Published in final edited form as:

Water Res. 2007 June ; 41(12): 2672–2678. doi:10.1016/j.watres.2007.02.041.

Ultrasonically Induced Degradation of 2-methylisoborneol and geosmin

Weihoa Song and Kevin E. O'Shea

Department of Chemistry and Biochemistry, Florida International University, University Park, Miami, FL 33199, USA, Tel: 1.305.348.3968; Fax: 1.305.348.3772

Kevin E. O'Shea: osheak@fiu.edu

Abstract

2-methylisoborneol (MIB) and geosmin (GSM) are taste and odor compounds produced by cyanobacteria in surface waters. While the strong odors and musty flavors of MIB and GSM are generally associated with poor water quality, the removal of these semi-volatile compounds presents a significant challenge to drinking water providers. Likewise in aquaculture, accumulation of these compounds in fish meat leads to quality problems and reduces marketability. Conventional water treatments are ineffective at removing low concentration of odor compounds. We report herein ultrasonic irradiation at 640 kHz leads to rapid degradation of MIB and GSM. While radical processes generally dominate during ultrasonic induced degradation, pyrolysis appears to be responsible for a significant fraction of the observed degradation. Several pyrolytic products from MIB and GSM have been identified and degradation pathways are elucidated. The degradation of MIB and GSM follows the first order kinetics and the rate constants are 0.07 and 0.12 min⁻¹, respectively. These results suggest ultrasonic irradiation maybe applicable as an effective method for removal of taint compounds from potable water supplies and fish farms.

Keywords

2-methylisoborneol; Geosmin; ultrasonic irradiation; pyrolysis

1. Introduction

Taste and odor (T&O) problems are common in water utilities (Lalezary 1984, Lalezary et al. 1986a). The most prevalent T&O customer complaints are in regard to earthy-musty odors. Microbial by-products, such as alicyclic alcohols 2-methylisoborneol (MIB), *trans*-1, 10-dimethyl-*trans*-9-decalol (GSM), isopropyl methoxy pyrazine (IPMP), or trichloroanisole (TCA) are usually sources of the earthy-musty odors. MIB and GSM, microbial by-products associated with blue-green algae and aquatic actinomycetes, are the most common odorants (Burlingame et al. 1986, Lalezary et al. 1986b). Extremely low levels of MIB and GSM cause undesirable tastes and odors. The human threshold concentration for detecting these compounds is typically 4–10 ng/L for MIB and GSM. (Suffet 1996, Rashash et al. 1997)

© 2007 Elsevier Ltd. All rights reserved.

Correspondence to: Kevin E. O'Shea, osheak@fiu.edu.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Previous research concluded that conventional treatment (coagulation / flocculation / sedimentation / filtration) are ineffective in removing MIB and GSM from drinking water (Bruce et al. 2002). MIB and GSM have relatively low molecular weights, moderate hydrophobicity and moderate solubility. Air stripping systems are not economical for MIB and GSM removal due to their low Henry's constants. Powdered activated carbon (PAC) or granular activated carbon (GAC) adsorption can remove most odorants (Suffet et al. 1995), but may require relatively high doses and exhibit reduced efficiency in natural water due to the presence of other organics. Chlorine and chlorine-dioxide are ineffective for treatment of modest levels of MIB and GSM. Ozone, a powerful oxidant, is efficient for degradation of MIB and GSM (Nerenberg et al. 2000). Water utilities use ozone to achieve multiple objectives, including pathogen inactivation, TOC removal improvement, mineral oxidation, and synthetic organic chemical oxidation. Unfortunately dissolved organic material (DOM) in the raw water can rapidly deplete ozone, resulting in incomplete oxidation of MIB and GSM. Ozonation can produce hazardous oxidation by-products, especially in waters containing bromide ions (Br^-) where carcinogenic bromate (BrO_3^-) is formed. MIB and GSM are biodegradable, but information regarding their removal in biological filters used in water treatment plants (WTP) is limited (Nerenberg et al. 2000).

Advanced oxidation technologies (AOTs) are attractive alternatives to traditional water treatments and have received considerable attention recently. AOTs involve the generation of $\bullet\text{OH}$ as the predominant species responsible for the degradation of pollutants. Several reports indicated that TiO_2 photocatalysis and $\text{UV}/\text{H}_2\text{O}_2$ effectively remove MIB and GSM from drinking water and $\bullet\text{OH}$ is the predominant species responsible for their degradation (Linden et al. 2002, Lawton et al. 2003, Rosenfeldt et al. 2005). Ultrasonic irradiation, an AOT, has been studied for the oxidation of organics, destruction of pathogenic organisms, and treatment of water and wastewater either as a sole means of treatment or in combination with other oxidation processes such as ozone, UV irradiation and photocatalysis (Adewuyi 2005a, b). Unlike other AOTs, ultrasound does not require addition of chemicals and can be used for treatment of turbid solutions. Ultrasonic irradiation promotes the growth and collapse of gas bubbles (cavitation), leading to extreme conditions (5000 K, 1000 atm) under which the pyrolysis of water produces $\bullet\text{H}$ and $\bullet\text{OH}$. In most cases, the reaction pathways observed for ultrasonic induced degradation of dissolved organic compounds in aqueous media involve hydroxyl radical oxidation, pyrolysis and supercritical oxidation (Suslick et al. 1986).

Our previous studies have shown that ultrasonic irradiation can quickly and effectively degrade cyanobacterial toxins produced by blue-green algae (Song et al. 2005, Song et al. 2006). We report herein the rapid ultrasonic induced degradation of MIB and GSM. Experiments involving hydroxyl radical scavengers suggest pyrolysis is responsible for the degradation of MIB and GSM during ultrasonic irradiation. We identified several degradation products and propose specific degradation pathways for MIB and GSM.

2. Experimental

2.1 Chemicals

2-methylisoborneol, geosmin, terephthalic acid disodium, *tert*-butyl alcohol and 1, 2-diphenylethane were purchased from Sigma-Aldrich. 65 μm PDMS-DVB SPME fibers were purchased from Supelco. All solutions were prepared using Milli-Q water.

2.2 Ultrasonic irradiation

An ultrasonic transducer UES 1.5-660 Pulsar (Ultrasonic Energy Systems, Inc.) equipped with a 500 mL glass reactor was fitted with a polyethylene window facing the transducer. The reaction vessel was centered at a distance of 4.50 cm from the face of horn. Since

modest heating is observed during ultrasonic irradiation, the entire assembly was submerged in an ice bath to maintain a constant temperature of 4 °C throughout the reaction process. (Peller et al. 2001, Song et al. 2006) Argon saturation was achieved by sparging the solution for 3 min prior to irradiation. In all cases, the reaction vessel was sealed under argon or air saturated conditions during irradiation.

2.3 Analytical methods

GSM and MIB were extracted from aqueous solution using solid-phase microextraction (SPME) procedure modified from a literature (Watson et al. 2000). Twenty mL samples were taken at various irradiation times, transferred to screw-capped, straight-sided headspace vials with a PTFE-faced silicone septa. Ten μL of 20 ppm 1,2-diphenylethane was added as internal standard. Sodium chloride (5 g) and a PTFE stirrer bar were added to the sealed vial which was placed in a 65 °C hot-block. The SPME fiber was extended into the headspace of the vial then exposed for 30 min while the sample was constantly stirred and maintained at 65 °C. The fiber was retracted and transferred to the injector of the GC-MS where the sample was thermally desorbed (250 °C for 1 min). A GC temperature gradient from 40 to 300 °C at a rate of 7.5 °C min^{-1} was employed with a final time of 5 min at 300 °C. The GC-MS measurements were carried out on a Hewlett-Packard model 6890 series II GC connected to a Hewlett-Packard model 5971A mass selective detector. The column used was a DB-5 (30 m $\times$ 0.25 μm $\times$ 0.25 mm).

3. Results and Discussion

The ultrasonic induced degradation of MIB and GSM were conducted at 640 kHz as dilute aqueous air saturated solutions at 4 °C. The concentrations were determined using SPME-GC/MS analyses of the solutions at different treatment times. Control experiments established that the concentrations of MIB and GSM remain constant throughout the experimental process without ultrasonic irradiation. (No loss due to evaporation or adsorption). Upon ultrasonic induced degradation, MIB and GSM (10 $\mu\text{g/L}$) are readily degraded and within 10 min less than 50 % of the starting material remains, as illustrated in Fig. 1. After 40 min irradiation, over 90 % decomposition of both compounds was achieved. Ultrasonically induced transformation of organics in aqueous media often follows first-order kinetics as described by eq 1 (Colussi et al. 1999).

$$\ln(C/C_0) = -k * t \quad (1)$$

Plots of $\ln C/C_0$ versus time indicate first-order degradation kinetics for MIB and GSM. The first-order rate constants for MIB and GSM determined from these plots are 0.07 and 0.12 min^{-1} , respectively. These results clearly establish that ultrasonic irradiation can lead to the rapid decomposition of MIB and GSM, via a process that is effectively modeled ($R^2=0.997$, 0.999) by first order kinetics. Under argon-saturated conditions, the first order decay rates of MIB and GSM are increased to 0.16 and 0.17 min^{-1} , respectively. The increase in the degradation under argon-saturation is likely the result of increased cavitation temperatures which increases both the yield of OH radical and direct pyrolysis.

While the ultrasonic induced degradation of organic compounds is a complex process, the chemical effects of ultrasound are due to the phenomenon of acoustic cavitation. Ultrasonic irradiation promotes the growth and collapse of gas bubbles (cavitation), with the concomitant release of heat. The substrate molecules can undergo degradation by three different pathways depending on their chemical properties: i.e. hydrophobicity, volatility and Henry's law constant. These reaction pathways typically occur in specific regions: pyrolytic reactions inside the vapor regions; oxidation by hydroxyl radical in the bulk

medium; supercritical oxidation and hydrolysis in the hydrophobic interface as shown in Fig. 2. Recent studies demonstrated that Henry's law constant, the hydrophobic parameters such as water solubility and octanol- water partition coefficient have a substantial effect on the ultrasonic degradation rate (Goel et al. 2004, Wu and Ondruschka 2005). These parameters might be strongly associated with the rate of solute transfer rate from bulk liquid to cavitation bubbles during the sonochemical destruction of organic chemicals. As the vapor pressure increases, more solutes diffuse into the bubbles and become susceptible to pyrolytic decomposition upon bubble collapse.

The physical properties of MIB and GSM (Pirbazari et al. 1992) are summarized by Pirbazari in Table 1. GSM is more hydrophobic than MIB as indicated by its lower aqueous solubility and greater Kow. GSM is more volatile and more easily transferred from bulk liquid to cavitation bubbles and subsequently decomposed. The faster degradation rate of GSM compared MIB suggests that the processes in the vapor and hydrophobic interfacial regions are critical to the degradation.

To further explore the degradation pathway of MIB and GSM, •OH scavengers, terephthalate (TA) and *tert*-butyl alcohol (TBA) were added during irradiation. TA, a dianion under our experimental conditions, will reside in the bulk solution and is excluded from the interfacial and vapor phase regions. On the other hand, TBA is a volatile hydroxyl radical scavenger and is expected to scavenge the hydroxyl radicals in the vapor and interfacial regions.

The effect of hydroxyl radical scavengers on the sonolysis of MIB and GSM was determined by sonicating 10 ppb MIB in the presence of 1.0 ppm TBA or 1.0 ppm TA respectively. Neither hydroxyl radical scavengers had a pronounced affect on the degradation rate of MIB or GSM during ultrasonic irradiation as illustrated in Fig. 3. Since the degradation of MIB and GSM is not dramatically reduced in the presence of the 100-fold excess of •OH scavengers, radical mediated degradation in the bulk, interfacial, or vapor regions is insignificant. These results suggest pyrolysis in the interfacial and vapor regions are the predominant. Based on these results we propose the substrates are transferred from bulk liquid to vapor regions of the cavitation bubbles. The rate of transfer of MIB and GSM from bulk liquid to vapor phase should play a key role under ultrasonic induced degradation of MIB and GSM. The compounds may be concentrated in the vapor phase during the compression-expansion cycles of cavitation and subsequent degradation via pyrolysis upon cavitation collapse.

The degradations of MIB and GSM over a concentration range of 10 ppb – 1.0 ppm exhibit apparent first-order kinetics. The first-order rate constants did not differ significantly over this concentration range, as shown in table 2. If hydroxyl radical mediated oxidation was a significant degradation pathway, the degradation rates are expected to be dependent on the initial substrate concentration. Our observation that the rates of decay of both MIB and GSM under sonolysis follow first-order kinetics over a wide concentration range strongly suggests that decay processes are primarily a result of pyrolysis processes.

Degradation pathways of MIB and GSM

Product studies were pursued in an attempt to better understand the processes and define the degradation pathways. For pyrolytic transformations molecular eliminations can compete with simple bond scissions leading to free radicals. GC/MS analyses of the degradation products of MIB indicate the formation of two directly dehydrated products: 2-methyl-2-bornene (2) and 2-methylenebornane (3). Dehydration and rearrangement leads to 1-methylcamphene (4) which was identified under our experimental conditions. Molecular elimination of H₂O plays a key role during pyrolytic degradation of MIB. Camphor (5) was

also an observed degradation product, which can be explained by elimination of methane from MIB.

With respect to pyrolytic bond scission, dissociation of C-C bond is more likely than C-O or C-H bonds based on relative homolytic bond dissociation energies. Typical literature values of bond dissociation energies are C-H (99 kcal/mol), C-C (83 kcal/mol), C-O (86 kcal/mol), O-H (111 kcal/mol) (Streitwieser and Heathcock 1981). Significant pyrolytic scission of bonds can occur during cavitation collapse which can produce temperatures up to 5000 K and pressures to 1000 atm (Suslick et al. 1986). MIB, a tertiary alcohol, is susceptible to C-C dissociation and subsequent skeletal rearrangement. 1, 2-dimethyl-4-(prop-1-en-2-yl) cyclohex-1-ene (6) and 1, 2-dimethyl-4-(propan-2-ylidene) cyclohex-1-ene (7) were the observed products and are nicely rationalized via C-C homolytic bond scissions leading to ring opening pathways.

Dehydration reactions were also observed during the ultrasonic degradation of GSM. Compounds 9 and 10 are products of simple dehydrations. Subsequent dehydrogenations yield observed products 12 and 13. A ring opening reaction can form compound 11.

The results indicate that ultrasonic induced degradation demonstrates significant potential for the rapid removal of these compounds that present taint problems to drinking water and aquaculture industries. Since pyrolysis, not hydroxyl radical, is responsible for the degradation, we proposed that the degradation of these compounds by ultrasound would not be inhibited by hydroxyl radical scavengers presented in natural water, such as CO_3^{2-} , HCO_3^- and humic substances. Furthermore primary byproducts of MIB and GSM are alkenes which do not generally possess odor or taste problems. We plan, in future work in our laboratory, to optimize the degradation process under a variety of water quality conditions.

4. Conclusion

To the best of our knowledge, this paper is the first report on the remediation of MIB and GSM from water by ultrasonic irradiation. These compounds can be effectively and rapidly degraded by ultrasonic irradiation. Degradations of MIB and GSM exhibit apparent first-order degradation kinetics and the rate constants are constant over the concentration range of 10 ppb to 1.0 ppm. Hydroxyl radical scavenger experiments indicate pyrolysis plays the major role in the degradation. The degradation rate of GSM is higher than MIB due to higher Henry's law constant. Dehydration and open ring compounds are the main products identified by GC-MS. Ultrasonic induced degradation may be an applicable method for removal of MIB and GSM from drinking water or aquaculture industrials. However, since the general application of ultrasound for water treatment can be costly, careful evaluation of the economic feasibility is required prior to large scale treatment.

Acknowledgments

K.E.O. gratefully acknowledges support from the NIH/NIEHS (Grant S11ES11181). W.S. is supported by a Presidential Dissertation Fellowship from the University Graduate School at FIU. We thank the reviewers for valuable insight and suggestions.

References

- Adewuyi YG. Sonochemistry in Environmental Remediation. 1 Combinative and Hybrid Sonophotocatalytic Oxidation Processes for the Treatment of Pollutants in Water. *Environ Sci Technol*. 2005a; 39 (10):3409–3420. [PubMed: 15952344]

- Adewuyi YG. Sonochemistry in Environmental Remediation. 2 Heterogeneous Sonophotocatalytic Oxidation Processes for the Treatment of Pollutants in Water. *Environ Sci Technol*. 2005b; 39 (22): 8557–8570. [PubMed: 16323748]
- Bruce D, Westerhoff P, Brawley-Chesworth A. Removal of 2-methylisoborneol and geosmin in surface water treatment plants in Arizona. *J Water Supply Res T*. 2002; 51 (4):183–197.
- Burlingame GA, Dann RM, Brock GL. A Case-Study of Geosmin in Philadelphia Water. *J Am Water Works Ass*. 1986; 78 (3):56–61.
- Colussi AJ, Hung HM, Hoffmann MR. Sonochemical Degradation Rates of Volatile Solutes. *J Phys Chem*. 1999; 103:2696–2699.
- Goel M, Hu HQ, Mujumdar AS, Ray MB. Sonochemical decomposition of volatile and non-volatile organic compounds- a comparative study. *Water Res*. 2004; 38 (19):4247–4261. [PubMed: 15491671]
- Lalezary S, Pirbazari M, McGuire MJ. Evaluating Activated Carbons for Removing Low Concentrations of Taste-Producing and Odor-Producing Organics. *J Am Water Works Ass*. 1986a; 78 (11):76–82.
- Lalezary S, Pirbazari M, McGuire MJ. Oxidation of 5 Earthy Musty Taste and Odor Compounds. *J Am Water Works Ass*. 1986b; 78 (3):62–69.
- Lalezary S, Pirbazari M, McGuire MJ, Krasner SW. Air Stripping of Taste and Odor Compounds from Water. *J Am Water Works Ass*. 1984; 76 (3):83–87.
- Lawton LA, Robertson PKJ, Robertson RF, Bruce FG. The destruction of 2-methylisoborneol and geosmin using titanium dioxide photocatalysis. *Appl Catal B: Environ*. 2003; 44 (1):9–13.
- Linden, K.; Rosenfeldt, E.; Johnson, S.; Melcher, B. Direct UV and UV oxidation process for treatment of taste and odor causing compounds in water. *Proceedings - Water Quality Technology Conference*; 2002. p. 511-520.
- Nerenberg R, Rittmann BE, Soucie WJ. Ozone/biofiltration for removing MIB and geosmin. *J Am Water Works Ass*. 2000; 92 (12):85–95.
- Peller J, Wiest O, Kamat PV. Sonolysis of 2,4-Dichlorophenoxyacetic Acid in Aqueous Solutions. Evidence for OH-Radical-Mediated Degradation. *J Phy Chem A*. 2001; 105:3176–3181.
- Pirbazari M, Borow HS, Craig S, Ravindran V, McGuire MJ. Physical Chemical Characterization of Five Earthy-Musty-Smelling Compounds. *Wat Sci Tech*. 1992; 25 (2):81–88.
- Rashash DMC, Dietrich AM, Hoehn RC. FPA of selected odorous compounds. *J Am Water Works Ass*. 1997; 89 (4):131–141.
- Rosenfeldt EJ, Melcher B, Linden KG. UV and UV/H₂O₂ treatment of methylisoborneol (MIB) and geosmin in water. *J Water Supply Res T*. 2005; 54 (7):423–434.
- Song W, De La Cruz A, Rein K, O'Shea KE. Ultrasonically Induced Degradation of Microcystin-LR and -RR: Identification of Products, Effect of pH, Formation and Destruction of Peroxides. *Environ Sci Technol*. 2006; 40 (12):3941–3946. [PubMed: 16830565]
- Song W, Teshiba T, Rein K, O'Shea KE. Ultrasonically induced degradation and detoxification of microcystin-LR (Cyanobacterial toxin). *Environ Sci Technol*. 2005; 39 (16):6300–6305. [PubMed: 16173596]
- Streitwieser, JA.; Heathcock, CH. *Introduction to Organic Chemistry*. 2. Macmillan Publishing Co; London: 1981.
- Suffet IH. AWWA Taste and Odor Survey. *J Am Water Works Ass*. 1996; 88 (4):168.
- Suffet, IH.; Ho, J.; Chou, D.; Khiari, D.; Mallevialle, J.; Kawczynski, E. *Advances in Taste-and-Odor Treatment and Control*. American Water Works Association; 1995.
- Suslick KS, Hammerton DA, Cline RE. Sonochemical hot spot. *J Am Chem Soc*. 1986; 108 (18): 5641–5642.
- Watson SB, Brownlee B, Satchwill T, Hargesheimer EE. Quantitative analysis of trace levels of geosmin and MIB in source and drinking water using headspace SPME. *Water Res*. 2000; 34 (10): 2818–2828.
- Wu Z, Ondruschka B. Roles of Hydrophobicity and Volatility of Organic Substrates on Sonolytic Kinetics in Aqueous Solutions. *J Phys Chem A*. 2005; 109 (29):6521. [PubMed: 16833997]

Figure 1.

The destruction of 2-methylisoborneol and GSM using ultrasonic irradiation. Analyses were performed in triplicate, and the error bars indicate the standard deviation of the mean. Insert represents the first order plots for the degradation MIB and GSM.

Figure 2.
Schematic illustration of cavitating bubble caused by ultrasonic irradiation.

Figure 3. Degradation of MIB (a) and GSM (b) in aqueous solution and in the presence of hydroxyl radical scavengers TA and TBA. Analyses were performed in triplicate, and the error bars indicate the standard deviation of the mean.

Scheme 1.

Proposed products from sonolysis of MIB in aqueous saturation based on GC/MS analyses.

Scheme 2.

Proposed products from sonolysis of GSM in aqueous saturation based on GC/MS analyses.

Table 1

Physical properties of MIB and GSM (Pirbazari et al. 1992)

Parameter	MIB	GSM
Structure
Boiling Point (°C)	196.7	165.1
Aqueous solubility (mg/L)	194.5	150.2
Kow	3.13	3.7
Henry's Law Constant	5.76×10^{-5}	6.66×10^{-5}

Table 2

First-order reaction rate constants and correlation coefficients R^2 for the sonolysis of MIB and GSM at different initial concentrations.

MIB	k (min^{-1})	R^2	GSM	k (min^{-1})	R^2
10 ppb	0.070 ± 0.010	0.9969	10 ppb	0.12 ± 0.009	0.9991
100 ppb	0.067 ± 0.008	0.9973	100 ppb	0.12 ± 0.009	0.9932
1.0 ppm	0.063 ± 0.007	0.9916	1.0 ppm	0.11 ± 0.007	0.9974