accelerated by radical-type chain reactions. However, ozone-refractory compounds in reaction 11 may compete with O$_3$ for ‘OH(O3).

Up to now, two methods have been available for the detection and/or determination of HO$_2$/$O_2^-$ in ozone decomposition reactions: a) the kinetic spectroscopy in pulse radiolysis of aqueous ozone solutions,$^{2,7,8}$ b) the reduction of tetrantromethane (TNM, C(NO$_2$)$_2$H) as an HO$_2$/$O_2^-$ indicator.$^{8}$ In the kinetic spectroscopy method, both HO$_2^-$ and O$_2^-$ formed in the decomposition of electron-irradiated aqueous ozone have distinct absorption spectra ($\epsilon_{220nm}$ = 1,350 M$^{-1}$ cm$^{-1}$ and $\epsilon_{220nm}$ = 1,900 M$^{-1}$ cm$^{-1}$) at pH 2 and 10.5, respectively.$^{2,7,8}$ This method, however, has been limited in O$_3$ solution by the spectrum overlapping since many chemical species, i.e., ‘OH ($\epsilon_{220nm}$ = 550 M$^{-1}$ cm$^{-1}$)$^{11}$ and O$_3$ ($\epsilon_{220nm}$ = 516 M$^{-1}$ cm$^{-1}$ as estimated value) (see Appendix), absorb strongly at wavelength 220 nm. The use of the kinetic spectroscopy has only focused on the rate constant data of HO$_2$/$O_2^-$ with ozone.$^{2,7,8}$ In the TNM method, the reaction of TNM with HO$_2$/$O_2^-$ at diffusion-controlled rate ($k = 2 \times 10^6$ M$^{-1}$ s$^{-1}$) produces the nitroform...
anion, $\text{C(NO}_3\text{)}_2^- (\text{NF}^-)$ with intense optical absorbance ($\varepsilon_{280\text{nm}} = 15,000 \text{ M}^{-1}\text{cm}^{-1}$).\(^8\) However, the spectrophotometric method using TNM has suffered from low sensitivity,\(^9\) and a consumption of NF$^-\text{ by ozone as well as a rapid production of NF}^+\text{ by the hydrolysis of TNM has to be taken into account.}^1\) This method has high uncertainty for the quantitative determination of HO$_2$/O$^\cdot_2\text{ concentration. However, information on the concentration of HO}_2$/O$^\cdot_2\text{ has been so far limited in earlier studies involving O}_3\text{ chemistry in aqueous solution.}

For an alternative method of determining the HO$_2$/O$^\cdot_2\text{, Kwon et al.}^{1,2}\) developed a new kinetic method as an analytical tool for the measurement of HO$_2$/O$^\cdot_2\text{ in aqueous solution. This new method is based on the reduction of Fe$^{3+}-\text{EDTA into Fe}^2$-EDTA by HO$_2$/O$^\cdot_2\text{ and the subsequent well-known Fenton-like (FL) reaction of H}_2\text{O and Fe}^2$-EDTA to yield the hydroxyl radicals, }\text{'OH (HL)}.$ Benzoic acid (BA) scavenges OHBA to produce hydroxylbenzoic acids (OHBA), which are analyzed by fluorescence detection ($\lambda_{ex} = 320 \text{ nm and } \lambda_{em} = 400 \text{ nm}$). The concentration of HO$_2$/O$^\cdot_2\text{ in ozone decomposition has been determined by the novel kinetic method using the experimentally determined half-life (1.2)). The new kinetic method has shown high sensitivity and simple calibration system. It can contribute significantly to the studies of HO$_2$/O$^\cdot_2$ at very low concentrations as well as of the basic function of HO$_2$/O$^\cdot_2$.

In this study, the optimization of the kinetic method in aqueous ozone decomposition and the quantitative determination of HO$_2$/O$^\cdot_2$ concentration are investigated. The reactions of O$_3$ with H$_2$O$_2$/HO$_2^-\text{ and HO}_2$/O$^\cdot_2^-\text{ produce the hydroxyl radicals, }\text{'OH (HL)}, through reactions of 3-4 and 8-9, which may interfere with the additional formation of OHBA. In addition, the OHBA formation may be resulted from the direct oxidative reaction of O$_3$ with BA:\(^5\)

\[
\text{O}_3 + \text{BA} \rightarrow \rightarrow \rightarrow \text{OHBA}
\]

Hence potential OHBA formation by reactions of O$_3$ and 'OH(O3) with BA should be effectively suppressed, which was performed by addition of HSO$_3^-$/SO$_2^-\text{ depending on the ozone solution pH.}

**Experimental Section**

**Materials.** Ozone is generated with a dioxygen (purity, 99.99%-fed ozone generator (Ozonix Triogen, model LAB2A). The aqueous stock solution of ozone is generated with bubbling the gas-Phase ozone through a gas-washing bottle (500 mL) filled with slightly acidic deionized water. The concentration of aqueous ozone stock solution is determined spectrophotometrically by measuring the absorbance at 258 nm (\(\varepsilon = 2,900 \text{ M}^{-1}\text{cm}^{-1}\)).\(^1\) Stock solution is then pipetted into a reaction flask where it is diluted in proper level with buffer solution. The solution pH is adjusted to the ranges between 4 and 10 with phosphate buffer (Sigma) and borate buffer (LabChem Inc.) along with H$_2$SO$_4$ and NaOH. Potential OHBA formation reactions by O$_3$ and OH(O3) with BA are quenched with NaSO$_3$ (Sigma). Ferric ethylenediaminetetra acetate (Fe$^{3+}$-EDTA), ferrous sulfate, ferric sulfate, sulfuric acid, sodium hydroxide, benzoic acid (BA), and 3% hydrogen peroxide are of reagent grade, and are purchased from Sigma-Aldrich. The concentration of the stock H$_2$O$_2$ solution is determined by using KMnO$_4$ titration method prior to use. Working solution of H$_2$O$_2$ is prepared daily by diluting the H$_2$O$_2$ stock in proper level with high-purity deionized water. The standard HO$_2$/O$^\cdot_2$ solution is prepared by the photolysis of H$_2$O$_2$ solution at wavelength 254 nm.\(^1\) All solutions are made with high-purity water from Millipore ultra-purification system (> 18 MΩ cm).

**HO$_2$/O$^\cdot_2$ measurement system in ozone process.** A schematic diagram for HO$_2$/O$^\cdot_2$ measurement is shown in Figure 1. The apparatus and the experimental procedures employed in the present study are similar to a previous study for except for the HSO$_3^-$/SO$_2^-\text{ and O}_3\text{ plots. All solutions are delivered by using peristaltic pump (Ismatec) with PTFE tubing (Cole-Parmer, i.d. 0.8 mm).}

During measurement of HO$_2$/O$^\cdot_2$, V1 (valve 1) and V2 (valve 2) are opened, while V3 and V4 are closed, and O$_3$ solution is delivered through the port 1 (P1, 0.23 mL/min). The OH-initiated decomposition of O$_3$ leads to the formation of HO$_2$/O$^\cdot_2$, 'OH(O3), and O$_2^-\text{ Solution of SO}_2^-\text{ is added through the port 2 (P2, 0.23 mL/min) eliminating the residual O}_3$ and 'OH(O3) which may react with BA to produce extra OHBA. Excess H$_2$O$_2$ in the port 3 (P3, 0.42 mL/min) destroys leftover HSO$_3^-$/SO$_2^-\text{ and is mixed with a premixed solution containing Fe}^{3+}$-EDTA (port 4, 0.23 mL/min) and BA (port 5, 0.23 mL/min). Fe$^{3+}$-EDTA is reduced by O$_2^-\text{ to Fe}^{2+}$-EDTA with $k_{13} = 2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}.$\(^9\)
Fe$^{3+}$-EDTA + $O_2^-$ \rightarrow Fe$^{2+}$-EDTA + O$_2$ \quad (13)

Subsequent Fenton-like reaction between Fe$^{3+}$-EDTA and
$H_2O_2(k_a = (2 \pm 1) \times 10^5 \text{M}^{-1} \text{s}^{-1})$ leads to the production of
$OH(\cdot)$ and the regeneration of Fe$^{2+}$-EDTA:\ref{14}

Fe$^{3+}$-EDTA + $H_2O_2$ \rightarrow Fe$^{2+}$-EDTA + $OH^-$ + $OH(\cdot)$ \quad (14)

Then, $OH(\cdot)$ produces OHBA in the presence of BA with
a nearly diffusion-controlled rate constant of $k_{15} = 4.3 \times 10^9$
M$^{-1} \text{s}^{-1}$ in KTR1 (knoted tubing reactor 1).\ref{15}

$OH(\cdot) + \text{BA} \rightarrow \text{OHBA}$ \quad (15)

After, 0.05 N NaOH through the port 6 (P6, 0.23 mL/min)
is added to raise pH level above 11 at which the fluorescence
signal of OHBA can be maintained at a maximum level.
The mixed solution occasionally causes the formation of air
bubbles in the effluent stream, which is removed by a glass
debubbler (GD) prior to the fluorometer (FM) in order to
prevent a noise signal by the air bubbles.

The OHBA fluorescence is then measured with a fluorometer (Waters 474 model) equipped with a 16 $\mu$L flow-
through cell using $\lambda_{ex} = 320 \text{nm} / \lambda_{em} = 400 \text{nm}$ with slit-
width of 40 nm. The fluorescence signal is transferred to a
data acquisition system, Auto-chrowin (Younglin, Korea),
consisting of an analog-to-digital converter (A/D) with a
personal computer (PC).

**Calibration procedures for $HO_2^/-$**. The calibration
employed in this work is described in detail in the previous
study.\ref{12} Briefly, during calibration of the system, V3 and V4
are opened, while V1 is by-passed and V2 is closed. All
working solutions containing 4 mM $H_2O_2$, 20 $\mu$M Fe$^{3+}$-
EDTA, 1 mM benzoic acid (BA), and 0.05 N NaOH are
passed through the appropriate ports under UV lamp-off and
the base lines are monitored. $H_2O_2$ solution ($\text{cm} \text{mol}^{-1} \text{cm}^{-1} \text{M}^{-1}$) placed in UV irradiation under lamp-on using a 4W
low pressure Hg lamp ($\lambda_{em} = 254 \text{nm}$, Philips) is photo-
decomposed to produce two OH radicals. Most of the OH
radicals formed under UV irradiation react with residual
$H_2O_2$ giving HO$_2^-$:

$H_2O_2 + h \nu \rightarrow 2 \cdot OH$ \quad (16)

$\cdot OH + H_2O_2 \rightarrow HO_2^- + H_2O$ \quad (17)

where $k_{17} = 2.7 \times 10^7 \text{M}^{-1} \text{s}^{-1}$.\ref{9}

In the absence of additives, HO$_2^-$ and $O_2^-$ in knotted
tubing reactor 2 (KTR2) are disproportionated by self-
reactions of 18 and 19 according to the empirically observed
pH-dependent rate constant, $k_{obs}$.\ref{9}

HO$_2^- + $HO$_2^- \rightarrow H_2O_2 + O_2$ \quad (18)

HO$_2^- + $O$_2^- \rightarrow HO_2^- + O_2$ \quad (19)

$k_{obs} = [k_{18} + k_{19}(K_{18/2}[H^+])]/(1 + K_{18/2}[H^+])^2$ \quad (I)

where $k_{obs}$ can be calculated at a given pH using $k_{18} = (8.3 \pm 0.7) \times 10^7 \text{M}^{-1} \text{s}^{-1}$, $k_{19} = (9.7 \pm 0.6) \times 10^7 \text{M}^{-1} \text{s}^{-1}$, and $K_{HO_2^-} = 1.6 \times 10^7 \text{M}$ as recommended values.\ref{10} The rate of second-
order reaction mainly given by the reactions of 18 and 19 is

$$
\frac{d[HO_2^-/O_2^-]}{dt} = k_{obs}[HO_2^-/O_2^-]^2
$$

(II)

The solution of equation (II) is

$$
k_{obs} \times \frac{1}{t} = \frac{[HO_2^-/O_2^-]_0 - [HO_2^-/O_2^-]}{[HO_2^-/O_2^-]_0 \times [HO_2^-/O_2^-]} \cdot \text{SR} = \frac{A_0 - A}{A_0 \cdot A_1}
$$

(III)

where the signal ratio (SR) can be defined as $(A_0 - A_1)/(A_0 \cdot A_1)$ where $A_0$ is signal height of fluorescent OHBA at KTR2
of 0 m and $A_1$ is signal heights at KTR2 of 1, 2, 3, and 4 m,
respectively. Since $[HO_2^-/O_2^-]_{1/2}$ is equal to $[HO_2^-/O_2^-]_{0/2}$
at the half-life $(t_{1/2})$, equation (III) becomes

$$
[HO_2^-/O_2^-]_{0/2} = \frac{1}{k_{obs} \times t_{1/2}}
$$

(IV)

In the case of the second-order reaction, the $t_{1/2}$ is
inversely proportional to the initial concentration of $HO_2^/-$.
Thus, the concentration of $HO_2^/-$ can readily be
determined from the $t_{1/2}$ of $HO_2^/-$ decay in the aqueous
solution with calculated $k_{obs}$ at a given pH.

![Figure 2](image-url)

**Figure 2. A:** Plot of SR vs. reaction time with straight line: $[BA] = 1 \text{M}$, $[H_2O_2] = 4 \text{M}$, $[Fe^{3+}$-EDTA] = 20 $\mu$M, and [NaOH] = 0.05 N. **B:** Linear plot of fluorescence signal intensity versus concentration of $HO_2^/-$; pH = 6.11 and same as A. Figure 2 B is fitted by the least squares method using the SigmaPlot (ver. 8.0).
The half-life \( (t_{1/2}) \) of \( \text{HO}_2/\text{O}_2^- \) is experimentally measured with plotting linear relationship of \( \text{SR} \) vs reaction time based on each length of KTR2. Since self-reactions of 18 and 19 occur in KTR2, the concentrations of \( \text{HO}_2/\text{O}_2^- \) can be expected to decrease with increasing length of KTR2, which are stepwise varied as 0, 1, 2, 3, and 4 m. Hence the fluorescence intensity of OHBA corresponding to the concentration of \( \text{HO}_2/\text{O}_2^- \) is decreased with increasing length of KTR2, which is converted into reaction time by the constant flow rate through KTR2 and their constant volumes. A plot of \( \text{SR} \) vs reaction time gives a straight line (Figure 2a) as expected, which produces a pair of slope and intercept at a given pH. From this slope and intercept, we derived the half-life \( (t_{1/2}) \) as following equation (V):

\[
\text{SR}_{1/2} = \text{Slope} \times t_{1/2} + \text{Intercept (V)}
\]

where \( \text{SR}_{1/2} \) is the SR of half-life and becomes identical with \( 1/A_o \) at \( t_{1/2} \). Consequently, a given concentration of \( \text{HO}_2/\text{O}_2^- \) is kinetically calculated from the equation (IV), based on the measured \( 1/A_o \) and calculated \( k_{obs} \) at a given pH.

The fluorescence intensity using various irradiation time of \( \text{H}_2\text{O}_2 \) to produce different quantities of \( \text{HO}_2/\text{O}_2^- \) is linear at pH 6.12 as shown in Figure 2b.

**Results and Discussion**

**Potential interferences and their elimination.** As mentioned earlier, \( \text{OH}_{(o)} \) and \( \text{O}_2 \) are considered as potential interfering oxidants for the use of the kinetic method. The fluorescence intensity of OHBA against various concentrations of \( \text{O}_2 \) in the absence of \( \text{Fe}^{3+}-\text{EDTA} \) is given in Figure 3, which shows a reasonable response to \( \text{OH}_{(o)} \) and \( \text{O}_2 \). The possible formation pathways of OHBA may be resulted from the hydroxylation of BA by \( \text{O}_2 \) (reaction 12) and \( \text{OH}_{(o)} \) (reaction 15).

Although the direct hydroxylation of BA by \( \text{O}_2 \) \( (k_{12} = 1.2 \text{ M}^{-1}\text{s}^{-1}) \) is negligible, \( \text{O}_2 \) decomposition in water can continuously generate \( \text{OH}_{(o)} \) which reacts very rapidly with BA \( (k_{15} = 4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}) \) to produce OHBA.\(^5\) Thus, \( \text{OH}_{(o)} \) and \( \text{O}_2 \) have to be eliminated prior to their reactions with \( \text{Fe}^{3+}-\text{EDTA}/\text{H}_2\text{O}_2/\text{BA} \) for \( \text{HO}_2/\text{O}_2^- \) determination using the kinetic method. This prompted us to seek a proper scavenging compound that would suppress \( \text{OH}_{(o)} \) and \( \text{O}_2 \) while minimizing the quenching of the fluorescence signal of OHBA generated from \( \text{OH}_{(o)} \).

Several compounds such as formate (\( \text{HCOO}^- \)), alcohols \( (\text{i.e., methanol and ethanol}), \) nitrite (\( \text{NO}_2^- \)), and sulfate (\( \text{SO}_4^{2-} \)) were considered as scavengers for suppressing both \( \text{OH}_{(o)} \) and \( \text{O}_2 \). Formate, methanol, and ethanol, however, lead to a production of additional \( \text{HO}_2/\text{O}_2^- \) in the presence of \( \text{OH}_{(o)} \) and react very slow with \( \text{O}_2 \) \( k = 0.02-100 \text{ M}^{-1}\text{s}^{-1} \). In addition, nitrite reacts fast not only with \( \text{OH}_{(o)} \) and \( \text{O}_2 \) but also with \( \text{HO}_2/\text{O}_2^- \). Hence, formate, alcohols, and nitrite are not proper scavengers in the kinetic method for \( \text{HO}_2/\text{O}_2^- \) determination. On the other hand, it has been well known the chain oxidation mechanism of \( \text{H}_2\text{SO}_4/\text{SO}_3^{2-} \) in aqueous solution. As expected from kinetic considerations, \( \text{H}_2\text{SO}_4/\text{SO}_3^{2-} \) is considered as a possible scavenger of both \( \text{OH}_{(o)} \) and \( \text{O}_2 \). The interfering effects of \( \text{O}_2 \) and \( \text{OH}_{(o)} \) in the kinetic method may be effectively suppressed by addition of \( \text{H}_2\text{SO}_4/\text{SO}_3^{2-} \) as follow:\(^{4,25,56,20}\)

\[
\begin{align*}
\text{O}_2 + \text{SO}_3^{2-} &\rightarrow \text{products} \\
\text{O}_2 + \text{H}_2\text{SO}_4^- &\rightarrow \text{products} \\
\text{OH}_{(o)} + \text{SO}_3^{2-} &\rightarrow \text{HO}^- + \text{SO}_4^{2-} \\
\text{OH}_{(o)} + \text{H}_2\text{SO}_4^- &\rightarrow \text{H}_2\text{O} + \text{SO}_4^{2-} \\
\text{O}_2^- + \text{SO}_3^{2-} + \text{H}_2\text{O} &\rightarrow \text{SO}_4^{2-} + \text{HO}_2^- + \text{OH}^- \\
\text{HO}_2^- + \text{H}_2\text{SO}_4^- &\rightarrow \text{products} \\
\text{H}_2\text{SO}_4^- &\leftarrow \text{SO}_3^{2-} + \text{H}^+ \quad \text{pK}_a = 7.2
\end{align*}
\]

where \( k_{20} = 1.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \), \( k_{21} = 3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \), \( k_{22} = 5.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \), \( k_{23} = 4.5 \times 10^4 \text{ M}^{-1}\text{s}^{-1} \), \( k_{24} = 82 \text{ M}^{-1}\text{s}^{-1} \), and \( k_{25} = 0.1 \text{ M}^{-1}\text{s}^{-1} \). \( \text{O}_2 \) and \( \text{OH}_{(o)} \) react rapidly with \( \text{H}_2\text{SO}_4/\text{SO}_3^{2-} \) at nearly diffusion-controlled rate (reactions of 20, 22, and 23), whereas \( \text{HO}_2/\text{O}_2^- \) reacts very slow with \( \text{H}_2\text{SO}_4/\text{SO}_3^{2-} \). \( \text{SO}_4^{2-} \) formed in reactions 22-24a would be removed by dissolved \( \text{O}_2 \) with \( k_{29} = 1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \).

\[
2\text{SO}_3^{2-} + \text{O}_2 \rightarrow \rightarrow \rightarrow 2\text{SO}_4^{2-} \tag{26}
\]

In order to examine the scavenging effect of \( \text{H}_2\text{SO}_4/\text{SO}_3^{2-} \) on both \( \text{OH}_{(o)} \) and \( \text{O}_2 \), the kinetic method for \( \text{H}_2\text{O}_2/\text{O}_2^- \) measurement is evaluated without and with \( \text{Fe}^{3+}-\text{EDTA} \). In the absence of the \( \text{Fe}^{3+}-\text{EDTA} \), Figure 4 shows the dependence of the fluorescence intensity of OHBA on \( \text{H}_2\text{SO}_4/\text{SO}_3^{2-} \) concentration at various pH conditions of 4.11-8.35. The fluorescence intensity of OHBA is rapidly decreased by gradually increasing \( \text{H}_2\text{SO}_4/\text{SO}_3^{2-} \) concentrations in the ranges of 0.001-0.01 mM and is slowly decreased thereafter. It suggests that \( \text{H}_2\text{SO}_4/\text{SO}_3^{2-} \) effectively eliminates residual \( \text{O}_2 \) and \( \text{OH}_{(o)} \) formed by ozone decomposition. After eliminating \( \text{O}_2 \) and \( \text{OH}_{(o)} \), residual \( \text{SO}_3^{2-} \) may compete
Determination of Hydroperoxy/superoxide Anion Radical (HO$_2$·/O$_2$·−).


with BA for ·OH (FL). This competing reaction would be eliminated by the oxidation of residual HSO$_3$−/SO$_3^{2−}$ by excess H$_2$O$_2$ prior to the Fenton-like reaction. On the other hand, in the presence of Fe$^{3+}$-EDTA the fluorescence intensity of OHBA is measured at pH 4.9 as shown in Figure 5. The fluorescence intensity of OHBA is rapidly decreased by gradually increasing sulfite concentration in the ranges of 0-0.1 mM and thereafter reaches a steady fluorescence intensity. This rapid decrease of the fluorescence signal indicates that residual O$_3$ and ·OH(O$_3$) formed by O$_3$ decomposition are properly eliminated by sulfite, and the steady fluorescence signal of OHBA is caused by HO$_2$·/O$_2$·− through the reduction of Fe$^{3+}$-EDTA into Fe$^{2+}$-EDTA followed by the Fenton-like reaction of H$_2$O$_2$ and Fe$^{2+}$-EDTA in the presence of BA. These results suggest that the kinetic method using HSO$_3$−/SO$_3^{2−}$ can be used to determine the steady-state concentration of HO$_2$/O$_2$− formed in O$_3$ decomposition.

**Determination of HO$_2$/O$_2$−.** The steady-state concentration of HO$_2$/O$_2$− in aqueous O$_3$ solution was measured by using the kinetic method as a function of initial O$_3$ concentration at pH 4.9 using a continuous flow system as shown in Figure 6. The concentration of HO$_2$/O$_2$− increases with increasing the O$_3$ concentration, which shows a reasonable linearity within the experimental error. These results suggest that the steady-state HO$_2$/O$_2$− concentration is proportional to the O$_3$ concentration at a given pH.

The steady-state concentration of HO$_2$/O$_2$− generated during O$_3$ decay shows pH dependence in the range of pH 4-7.59 as shown in Figure 7 and in Table 1, and they are ranging from 2.49 (± 0.10) × 10$^{-7}$ M (pH = 4.17) to 3.01 (± 0.07) × 10$^{-10}$ M (pH = 7.59) at [O$_3$]$_o$ = 60 μM. The pH
dependence of HO$\cdot$/$O_2^-$(±) concentration is distinguished from the different reactivities of HO$\cdot$ and $O_2^-$ on O$_2$ molecules. Based on $pK_a$ (HO$_2$) ~ 4.8, at low pH condition [HO$^·$/[O$_2^-$] ratio is high and HO$_2$ reacts very slow with $O_2$ ($k_7 < 10^5$ M$^{-1}$s$^{-1}$)). Thus, the steady-state concentration of HO$_2^·$ is relatively high. On the other hand, as the pH increases, [HO$^·$/[O$_2^-$] ratio rapidly decreases. Since the reaction between $O_2^-$ and $O_3$ ($k_6$ ~ 1.52 (± 0.05) × 10$^9$ M$^{-1}$s$^{-1}$) is very fast, the loss rate of $O_2^-$ by $O_3$ is increased as pH increases. Thus, its concentration obtained by the kinetic method is relatively low or even undetectable at higher pH (> 8).

However, any quantitative concentration of HO$^·$/O$_2^-$ measured in the ozone decomposition in water has not been found from a number of previous studies. Staeelin et al. reported without specifying pH condition that the steady-state concentration of HO$^·$/O$_2^-$ was estimated to be ≤ 10$^{-6}$ M, assuming that formation rate of HO$^·$/O$_2^-$ is ≤ 10$^{-10}$ M/s and ozone concentration of ≤ 10$^{-7}$ M controls its consumption rate. It is notorious that the steady-state concentrations of HO$^·$/O$_2^-$ measured in this study find a reasonable agreement with their results.

### Conclusions

The concentration of HO$^·$/O$_2^-$ in ozone decomposition has been determined by the novel kinetic method using the experimentally determined half-life ($\tau_{1/2}$) of HO$^·$/O$_2^-$. HO$^·$/O$_2^-$ formed in ozone decomposition reduce Fe$^{3+}$/EDTA into Fe$^{2+}$/EDTA and subsequently the well-known Fenton-like (FL) reaction of H$_2$O$_2$ and Fe$^{2+}$/EDTA produces the hydroxyl radicals, $\cdot$OH$_{FL1}$. Benzoic acid (BA) scavenges $\cdot$OH$_{FL1}$ to produce OHBA, which are analyzed by fluorescence detection ($\lambda_{ex} = 320$ nm and $\lambda_{em} = 400$ nm). In this study, potential interferences of $O_3$ and the hydroxyl radicals, $\cdot$OH($OH$), are suppressed by HSO$_3$/SO$_2^-$. The steady-state concentration of HO$^·$/O$_2^-$ is proportional to the $O_3$ concentration at a given pH. However, the steady-state concentration of HO$^·$/O$_2^-$ in ozone decomposition is inversely proportional to pH values. This pH dependence is due to significant loss of $O_3^-$ by $O_3$ at high pH conditions. The steady-state concentrations of HO$^·$/O$_2^-$ are in the range of 2.49 (± 0.10) × 10$^{-9}$ M (pH = 4.17) ~ 3.01 (± 0.07) × 10$^{-9}$ M (pH = 7.59) at [O$_3$]$_b$ = 60 μM.

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### References


### Appendix

**Estimation for the extinction coefficient of aqueous ozone**

Up to now, previous studies are not presenting the extinction coefficient of aqueous ozone for the wavelength range 200 to 240 nm because of the instability of ozone in water. In this study, the extinction coefficient of ozone in water at 220 nm is extrapolating from the cross section of ozone, based on the well-known $\varepsilon_{\text{max}} = 2900$ M$^{-1}$cm$^{-1}$. The cross section of gaseous ozone in the atmosphere have a value of 1.12 × 10$^{-20}$ cm$^2$ at 258 nm and 1.99 × 10$^{-22}$ cm$^2$ at 220 nm, respectively. The cross section values of gaseous ozone in the atmosphere can get from NASA.