Decomposition of Geosmin in Aqueous Solution by Sonication

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Geosmin was decomposed by sonication in aqueous solutions saturated with various gaseous envelopes. The order of the decomposition rate of geosmin under the atmosphere was as follows ; argon > oxygen ≧ air > nitrogen.

In recent years, many researches on sonochemical decomposition of contaminants such as pentachlorophenol,[1] p-nitrophenol,[2] chlorinated hydrocarbons,[3,4] and chlorofluorocarbons[5,6] in aqueous solution have been reported. The ultrasonic irradiation of aqueous solutions could be an advantageous method to investigate the reactivity of hydroxyl radicals which play a significant role upon environmental chemistry as well as to investigate the thermal effects caused by ultrasound. Earthy-musty odors compounds such as geosmin in drinking water have come to be recognized world-wide as an index of deterioration of the drinking water. These bicyclic-structural earthy-musty odors compounds have low odor threshold.[7] For removing these compounds in water, adsorption methods using activated carbon,[8,9] zeolites,[10,11] and adsorption decomposition methods by ozone/active carbon[12] or an acclimatized biofilm reactor[13] have been investigated.

However, the decomposition and deodorization of these compounds by ultrasonic irradiation have not been reported.

In this research, we report the results of sonochemical decomposition of geosmin.

Geosmin and t-butyl alcohol (t-BuOH) were obtained from Wako Pure Chemicals. All chemicals were of at least 99 % purity and were used without further purification. Bubbling gases (argon, oxygen and nitrogen) of four-nine grade were purchased from Osaka Sanso, and water was purified in Millipore system (Milli-Q Labo). A multiwave ultrasonic generator (Kaijo 4021) and a barium titanate oscillator of 65 mm ϕ were used for ultrasonic irradiation and operated at 200kHz with an input intensity of 200W. A cylindrical glass vessel of 65 mm ϕ with total volume of 150mL was used for ultrasonic irradiation. The vessel has a side arm with a silicon rubber septum for gas bubbling, solute injection or sample extraction, and the vessel was fitted at a constant position of a nodal plane of the ultra-sound wave (λ /2 ; 3.8mm upon the oscillator). During the irradiation the vessel was closed. The solution was bubbled by enveloping gases for 30 minutes before irradiation. The concentration of geosmin was determined by a gas chromatograph (Hewlett-Packard 5890) with a capillary column (DB Ultra-1).

Figure 1 shows the time-profiles of geosmin during a sonication under air atmosphere. The decomposition rate of geosmin by ultrasonic irradiation was dependent on concentration of geosmin, and the initial decomposition rates are as follows; 0.9 x10^{-3} μ M (1 M = 1 mol dm^{-3}) sec^{-1} at 0.6 μ M , 3.2x10^{-3} μ M sec^{-1} at 3.3 μ M, and 16.9x10^{-3} μ M sec^{-1}at 33 μ M. Figure 2 shows a pH change of the sample solution during sonication of geosmin (3.3 μ M) under air. The pH dropped from its initial value of 7.0 to 3.2 at the end of run. It is known that nitrate and/or nitrite anion are produced during a sonication of aqueous solution under air atmosphere and thus, the pH of the aqueous solution usually decreases with sonication time under air atmosphere. In order to examine the effect of pH on the decomposition of geosmin by sonication, the decomposition rate of geosmin in buffer solution was measured at various pH ranging from 3.9 to10. As shown in Figure 3, the rate increased slightly with decreasing pH of the sample solution.

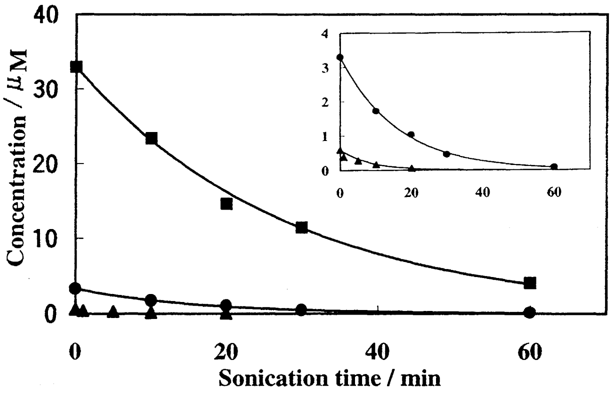

Figure 1. Decomposition of geosmin by ultrasonic irradiation under air. ▲;0.6 μM,●; 3.3 μM,■; 33 μM.

Acoustic cavitation refers to the formation and collapse of small gas or vapour-filled cavities (bubbles) in liquids exposed to ultrasound.[14] In aqueous solution, thermal decomposition of water vapor is generated to hydroxyl radicals and hydrogen atoms in the collapsing cavities.[14] It is known that the efficiency of acoustic cavitation is dependent upon the dissolved gas. Table 1 indicates the decay rates of geosmin (33 μ M) in aqueous solutions saturated with various gases. The order of the initial decomposition rate is as follows; argon > oxygen ≧ air > nitrogen. Specific heat ratio (γ = C_p/C_v) of the envelope gas

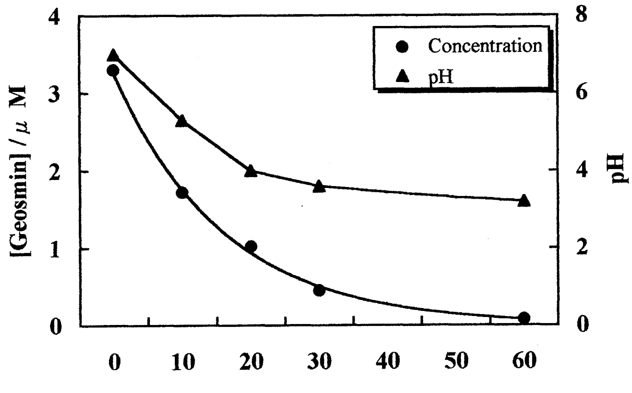

Figure 2. Change in geosmin concentration and pH versus sonication time under air.
[Geosmin]$_i$ = 3.3 μ M, initial pH = 7.0.

used are listed in Table 1, and the results show that the decomposition rate was increased with increasing γ value of the envelope gas.

The temperature in a collapsing cavity was derived[15] as $T_f = T_i\ [\ P_f\ (\gamma\text{-}1)\ /\ P_i\ ]$ where T_f and P_f are final temperature and pressure, and T_i and P_i are initial temperature and pressure in cavities, respectively. T_f is higher under argon than the other gases because of the higher γ value of argon than that of the other gases, therefore, the rate of ·OH radical formation would be faster under argon than under the other gases, and thermal decomposition of geosmin would also effectively occur if this compound exists in this region or it's surroundings of high temperature. The decomposition rates under oxygen or air were slightly faster than that under nitrogen irrespective of almost equal γ values of these gases. We assumed that oxygen scavenged H· radicals and resulting HOO· radicals contribute the decomposition of geosmin(eqs.1,2,3).

$$H_2O \xrightarrow{)))} H\cdot + \cdot OH \qquad (1)$$

$$H\cdot + O_2 \rightarrow HOO\cdot \qquad (2)$$

$$\text{geosmin} + HOO\cdot \rightarrow \text{decomposition} \qquad (3)$$

The contribution of the radical reaction by ·OH radicals was examined by the addition of t-butyl alcohol, which is known as an effective ·OH radical scavenger, into the sample solution. Result is indicated in Figure 4. The decomposition of geosmin was suppressed about 60% by the t-BuOH addition. This result suggests that decomposition of about 60% proceeds via radical reaction and that of about 40% via thermal reaction in sonochemical decomposition of geosmin in water at the present experimental conditions.

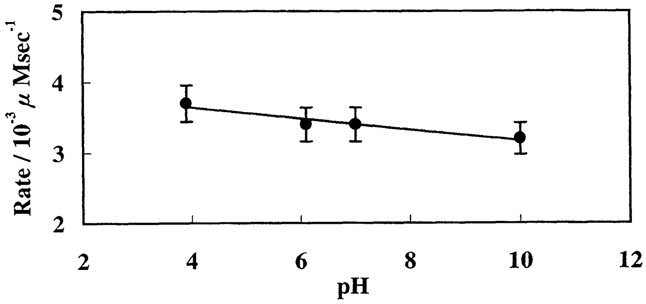

Figure 3. Effect of pH on the decay rate of geosmin by ultrasonic irradiation under air. $[\text{Geosmin}]_i = 3.3\ \mu$ M.

Table 1. Comparison of initial decomposition rate of Geosmin[a] with specific heat ratio of atmospheric gases

Atmosphere	Rate[b]	SD[c]	Cp/Cv[d]
Argon	37.8	3.1	1.670
Oxygen	17.3	1.6	1.396
Air	16.9	1.7	1.402
Nitrogen	15.3	1.4	1.401

[a] $[\text{Geosmin}]_i = 33\ \mu$ M. [b] Initial decomposition rate (x $10^{-3}\ \mu$ Msec^{-1}). [c] Standard deviation. [d] J.Hilsenrath et al., "Tables of Thermal Properties of Gases", NBS Circular, 564 (1955). At 1atm, 300K.

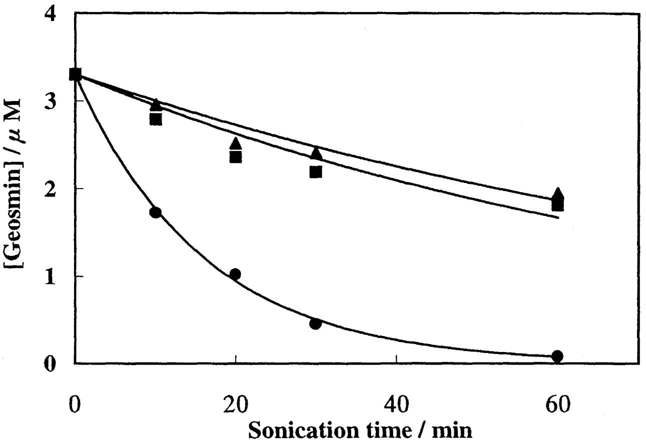

Figure 4. Effect of t-BuOH addition on the decay of geosmin by ultrasonic irradiation under air. $[\text{Geosmin}]_i = 3.3\ \mu$ M, ●; no addition, ■; 0.3mM addition, ▲; 3.3mM addition.

References and Notes

1 C. Petrier, M. Micolle, and G. Reverdy, *Environ. Sci.Technol.*, **26**, 1639 (1992).
2 A. Kotronarou, G. Mills, and M. R. Hoffmann, *J. Phys.Chem.*, **95**, 3630 (1991).
3 H. M. Cheung, M. Bhatnagar, and G. Lansen, *Environ. Sci. Technol.*, **25**, 1510 (1991).
4 K. Inazu, Y. Nagata, and Y. Maeda, *Chem. Lett.*, **1993**, 57.
5 H. M. Cheung and S. Kurup, *Environ. Sci. Technol.*, **28**, 1619 (1994).
6 Y. Nagata, K. Hirai, and Y. Maeda , *Chem. Lett.*, **1995**, 203.
7 N. N. Gerber, *Tetrahedron Lett.*, **1968**, 2971.
8 D. R.Herzing, V. L. Snoeyink, and N. F.Wood, *J. Am.Wat. Wks Ass.*, **69**, 223 (1977).
9 S. Lalezary-Craig, M. Pirbazari, M. S.Dale, T. Tanaka,and M. J. McGuire, *J. Am. Wat. Wks Ass.*, **80**,73 (1988).
10 J. Ellis and W. Korth, *Wat. Res.*, **27**, 535 (1993).
11 " *Guidelines for Mastering the Properties of Molecular-sieves,* " ed by E. G. Derouane, Plenum Press, New York (1990).
12 A. Ando, M. Miwa, Kajinom, and S. Tatsumi, *Wat. Sci. Technol.*, **25**, 299 (1992).
13 K. Egashira, K. Ito, and Y.Yoshii, *Wat. Sci. Technol.*, **25**,307 (1992).
14 "*Ultrasonics,* " ed by R.E. Apfel, Academic Press, New York (1981).
15 A. Kotronarou, G.Mills, and M.R.Hoffmann, *J. Phys. Chem.*, **95**, 3630 (1991).