A kinetic study of resorcinol-enhanced hydroxyl radical generation during ozonation with a power law type equation

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ABSTRACT

Hydroxyl (OH) radical is proposed as an important factor in the ozonation of water. It is necessary for the utilization of ozonation in the water treatment process to quantitatively determine the interaction among ozone, OH radical and dissolved substances during ozonation. In this study, the effect of humic acid on OH radical generation during ozonation was evaluated with ESR/spin-trapping/stopped-flow technique using resorcinol as a model compound of humic substances. The OH radical was trapped with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a stable adduct, DMPO-OH. The initial velocity \( v_0 \) of DMPO-OH generation increased as a function of ozone and resorcinol concentrations. The relation among ozone, resorcinol concentrations and the initial velocity \( v_0 \) of DMPO-OH generation was kinetically analyzed using a power law equation and the following equation was obtained:

\[
v_0 (\text{DMPO-OH} \times 10^{-6} \text{ M/s}) = (9.55 \times 10^{-5}) \times \text{resorcinol} (10^{-6} \text{ M}) \times \text{ozone} (10^{-6} \text{ M})^{1.9} + (3.09 \times 10^{-5}) \times \text{ozone} (10^{-6} \text{ M})^{1.72}.
\]

The equation fitted the experimental results very well. This equation indicated that in the presence of 1 \( \mu \)M resorcinol, 1/3 of ozone concentration is enough to produce the same initial velocity of OH radical generation as that without resorcinol. The kinetic equation for the enhancing effect of resorcinol obtained in the present study should provide useful information to optimize the condition in ozone treatment process of water containing humic substances.

Keywords: Electron spin resonance (ESR); Hydroxyl radical; Ozonation; Power law, Resorcinol, Spin trapping, Stopped-flow,

INTRODUCTION

Ozone has the ability to oxidize various organic contaminants in water. In water purification, ozonation is widely employed to decompose the substances responsible for musty odors. In water, ozone may either react directly with dissolved substances or decompose to form secondary oxidants such as hydroxyl (OH) radicals, which may then lead to a series of radical chain reactions accompanied by further ozone consumption (Staehelin et al., 1984). Given that the OH radical formed from ozone decomposition is highly reactive with organic compounds (Andreozzi et al., 1999; Beltran et al., 1999; Westerhoff et al., 1999; Canton et al., 2003), it is important to understand the decomposition kinetics of ozone in natural water. Recently, Morioka et al. (1993) and Han et al. (2003) reported that humic substances might act as promoters, resulting to the generation of OH radicals during ozonation. Furthermore, humic substances produced synthetically from widely varying phenols, such as resorcinol, catechol, hydroquinone and others, appear to be chemically similar. Resorcinol is often used as a model compound of humic acid (Sato et al., 1987). However, the mechanism among humic
substances, OH radical and ozone remains unclear. Electron spin resonance (ESR) spectroscopy is widely used because of its sensitivity and selectivity; an ESR/spin-trapping technique has been developed to detect unstable radicals (Janzen et al., 1969). We succeeded in using the ESR/spin-trapping technique to directly determine OH radical generation in water during ozonation (Utsumi et al., 1994). Recently, we combined ESR/spin-trapping technique with stopped-flow method to determine the rate constant of OH radical generation (Han et al., 1998), and mathematically, we evaluated the effect of 3-chlorophenol on OH radical generation (Han et al., 2004). The relation among ozone concentration, amount of 3-chlorophenol and the initial velocity (ν₀) of DMPO-OH generation was kinetically analyzed using power law equation and the following equation was obtained: ν₀ (10⁻⁶ M/s) = (1.58 × 10⁻⁵) × [3-chlorophenol (10⁻⁶ M)] × [ozone (10⁻⁶ M)]².⁴⁰ + (3.09 × 10⁻⁵) × [ozone (10⁻⁶ M)]¹.⁷².

In this study, we used the power law type equation obtained from previous study in order to evaluate the enhancing effect of OH radical generation through the ESR/spin-trapping technique in the presence of phenol and resorcinol as model compounds of humic substances.

MATERIALS AND METHODS

Materials
Phenol and resorcinol were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Labotech Co. Ltd. (Tokyo, Japan) and stored at -20°C. Other chemicals commercially available were obtained with the highest grade. Phosphate buffer (0.1 M, pH 7.4) was prepared with pre-ozonated pure water, and all chemicals were dissolved in the buffer just before usage, as described previously (Han et al., 1998). An aqueous ozone solution was prepared by continuously bubbling ozone gas through distilled water using an absorber glass at 20°C; ozone was produced from highly pure oxygen (Fukuoka Oxygen Co., Fukuoka, Japan) with an ozone generator (PO-10, Fuji Electric Co., Kanagawa, Japan). The concentration of aqueous ozone was determined by the Indigo method (Bader et al., 1981).

ESR Measurements
The initial velocity of DMPO-OH generation was obtained using a technique that combined a rapid data acquisition system with an ESR spectrometer (RE-1X, JEOL, Tokyo, Japan) and a stopped-flow system (Ohtsuka Electric Co. Ltd., Osaka, Japan). The OH radicals trapped with DMPO, as described previously (Han et al., 1998; Utsumi et al., 2003; Han et al., 2003), and the ESR signal were recorded with a rapid data acquisition system in order to accurately analyze the initial velocity of OH radical generation. The buffer solution containing DMPO (100 mM) and resorcinol (0.5, 1.0, and 2.0 μM), or phenol (0.5, 1.0, and 2.0 μM) was rapidly mixed with different concentrations of aqueous ozone (10, 20, 40, 60, and 80 μM) at room temperature using a stopped-flow system. The second line of the quartet ESR signals was acquired after a 1- to 2-sec interval in a computer using an ESR spectrometer. The DMPO-OH concentration was determined by comparing the signal intensity to that of a standard solution of diphenyl-2-picrylhydrazyl. ESR measurement conditions were 10 mW of
microwave (9.44 GHz) and 0.20 mT of field modulation (100 kHz).

RESULTS AND DISCUSSION
Effect of resorcinol on DMPO-OH generation
In order to confirm whether or not OH radical is measured with a computer-controlled ESR system, a full ESR spectrum of DMPO-adduct was recorded as described previously (Han et al., 1998; Utsumi et al., 2003; Han et al., 2003). The spectrum was composed of quartet lines having peak height ratio of 1:2:2:1. The ESR parameters (hyperfine constants $a_N=1.49$ mT, $a_H=1.49$mT and $g$-value= 2.0055) coincided with those of DMPO-OH adduct as previously demonstrated (Han et al., 1998; Utsumi et al., 2003), confirming that the quartet signal is DMPO-OH adduct.

ESR/stopped-flow experiment was carried out to accurately determine the initial velocity of DMPO-OH generation. Although ESR spectroscopy is one of the most sensitive methods for radical detection, the amounts of DMPO-OH generated from 10 μM of ozone was the lowest detectable limit with ESR spectroscopy. Therefore, 10-80 μM of aqueous ozone was rapidly mixed with DMPO solution containing 1 μM of phenol or resorcinol at room temperature, and the second line of the quartet ESR signal of the DMPO-OH adduct was acquired using the ESR/stopped-flow technique.

Table 1 summarizes the initial velocities of DMPO-OH generation at different concentration of ozone with/without phenol or resorcinol.

<table>
<thead>
<tr>
<th>Concentration of ozone (μM)</th>
<th>10 20 40 60 80</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.003 0.006 0.023 0.082</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.024 0.047 0.131 0.314</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>0.017 0.046 0.125 0.325 0.581</td>
</tr>
</tbody>
</table>

We previously showed the power law curves during 0-80 μM of the ozone concentration (Han et al., 2004). The power law curves, $v_0 (10^{-6} \text{ M/s}) = A \times \text{[ozone (10^{-6} M)]}^n$, were fitted very well to previously observed data. Therefore, we fitted these data to the power law curves. The reaction equation of DMPO-OH generation during ozonation in the absence of phenol or resorcinol is expressed as $v_0 (10^{-6} \text{ M/s}) = (3.09 \times 10^{-5}) \times \text{[ozone (10^{-6} M)]}^{1.72}$.

Kinetic analysis of OH radical generation enhanced by resorcinol
Stachelin et al. (1984) established the idea that ozonation is initiated by decomposition of O₃ with OH and propagated by the reaction of ·O₂⁻ with O₃ to produce OH radical; and the complicated reaction cascade has been called the SBH model. In SBH model, OH radicals are produced via several cyclic chain reactions. In previous study (Han et al., 2004), we estimated the schemes of elementary reactions and $k_1$ and $k_2$ indicate the apparent rate constants, respectively. Similarly, in this study, it still remains unclear what reactions in the cascade are affected by resorcinol and phenol. However, the velocity of the rate limiting step seems to be increased by resorcinol and phenol in dose dependent manner.
The schemes of elementary reactions are shown below and $k_1$ and $k_2$ indicate the apparent rate constants, respectively.

$$
\text{O}_3 \xrightarrow{k_1} \cdot \text{OH} \quad (1)
\text{O}_3 + \text{Resorcinol (or, Phenol)} \xrightarrow{k_2} \cdot \text{OH} \quad (2)
$$

The global power law equation for OH radical generation during ozonation of water including resorcinol or phenol, should have the form:

$$
\frac{d[\text{DMPO-OH}]}{dt} \approx \frac{d[\cdot \text{OH}]}{dt} = k_2[\text{Resorcinol (or, Phenol)}]^l [\text{O}_3]^m + k_1[\text{O}_3]^n \quad (3)
$$

where we set $d[\cdot \text{OH}]/dt$ to $v_0 \ (10^{-6} \text{ M/s})$.

In the present experimental condition, the concentration of DMPO (100 mM) is 1000-10000 times higher than that of ozone. The reaction of OH radical with DMPO is reported to be second-order kinetic and its rate is $2.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Finkelstein et al., 1980). These facts imply that the reaction between OH radical and DMPO is not rate limiting, indicating that the DMPO-OH level should be equal to that of the OH radical. In fact, the obtained initial velocities of DMPO-OH generation using Eq. (3) at different ozone concentrations shown in Figure 3 were fitted with a power law equation very well:

$$
v_0 \ (10^{-6} \text{ M/s}) - k_1[\text{ozone (10}^{-6} \text{ M})] = A \times [\text{ozone (10}^{-6} \text{ M})]^m,
$$

where $A = k_2[\text{Resorcinol (or, Phenol) (10}^{-6} \text{ M})]^l$.

Figure 1 - Relationship between the initial velocities of DMPO-OH generation and ozone concentration using the power law equation; $v_0 \ (10^{-6} \text{ M/s}) - k_1[\text{ozone (10}^{-6} \text{ M})] = A \times [\text{ozone (10}^{-6} \text{ M})]^m$, (A = $k_2[\text{Resorcinol (or, Phenol) (10}^{-6} \text{ M})]^l$). The initial velocities in the mixture of phenol (●) or resorcinol (▼) and ozone (10, 20, 40, 60, or 80 µM) were calculated using the Eq. (3), and were plotted against ozone concentration.
In order to obtain \( k_2[^{\text{Resorcinol (or, Phenol)}} (10^{-6} \text{ M})] \), \( A \) was calculated by substituting the generated initial velocity \( (\nu_0 (10^{-6} \text{ M/s); resorcinol - 0.5 \mu\text{M:0.029, 2 \muM:0.071; phenol - 0.5 \muM:0.015, 2 \muM:0.043}) \) at 20 \( \mu\text{M ozone to Eq. (3)}. \) Table 2 lists the value of \( A \) and \( m \) of the resulting power law equation and their correlation coefficients from the plots of initial velocities of DMPO-OH generation versus ozone concentration.

**Table 2.** Parameters of the power law equation used to fit the experimental data.

<table>
<thead>
<tr>
<th>Phenol</th>
<th>A</th>
<th>m</th>
<th>R²</th>
<th>Resorcinol</th>
<th>A</th>
<th>m</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.25  \times 10^{-5}</td>
<td>1.9</td>
<td>Calculated</td>
<td>7.98  \times 10^{-5}</td>
<td>1.9</td>
<td>Calculated</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>5.26  \times 10^{-5}</td>
<td>1.9</td>
<td>0.99</td>
<td>1.22  \times 10^{-4}</td>
<td>1.9</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.27  \times 10^{-4}</td>
<td>1.9</td>
<td>Calculated</td>
<td>2.22  \times 10^{-4}</td>
<td>1.9</td>
<td>Calculated</td>
<td></td>
</tr>
</tbody>
</table>

The data used for curve fitting are shown in Fig. 1. The equation, \( \nu_0 (10^{-6} \text{ M/s}) - k_1[^{\text{[ozone(10^{-6} \text{ M})]}]} = A \times [\text{ozone (10^{-6} \text{ M})}]^m \), \( (A = k_2[^{\text{resorcinol (or, phenol)} (10^{-6} \text{ M})}]) \), was used for the curve fitting and calculation. The symbol of \( A \), \( m \) and \( R^2 \) stand for the rate constant, reaction order for overall rate equation (Eq. 3), and the square of the correlation coefficient, respectively. The value of \( A \) was calculated using the generated initial velocity at 0.5 \( \mu\text{M and 2 \muM of resorcinol or phenol with 20 \muM ozone.} \)

Figure 2 demonstrates the relations of the rate constant \( (A = k_2[^{\text{resorcinol (or, phenol)} (10^{-6} \text{ M})}] \) in the power law equation with the concentration of resorcinol or phenol. The linear relations with the square of the correlation coefficient of higher than 0.99 were obtained as follows, \( A, (k_2[^{\text{resorcinol]}]) = (9.55 \times 10^{-5}) \times [\text{resorcinol (10^{-6} \text{ M})}] \) and \( (k_2[^{\text{phenol]}]) = (6.45 \times 10^{-5}) \times [\text{phenol (10^{-6} \text{ M})}] \), respectively.

The present observation strongly confirmed that the enhancing efficiency of humic substances on OH radical generation during ozonation is that the factor \( A (k_2[^{\text{resorcinol (or, phenol)} (10^{-6} \text{ M})}] \) depends linearly on resorcinol or phenol concentrations.

![Figure 2](image_url)

**Figure 2 -** The relationship between the constant factor \( A (k_2[^{\text{resorcinol or phenol)}]) \) and resorcinol (a) and phenol (b) concentrations. The factors A were shown in Table 2.
CONCLUSION

The effect of resorcinol or phenol on OH radical generation during ozonation was evaluated with the initial velocities of OH radical spin-adduct generation using an ESR/stopped flow apparatus. The OH radicals generated were converted into the stable DMPO-OH as a spin-adduct, and the initial velocities of DMPO-OH generation were analyzed as a function of the concentration of ozone and resorcinol or phenol.

The relation among ozone concentration, amount of resorcinol or phenol and the initial velocity ($v_0$) of DMPO-OH generation was kinetically analyzed using power law equation and the following equations were obtained: $v_0$ ($10^{-6}$ M/s) = $(9.55 \times 10^{-5}) \times [\text{resorcinol} \ (10^{-6} \text{ M})] \times [\text{ozone} \ (10^{-6} \text{ M})]^{1.9} + (3.09 \times 10^{-5}) \times [\text{ozone} \ (10^{-6} \text{ M})]^{1.72}$ and $v_0$ ($10^{-6}$ M/s) = $(6.45 \times 10^{-5}) \times [\text{phenol} \ (10^{-6} \text{ M})] \times [\text{ozone} \ (10^{-6} \text{ M})]^{1.9} + (3.09 \times 10^{-5}) \times [\text{ozone} \ (10^{-6} \text{ M})]^{1.72}$. The presence of resorcinol might increase the enhancing effect of OH radical generation 1.5-fold that of phenol itself.

Power law type rate equations are usually adopted to correlate the experimental data in laboratory-scale and pilot-plant scale reactors, and even used to design full-scale reactors. The kinetic equation obtained in the present study should provide useful information to optimize the condition in ozone treatment process of water containing phenolic compounds.

ACKNOWLEDGEMENT

This work was supported in part by Grants-in-Aid of Scientific Research for Research in Priority Areas, for Cooperative Research, for General Science Research, and for Developmental Scientific Research from the Ministry of Education, Science, Sports, and Culture, by the Fundamental Research Fund for the Environmental Future from Environmental Agency, Government of Japan, and by the grant from Takeda Science Foundation.

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