

A kinetic study of enhancing effect by phenolic compounds on the hydroxyl radical generation during ozonation

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Abstract Ozone decomposition in aqueous solution proceeds through a radical type chain mechanism. These reactions involve the very reactive and catalytic intermediates O_2^- radical, OH radical, HO_2 radical, OH^- , H_2O_2 , etc. OH radical is proposed as an important factor in the ozonation of water among them. In the present study, the enhancing effects of several phenolic compounds; phenol, 2-, 3-, 4-monochloro, 2,4-dichloro, 2,4,6-trichlorophenol on OH radical generation were mathematically evaluated using the electron spin resonance (ESR)/spin-trapping technique. OH radical was trapped with a 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a stable adduct, DMPO-OH. The initial velocities of DMPO-OH generation in ozonated water containing phenolic compounds were quantitatively measured using a combined system of ESR spectroscopy with stopped-flow apparatus, which was controlled by homemade software. The initial velocities of DMPO-OH generation increased as a function of the ozone concentration. The relation among ozone concentration, amount of phenolic compounds and the initial velocity (v_0) of DMPO-OH generation was mathematically analyzed and the following equation was obtained, v_0 (10^{-6} M/s) = ($A' \times [\text{PhOHs}] (10^{-9} \text{ M}) + 0.0005$) exp ($60 \times [\text{ozone}] (10^{-9} \text{ M})$). The equation fitted very well with the experimental results, and the correlation coefficient was larger than 0.98.

Keywords Electron spin resonance (ESR); hydroxyl radical; ozonation; phenolic compounds

Introduction

Ozonation is widely used in water purification procedures to decompose the substances responsible for musty odors. Ozonation produces hydroxyl (OH) radicals via the decomposition of O_3 promoted by OH^- (Staehelin *et al.*, 1984). Given that the OH radical formed from ozone decomposition is highly reactive with organic compounds (Hoigne *et al.*, 1976; Buxton *et al.*, 1988), it is important to understand the decomposition kinetics of ozone in natural water. Recently, some kinetic models were provided to explain the efficacy of OH radicals in advanced oxidation processes using OH radical scavengers (Andreozzi *et al.*, 1999; Beltran *et al.*, 1999; Westerhoff *et al.*, 1999; Canton *et al.*, 2003). However, there have been very few papers which determined the amount and the dynamics of OH radical directly.

There is growing public concern about the widespread contamination of surface and ground waters by various organic compounds over the past several decades. In particular, like many phenolic compounds, chlorophenols are used widely in the manufacture of pesticides and other industrial chemicals (Paasivirata *et al.*, 1985) and are also found as a consequence of their accidental formation during the disinfection of phenol-containing water by means of chlorination (Ahlborg *et al.*, 1980; Xu *et al.*, 1997). Trapido *et al.* (1995) reported that chlorophenols react with ozone, affecting the efficiency of ozone. Moreover, ozonation converts dissolved organic substances to various toxic intermediates (Sayato *et al.*, 1987).

In order to detect free radicals, electron spin resonance (ESR) spectroscopy is widely utilized because of its sensitivity and selectivity, and the ESR/spin-trapping technique has

been developed to detect unstable radicals (Janzen *et al.*, 1969). We have succeeded in direct determination of OH radical generation in water during ozonation using ESR/spin-trapping technique (Utsumi *et al.*, 1994). Recently, we combined the ESR/spin-trapping technique with the stopped-flow method to determine the rate constant of OH radical generation, and demonstrated the enhancing effect of phenol derivatives on OH radical generation during ozonation (Han *et al.*, 1998a; Utsumi *et al.*, 1998). We also clarified the generation of semiquinone radical as an intermediate of phenol during ozonation (Han *et al.*, 1998b). However, the precise reaction rate was not determined with the ESR/spin-trapping technique, because the technique is not sufficient to acquire the data as quick as the rate constants of OH radical generation.

The objective of this study was to determine the initial velocity of the OH radical generation during ozonation in the presence of several phenolic compounds using the combined technique of rapid data acquisition system with ESR/spin-trapping/stopped-flow apparatus, and obtained the enhancing effect of the mathematical relation on the ozone concentration.

Materials and methods

Materials

Phenolic compounds; phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol 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 were of the highest grade commercially available. 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 use as described previously (Han *et al.*, 1998a). 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), as described previously (Han *et al.*, 1998a; Utsumi *et al.*, 1998). 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 were trapped with DMPO, as described previously (Han *et al.*, 1998a), and the ESR signal was recorded with a rapid data acquisition system in order to analyze the initial velocity of OH radical generation more precisely. The buffer solution containing DMPO (100 mM) and phenolic compounds (1.0 μM) was rapidly mixed with different concentrations of aqueous ozone (10, 20, 40, and 60 μM) at room temperature using a stopped-flow system; the second line of the quartet ESR signals was acquired at the interval of 1 or 2 sec with a personal computer through an ESR spectrometer. The DMPO-OH concentration was determined by comparing the signal intensity with 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

OH radical measurement with an ESR/computer system

In order to confirm whether or not the OH radical is measured with a computer-controlled ESR system, a full ESR spectrum of DMPO-adduct was recorded as described previously

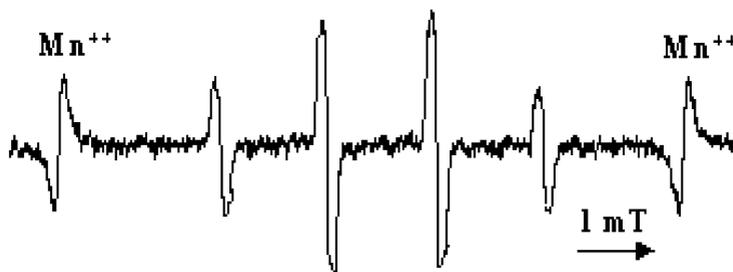


Figure 1 Typical ESR spectrum of DMPO-OH adduct generated during ozonation of water

(Utsumi *et al.*, 1994). Figure 1 shows the typical ESR spectrum obtained 5 min after mixing aqueous ozone with DMPO solution. The spectrum was composed of quartet lines having a 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 demonstrated previously (Han *et al.*, 1998a; Utsumi *et al.*, 1998), confirming that the quartet signal is DMPO-OH adduct.

Relation of ozone concentration with enhancing effect of phenolic compounds on OH radical generation

In order to quantify the enhancing effect of different phenolic compounds on OH radical generation during ozonation, the initial velocities of OH radical generation were estimated as those of DMPO-OH generation as described previously (Han *et al.*, 1998a; Utsumi *et al.*, 1998). In treating drinking water, 1–1.5 ppm of ozone is generally used, which corresponds to 20–30 μM ozone. Therefore, aqueous ozone at a concentration of 10–60 μM was rapidly mixed with DMPO solution containing 1.0 μM of phenolic compounds at room temperature, and the second line of the quartet ESR signal of DMPO-OH adduct was acquired at the interval of 1 or 2 sec using the ESR/stopped-flow technique. Figures 2a–2f demonstrate the time-course of DMPO-OH generation during ozonation in the solutions containing phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol, respectively. The amount of DMPO-OH increased gradually with time after mixing in an ozone dose-dependent manner.

The initial velocities of DMPO-OH generation at different ozone concentrations were obtained from the time-course curves shown in Figures 2a–2f, and plotted against ozone concentration (Figure 3). The enhancing effects of the phenolic compounds were dependent on the ozone dose, and the dose-dependency seemed to be exponential and not linear.

In fact, the initial velocities of DMPO-OH generation at different ozone concentrations shown in Figure 3 were fitted with an exponential equation very well: v_0 (10^{-6} Ms^{-1}) = $A \exp(B \times [\text{ozone} (10^{-6} \text{ M})])$. Table 1 lists the values of A and B of the resulting exponential equations and their correlation coefficients from the plots of DMPO-OH generation versus ozone concentration. The square correlation coefficients were higher than 0.99 in all cases, indicating that the equation fitted the curve very well in all cases. The variation in factor B was much smaller than the variation in factor A , and the average value of B (0.062) was similar to that obtained previously for 3-chlorophenol (0.057) (Utsumi *et al.*, 2003). Thus, using 0.06 of factor B , re-curve-fitting was carried out. Moreover, previously (Utsumi *et al.*, 2003), the relation of the pre-exponential factor with the concentration of 3-chlorophenol was obtained to be $\{(9.7 \times 10^3 \text{ nM}^{-1}) + 0.0005\}$. The re-curve-fitting gave again very high correlation coefficients (Table 1).

The data in Table 1 suggest that the enhancing effects of phenolic compounds on OH radical generation during ozonation can be compared using the pre-exponential factors. For

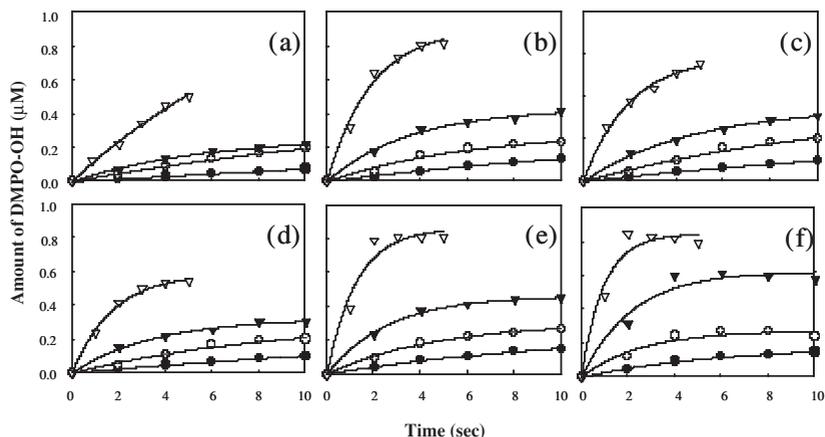


Figure 2 The time courses of DMPO-OH generation during ozonation of water containing different phenolic compounds (1 μM). A phosphate-buffered solution of DMPO (100 mM) with either (a) phenol, (b) 2-chlorophenol, (c) 3-chlorophenol, (d) 4-chlorophenol, (e) 2,4-dichlorophenol, or (f) 2,4,6-trichlorophenol was rapidly mixed with various concentrations of aqueous ozone [10 μM (●), 20 μM (○), 40 μM (▼), 60 μM (▽)] using a stopped-flow system at room temperature, and the peak area of the second line of the quartet ESR signals was acquired at the interval of 1 or 2 sec. The DMPO-OH concentration was determined by measurement conditions of 10 mM of microwave (9.44 GHz) and 0.020 mT of field modulation (100 kHz)

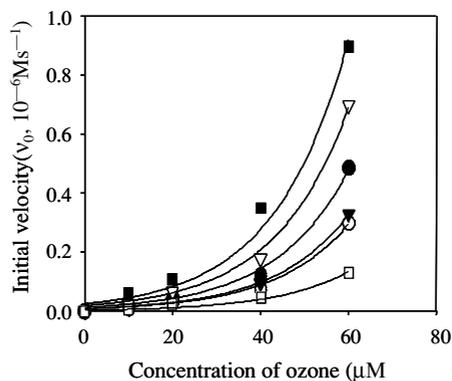


Figure 3 The relation between the initial velocities of DMPO-OH generation and the ozone concentration. The initial velocities of DMPO-OH generation in the mixture of aqueous ozone with phenol (□), 2-chlorophenol (●), 3-chlorophenol (○), 4-chlorophenol (▼), 2,4-dichlorophenol (▽), and 2,4,6-trichlorophenol (■) were obtained from the time-course of DMPO-OH generation shown in Figures 1a–1f, and were plotted against ozone concentration. The lines indicate the curve-fitted one with exponential equation $\{v_0 (10^{-6} \text{ Ms}^{-1}) = A \times \exp(B \times [\text{ozone} (10^{-6} \text{ M})])\}$

Table 1 The parameters of exponential equation used for curve-fitting of the experimental data

	Experimental			Calibrated		
	A	B	R ²	A'	B' (const.)	R ²
Phenol	0.0062	0.051	0.99	0.0037	0.06	0.98
2-chlorophenol	0.0088	0.067	0.99	0.0131	''	0.99
3-chlorophenol	0.0054	0.067	0.99	0.0081	''	0.99
4-chlorophenol	0.0079	0.063	0.99	0.0090	''	0.99
2,4-dichlorophenol	0.0129	0.067	0.99	0.0189	''	0.99
2,4,6-trichlorophenol	0.0252	0.060	0.99	0.0252	''	0.99

the mono-chlorophenols, such as 2-chlorophenol, 3-chlorophenol and 4-chlorophenol, the OH radical generation was enhanced 3.5-, 2.2- and 2.4-fold times that of phenol itself as a pre-exponential factor (A'), respectively. Furthermore, the enhancing effects of 2,4,6-trichlorophenol and 2,4-dichlorophenol on OH radical generation were 6.8- and 5.1-fold larger than that of phenol itself, respectively. The results indicate that the enhancing effect of phenolic compounds on OH radical generation during ozonation are shown to depend on the position and number of the chlorine substitution of phenol.

The data used for curve-fitting were demonstrated in Figure 3. The exponential equation of $\{v_0 (10^{-6} \text{ Ms}^{-1}) = A \times \exp(B \times [\text{ozone} (10^{-6} \text{ M})])\}$ was used for the curve-fitting and the values of A , B , and R^2 are the pre-exponential factors, exponential factors and square of the correlation coefficient, respectively. The values of A' and R'^2 are the pre-exponential factors and the square of the correlation coefficient obtained with the constant exponential factor (B'), respectively, where the exponential factor B' (0.06) was the average value of factors B .

Conclusion

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

The contamination of phenolic compounds at a practical level increases distinguishably the OH radical generation during ozonation and that the enhancement of OH radical generation by phenolic compounds may be predicted with the following equation, $v_0 (10^{-6} \text{ Ms}^{-1}) = \{(A' \times 10^3) \times [\text{PhOHs} (10^{-9} \text{ M})] + 0.0005\} \exp(60 \times [\text{ozone} (10^{-9} \text{ M})])$, where the A' -value of each phenolic compound is demonstrated in Table 1.

The phenols with *ortho*-substituted chlorine had stronger enhancing effects than those substituted at the *meta* or *para* positions. 2,4,6-trichlorophenol had the strongest enhancing effect on OH radical generation, followed by 2,4-dichlorophenol. These results indicate that the enhancing effect of a chlorophenol on OH radical generation during ozonation depends on the position and number of the chlorine substitutions on the phenol.

Acknowledgements

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References

- Ahlborg, U.G. and Thunberg, T.M. (1980). Chlorinated phenols: occurrence, toxicity, metabolism and environmental impact. *CRC Crit. Rev. Toxicol.*, **7**, 1-35.
- Andreozzi, R., Caprio, V., Insola, A. and Marotta, R. (1999). Advanced oxidation processes (AOP) for water purification and recovery. *Cat. Tod.*, **52**, 51-59.
- Bader, H. and Hoigne, J. (1981). Determination of ozone in water by the indigo method. *Wat. Res.*, **15**, 449-456.
- Beltran, F.J., Rivas, J., Alvarez, P.M., Alonso, M.A. and Acedo, B. (1999). A kinetic model for advanced oxidation processes of aromatic hydrocarbons in water: Application to phenanthrene and nitrobenzene. *Ind. Eng. Chem. Res.*, **38**, 4189-4199.
- Buxton, G.V., Greenstock, C.L., Helman, W.P. and Ross, A.B. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution. *J. Phys. Chem. Ref. Data*, **17**(2), 513-886.

- Canton, C., Esplugas, S. and Casado, J. (2003). Mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light. *Applied Cat. B: Environ.*, **43**(2), 139–149.
- Han, S.K., Ichikawa, K. and Utsumi, H. (1998a). Quantitative analysis for the enhancement of hydroxyl radical generation by phenols during ozonation of water. *Wat. Res.*, **32**(11), 3261–3266.
- Han, S.K., Ichikawa, K. and Utsumi, H. (1998b). Generation of p-semiquinone radicals from chlorophenols in water during ozonation. *Wat. Res.*, **32**(6), 1978–1981.
- Hoigne, J. and Bader, H. (1976). The role of hydroxyl radical reaction in ozonation process in aqueous solutions. *Wat. Res.*, **10**, 377–396.
- Janzen, E.G. and Blackburn, B.J. (1969). Detection and identification of short-lived free radicals by an electron spin resonance trapping technique (Spin Trapping). Photolysis of organolead, -tin, and mercury Compounds. *J. Am. Chem. Soc.*, **91**, 4481–4490.
- Paasivirta, J., Heinola, K., Humppi, T., Karjalainen, A., Knuutinen, J., Mantykoski, K., Pauku, R., Piilola, T., Surma-Aho, K., Tarhanen, J., Welling, L., Vihonen, H. and Sarkka, J. (1985). Polychlorinate phenols, guaiacols and catechol in environment. *Chemosphere*, **14**, 469–491.
- Sayato, Y., Nakamura, K. and Ueno, H. (1987). Mutagenicity of products formed by ozonation of naphthoresorcinol in aqueous solutions. *Mutat. Res.*, **189**, 217–222.
- Stachelin, J., Buhler, R.E. and Hoigne, J. (1984). Ozone decomposition in water studied by radiolysis. 2.OH and HO₄ as chain intermediates. *J. Phys. Chem.*, **88**(24), 5999–6004.
- Trapido, M., Hirvonen, A., Veressinina, Y., Hentunen, J. and Munter, R. (1997). Ozonation, ozone/UV and UV/H₂O₂ degradation of chlorophenols. *Ozone Sci. Eng.*, **17**, 75–95.
- Utsumi, H., Hakoda, M., Shimbara, S., Nagaoka, H., Chung, Y. and Hamada, A. (1994). Active oxygen species generated during chlorination and ozonation. *Wat. Sci. Tech.*, **30**, 91–99.
- Utsumi, H., Han, S.K. and Ichikawa, K. (1998). Enhancement of hydroxyl radical generation by phenols and their relation intermediates during ozonation. *Wat. Sci. Tech.*, **38**(6), 147–154.
- Utsumi, H., Han, Y.H. and Ichikawa, K. (2003). Generation of hydroxyl radical during ozonation: Enhancement of hydroxyl radical generation by 3-chlorophenols. *Wat. Res.*, **37**, 4924–4928.
- Westerhoff, P., Aiken, G., Amy, G. and Debroux, J. (1999). Relationships between the structure of natural organic matter and its reactivity towards molecular ozone and hydroxyl radicals. *Wat. Res.*, **33**(10), 2265–2276.
- Xu, X., Huixian, Z. and Jinqi, Z. (1997). Formation of strong mutagen [3-chloro-4-(dichloromethyl)-5-hydroxyl-2(5h)-furanone] MX by chlorination of fractions of lake water. *Wat. Res.*, **31**(5), 1021–1026.