

Treatment of Volatile Organic Chemicals on the EPA Contaminant Candidate List Using Ozonation and the O_3/H_2O_2 Advanced Oxidation Process

WEI R. CHEN,[†] CHARLES M. SHARPLESS,[§]
KARL G. LINDEN,[§] AND
I. H. (MEL) SUFFET*,^{†,‡}

Department of Environmental Health Sciences, Environmental Science and Engineering Program, University of California at Los Angeles, Los Angeles, California 90095, and Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina 27708

Seven volatile organic chemicals (VOCs) on the EPA Contaminant Candidate List together with 1,1-dichloropropane were studied for their reaction kinetics and mechanisms with ozone and OH radicals during ozonation and the ozone/hydrogen peroxide advanced oxidation process (O_3/H_2O_2 AOP) using batch reactors. The three aromatic VOCs demonstrated high reactivity during ozonation and were eliminated within minutes after ozone addition. The high reactivity is attributed to their fast, indirect OH radical reactions with $k_{OH,M}$ of $(5.3\text{--}6.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Rates of aromatic VOC degradation are in the order 1,2,4-trimethylbenzene > *p*-cymene > bromobenzene. This order is caused by the selectivity of the direct ozone reactions ($k_{O_3,M}$ ranges from 0.16 to $304 \text{ M}^{-1} \text{ s}^{-1}$) and appears to be related to the electron-donating or -withdrawing ability of the substituent groups on the aromatic ring. The removal rates for the five aliphatic VOCs are much lower and are in the order 1,1-dichloropropane > 1,3-dichloropropane > 1,1-dichloroethane > 2,2-dichloropropane > 1,1,2,2-tetrachloroethane. The second-order indirect rate constants for the aliphatic VOCs range from 0.52×10^8 to $5.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The relative stability of the carbon-centered intermediates seems to be related to the relative reactivity of the aliphatic VOCs with OH radicals. Except for 1,3-dichloropropane, ozonation and the O_3/H_2O_2 AOP are not effective for the removal of other aliphatic VOCs. Bromide formation during the ozonation of bromobenzene indicates that bromate can be formed, and thus, ozonation and O_3/H_2O_2 AOP may not be suitable for the treatment of bromobenzene.

Introduction

The ozonation and ozone/hydrogen peroxide advanced oxidation process (O_3/H_2O_2 AOP) have been used worldwide

as effective ways to achieve degradation of many contaminants during drinking water treatment. The knowledge of the effect of these processes on the emerging contaminants such as those on the U.S. EPA's Drinking Water Contaminant Candidate List (CCL and CCL2) (1, 2) is essential to the EPA's regulatory strategies on these chemicals. Information such as reaction rate constants and byproducts formation can be used as important factors in determining whether ozonation and O_3/H_2O_2 AOP are suitable for the treatment of a certain CCL pollutant.

Seven volatile organic chemicals (VOCs) that are on both the CCL and the CCL2 (1,1,2,2-tetrachloroethane, 1,1-dichloroethane, 1,3-dichloropropane, 2,2-dichloropropane, 1,2,4-trimethylbenzene, bromobenzene, and *p*-cymene), together with 1,1-dichloropropane, are evaluated for their treatability during ozonation and the O_3/H_2O_2 AOP. According to structure similarities and analytical methods, they are divided into two groups: the five chlorinated aliphatic compounds (i.e. 1,1,2,2-tetrachloroethane, 1,1-dichloroethane, 1,1-dichloropropane, 1,3-dichloropropane, and 2,2-dichloropropane) and the three substituted benzene compounds (i.e. 1,2,4-trimethylbenzene, bromobenzene, and *p*-cymene). In general, the aliphatic VOCs are not easily degraded by ozonation because of the chlorine substitutions and the lack of unsaturated bonds. Rate constants of direct ozonation reaction ($k_{O_3,M}$) of these chlorinated aliphatic VOCs are usually too small to be accurately measured (3); however, they are expected to react with OH radicals during ozonation at drinking water plants.

On the other hand, the reactions between aromatic VOCs and O_3 are highly electrophilic and selective (4). Aromatic rings with electron donor substituent groups (e.g., OH and CH_3) show higher reactivity toward ozone, whereas aromatic rings with electron-withdrawing substituents (e.g. Cl and NO_2) have lower ozone reactivity. Although a few second-order rate reaction constants with OH radicals ($k_{OH,M}$) have been measured (5), direct and indirect reaction rate constants ($k_{O_3,M}$ and $k_{OH,M}$) for most of these compounds remain unknown.

In this study, relative reactivities of the VOCs during ozonation were determined using batch-reactor ozonation (and O_3/H_2O_2 AOP) under ozone dosage, ozone residual, and contaminant concentration conditions similar to those in the conventional ozonation process. Second-order reaction rate constants of the VOCs with ozone and OH radicals ($k_{O_3,M}$ and $k_{OH,M}$) were measured in the ozonation and O_3/H_2O_2 AOP. Results of $k_{OH,M}$ were also confirmed using the UV/ H_2O_2 process. Reaction mechanisms and byproducts formation are discussed.

Methods and Materials

Reagents and Solutions. All chemicals were reagent or analytical grade and were used as received without further purification. VOCs of highest purity were obtained from Chem Service, Inc (West Chester, PA) and Sigma-Aldrich Co. (Milwaukee, WI). Due to the high volatility and the low water solubility of the VOCs, a 100 mM VOC primary stock solution was first prepared in dichloromethane (DCM) because DCM is relatively less reactive during ozonation ($k_{O_3} < 0.1 \text{ M}^{-1} \text{ s}^{-1}$) (4) and $k_{OH,DCM} = 9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (6)) than most other solvents (e.g., methanol and acetone). A 50 μM water stock solution was then made for spiking VOCs into the reactor to avoid loss of VOCs by volatilization to headspace during stirring if the DCM stock solution was used. Although DCM reacts slowly with OH radicals, the approach was deemed appropriate because only relative reactivity and competition kinetics were measured while keeping DCM to a minimal

* Corresponding author phone: (310)206-8230; fax: (310)206-3358; e-mail: msuffet@ucla.edu.

[†] Department of Environmental Health Sciences, University of California at Los Angeles.

[§] Department of Civil and Environmental Engineering, Duke University.

[‡] Environmental Science and Engineering Program, University of California at Los Angeles.

amount (i.e., 30 μM in the final reaction solution). In the experiments of $k_{\text{O}_3, \text{M}}$ measurement for which absolute rates were needed, VOCs were prepared directly from the pure compounds. A water bath ultrasonic system was used to facilitate dissolving.

Aqueous ozone stock solutions were prepared by continuously bubbling ozone produced by an oxygen-feed (oxygen >99%) ozonator (Osmonics OREC V Series, Phoenix, AZ) into Milli-Q water chilled in an ice–water bath (7). The concentration of ozone stock solution was ~ 35 mg/L. The pHs of all experiments were adjusted by adding orthophosphate buffers ($\text{H}_3\text{PO}_4/\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$) so that the total phosphate concentration in the final solution was 0.02 M.

Experiments. All experiments were performed in pH-buffered Milli-Q nanopure water at room temperature (22 $^\circ\text{C}$).

Ozonation and $\text{O}_3/\text{H}_2\text{O}_2$ AOP Experiments. Batch ozonation experiments were carried out using a 1-L dispenser system similar to that introduced by Hoigne and Bader (8). In a slow stirring reactor, an appropriate amount of Milli-Q water, buffer stock solution, organic stock solution, and aqueous ozone stock solution were successively added to satisfy the initial experimental conditions. At different time intervals, while one sample (10 mL) was dispensed into an indigo solution for residual aqueous ozone measurement, another sample (10 mL) was quenched by 1 mL of Na_2SO_3 solution (6 g/L) for measuring residual VOC concentrations. To avoid VOC loss due to volatilization to headspace, the samples for residual VOC measurement were filled to almost overflow so that when they were capped, no headspace was left. Samples were refrigerated for no more than 2 days before analysis. Both ozone and VOC kinetics were monitored for 40 min at pH 8.2, a usual drinking water pH. The initial concentrations of VOCs were ~ 0.2 μM (20–30 $\mu\text{g/L}$), whereas the ozone dosages applied were between 1.7 and 2.1 mg/L. The ozone residual was ~ 0.5 mg/L after 20 min of treatment and ~ 0.3 mg/L after 40 min of ozonation. This represents an approximate approach for an actual conventional ozonation process in which initial O_3 dosages are usually between 1 and 5 mg/L and 0.1–0.3 mg/L of O_3 residual is required after 20 min of treatment. An ozone blank experiment was conducted under similar conditions but without the addition of the VOCs and DCM solvent. A DCM control test was performed under the same ozonation and DCM concentration conditions as stated above but without the addition of the VOCs. Headspace addition experiments to test VOC loss during the experiments were performed under the same conditions by applying the same amount of Milli-Q water in lieu of the ozone stock solutions. During all of the experiments, the loss of VOCs due to volatilization caused by headspace addition during sampling was insignificant after applying methods such as limiting stirring, minimizing headspace, and headspace loss.

In the $\text{O}_3/\text{H}_2\text{O}_2$ AOP experiments, appropriate amounts of buffered water, VOC stock solution, and H_2O_2 solutions were added to four 250-mL amber bottles to achieve the same initial conditions. Then, four ozone doses (0, 2, 5, and 10 mg/L) were applied, and the residual VOCs were measured after the reactions were completed, that is, when the ozone was depleted. The applied H_2O_2 concentration was 0.1 mM. The initial molar ratios of $\text{H}_2\text{O}_2/\text{O}_3$ were 2.4, 0.96, and 0.48 for ozone doses of 2, 5, and 10 mg/L, respectively.

Determination of Rate Constants with O_3 and OH Radicals. The direct rate constants of the VOCs with ozone ($k_{\text{O}_3, \text{M}}$) were determined in a 1-L dispenser system (same as in the ozonation experiments) for all aromatic VOCs by both the ozone consumption method and the solute consumption method under pseudo-first-order conditions. pH 2 and 10 mM tertiary butanol were used in the experiments to eliminate any OH radical reactions. The ozone consumption

method involves determination of the ozone consumption rate constant (k_{O_3}) according to eq 1 by monitoring ozone decay while keeping pollutant concentration ($[\text{M}]_0$) constant and in excess ($7\times - 15\times$).

$$\ln\left(\frac{[\text{O}_3]_t}{[\text{O}_3]_0}\right) = -k_{\text{O}_3}[\text{M}]_0 t \quad (1)$$

Then, $k_{\text{O}_3, \text{M}}$ can be calculated by k_{O_3}/η , where η , the stoichiometric factor, is 2.5 for aromatic compounds (4). Rate constants were corrected by subtracting the rate constant of ozone loss in a blank experiment without VOCs but at the same pH and *tert*-butyl alcohol concentration. The blank was usually negligible except for slowly reacting compounds. The solute consumption methods measures $k_{\text{O}_3, \text{M}}$ directly by monitoring VOC decay over time under constant (usually $\leq 8\%$ variation) and excessive ozone concentrations ($213\times - 646\times$) by the following equation.

$$\ln\left(\frac{[\text{M}]_t}{[\text{M}]_0}\right) = -k_{\text{O}_3, \text{M}}[\text{O}_3] t \quad (2)$$

The indirect rate constants of VOCs with OH radicals ($k_{\text{OH}, \text{M}}$) were determined by competition kinetics using three methods: ozone alone, $\text{O}_3/\text{H}_2\text{O}_2$, and UV/ H_2O_2 . The reference compounds were 1,2,4-trimethylbenzene for the aromatic VOCs and 1,1-dichloroethane for the aliphatic VOCs. In ozone alone, $k_{\text{OH}, \text{M}}$ was calculated using eqs 3 and 4 from the predetermined overall reaction rate constants (k) (in the aforementioned ozonation experiments) as well as the $k_{\text{O}_3, \text{M}}$ values determined above and by applying the R_{ct} concept (9) (please refer to the Supporting Information for more explanations).

$$\ln\left(\frac{[\text{M}]_t}{[\text{M}]_0}\right) = -k \int_0^t [\text{O}_3] dt \quad (3)$$

$$k = k_{\text{OH}, \text{M}} R_{\text{ct}} + k_{\text{O}_3, \text{M}} \quad (4)$$

In the $\text{O}_3/\text{H}_2\text{O}_2$ method, eq 5 was applied to the previous $\text{O}_3/\text{H}_2\text{O}_2$ experiment for the calculation of $k_{\text{OH}, \text{M}}$,

$$k_{\text{OH}, \text{M}} = k_{\text{OH}, \text{R}} \times \ln\left(\frac{[\text{M}]_t}{[\text{M}]_0}\right) / \ln\left(\frac{[\text{R}]_t}{[\text{R}]_0}\right) \quad (5)$$

where R is the reference compound.

A sealed batch reactor (8 L) constructed of nickel-plated stainless steel was used for UV/ H_2O_2 experiments. It houses one 500-W medium-pressure Hg lamp (Hanovia-U.K.) in a quartz sleeve (GE type 214) centered in the reactor and has a stainless steel shutter that can be interposed between the lamp and the quartz sleeve. The outer wall of the reactor is hollow to allow cooling water to recirculate and moderate the reaction temperature. During the experiments, the solution was stirred with an impeller-type mixer attached via a Teflon bearing adapter on top. Stock VOC solutions were added via syringe through a septum in the top reagent port, which was also used for sampling. In a typical experiment, contaminants were spiked, followed by H_2O_2 , and the solution was allowed to mix for 10 min. A sample was then taken for initial concentration analysis, and then the experiment was commenced. Initial VOC concentrations were 0.2 μM , and H_2O_2 concentrations were 0, 25, and 50 mg/L. Samples were taken at time intervals sufficient to achieve UV fluences of 0, 330, 660, and 1000 mJ cm^{-2} (200–300 nm). To all samples, 0.2 mg/L catalase was added to quench residual H_2O_2 (10). The UV fluence rate was estimated by using 1 μM *N*-nitrosodimethylamine as an actinometer in separate experiments (11). The $k_{\text{OH}, \text{M}}$ was then determined

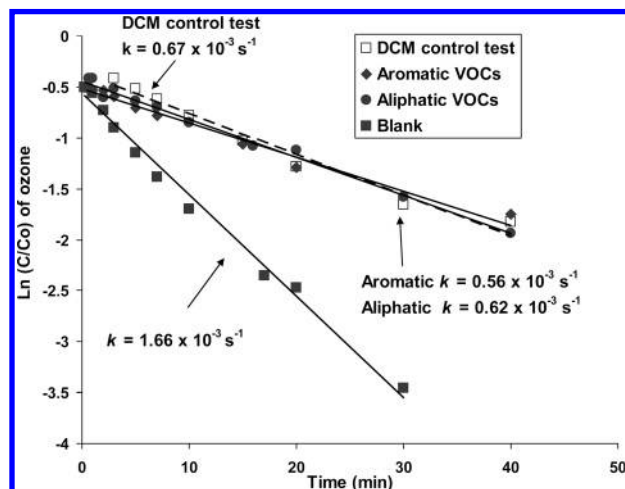


FIGURE 1. Ozone decay during the ozonation of aromatic and aliphatic VOCs at pH 8.2. $[O_3]_0 = 1.7\text{--}1.8$ mg/L. See Figures 2 and 3 for initial VOC concentrations. DCM control test (dashed line, with $30\text{ }\mu\text{M}$ DCM, $[O_3]_0 = 1.8$ mg/L) and ozone blank at $[O_3]_0 = 1.6$ mg/L are shown for comparison.

by averaging the rates of VOC degradation relative to the reference compounds at the two H_2O_2 levels (25 and 50 mg/L) by using eq 5.

Analytical Methods. Dissolved residual ozone was measured using the indigo method (12). A Perkin-Elmer Lambda 20 UV/visible spectrophotometer (Norwalk, CT) was used for the measurement of residual indigo absorbance with the cell path length at 1 or 5 cm. An HP 7695 purge and trap concentrator combined with a 6890 GC/MSD and a ChemStation system (Agilent, Palo Alto, CA) were used for the VOC analyses based upon EPA method 524.2. Purge and trap conditions were purge for 10 min, dry purge for 3 min, desorb for 1 min, and final bake for 8 min. A J & W Scientific (Folsom, CA) DB-624 capillary column ($30\text{ m} \times 0.25\text{ mm} \times 1.4\text{ }\mu\text{m}$) was used. The GC temperature programming was set as follows: initial temperature at $35\text{ }^\circ\text{C}$, hold for 4 min, ramp at $15\text{ }^\circ\text{C}/\text{min}$ to $200\text{ }^\circ\text{C}$, then hold for 0.1 min. Carrier gas (helium) was at a flow rate of $1\text{ mL}/\text{min}$; the injector temp was set at $200\text{ }^\circ\text{C}$. The MS conditions were set as follows: scan $25\text{--}260\text{ AMU}$ at $5.87\text{ scans}/\text{s}$; MS source temp at $230\text{ }^\circ\text{C}$; MS quad temp at $150\text{ }^\circ\text{C}$; t-line temp at $260\text{ }^\circ\text{C}$; and electron energy at 69.9 V . Standard fortification solutions for EPA method 524.2 were used to provide surrogates and internal standard for the VOC analyses. Bromide concentration in solution was determined using a Dionex-120 ion chromatograph (Sunnyvale, CA) with a $25\text{-}\mu\text{L}$ injection loop. Samples were run using an eluent containing 9 mM sodium carbonate at $1.0\text{ mL}/\text{min}$ through an AS9-HC $4 \times 250\text{ mm}$ analytical column and a $4 \times 50\text{ mm}$ AG9-HC guard column and were detected using a CS4 model conductivity detector with a DS4-1 stabilizer.

Results and Discussion

Ozonation and O_3/H_2O_2 AOP Experiments. Ozone kinetics followed first-order during all ozonation experiments (see Figure 1). The rate of ozone decay in the ozone blank experiment ($1.66 \times 10^{-3}\text{ s}^{-1}$) is significantly greater than that in the DCM control test ($0.67 \times 10^{-3}\text{ s}^{-1}$), indicating DCM solvent inhibits ozone decomposition by acting as an OH radical scavenger. The rates of ozone decay during the ozonation of both aromatic ($0.56 \times 10^{-3}\text{ s}^{-1}$) and aliphatic VOCs ($0.62 \times 10^{-3}\text{ s}^{-1}$) are very similar to that in the DCM control test. The similarity indicates that the addition of the VOCs during ozonation does not change the ozone/OH radical balance in a system with DCM. The low VOC concentrations have caused insignificant consumption of

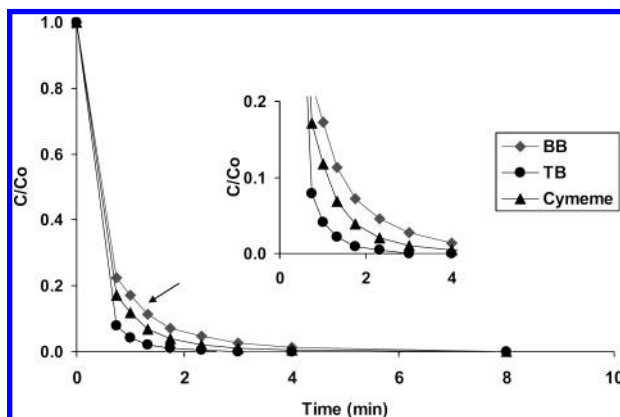


FIGURE 2. Ozonation of aromatic VOCs at pH 8.2. BB = bromobenzene, TB = 1,2,4-trimethylbenzene, and Cymene = *p*-cymene. $[O_3]_0 = 1.76\text{ mg}/\text{L}$, $[BB]_0 = 227\text{ nM}$, $[TB]_0 = 221\text{ nM}$, and $[Cymene]_0 = 132\text{ nM}$. ($\text{nM} = 10^{-9}\text{ M}$) The inner diagram amplifies the points of the outer diagram.

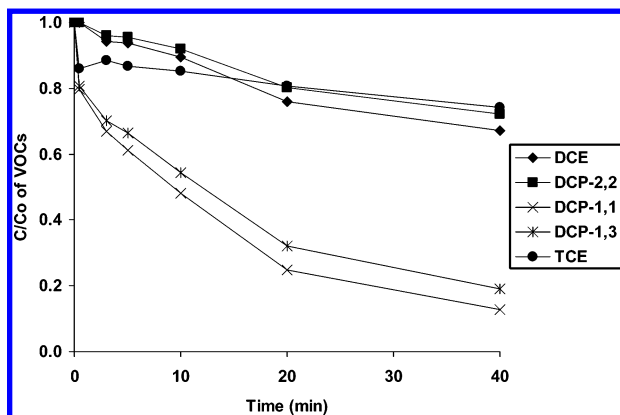


FIGURE 3. Ozonation of aliphatic VOCs at pH 8.2. $[O_3]_0 = 1.73\text{ mg}/\text{L}$. DCE = 1,1-dichloroethane, $[DCE]_0 = 146\text{ nM}$; DCP-2,2 = 2,2-dichloropropane, $[DCP-2,2]_0 = 113\text{ nM}$; DCP-1,1 = 1,1-dichloropropane, $[DCP-1,1]_0 = 186\text{ nM}$; DCP-1,3 = 1,3-dichloropropane, $[DCP-1,3]_0 = 206\text{ nM}$; and TCE = 1,1,2,2-tetrachloroethane, $[TCE]_0 = 180\text{ nM}$.

ozone and OH radicals; however, since OH radical production is hindered by the addition of DCM, slower degradation kinetics of the VOCs is expected, since most of the VOCs in this study are much more reactive toward OH radicals than ozone. Therefore, DCM is not competing with the VOCs for ozone or OH radicals but slows down the VOC kinetics by inhibiting the decomposition of ozone into the more reactive OH radicals. However, the slowed-down kinetics allows us to follow degradation kinetics for fast reacting chemicals, such as the aromatic VOCs. In real ozonation treatment of drinking water, there are always large amounts of background impurities in the water in forms such as dissolved organic matter ($2\text{--}12\text{ mg}/\text{L}$), carbonate, and bicarbonate ions ($50\text{--}250\text{ mg}/\text{L}$ as CaCO_3). These impurities can often act in a fashion similar to that of DCM to hinder the degradation of target chemicals.

The kinetics of VOCs differs in the ozonation process. Rates of aromatic VOC degradation are significantly greater than the degradation rates of the aliphatic VOCs (compare Figure 2 with Figure 3). All three aromatic VOCs are completely removed after 8 min of ozonation. The relative reactivity of aromatic VOCs during ozonation is in the order $1,2,4\text{-trimethylbenzene} > p\text{-cymene} > \text{bromobenzene}$. Because of the high removal rates of the aromatic VOCs by ozone alone, the use of H_2O_2 combined with ozone as AOP seems unnecessary in a relatively clean water matrix system. In contrast, none of the aliphatic VOCs is completely removed

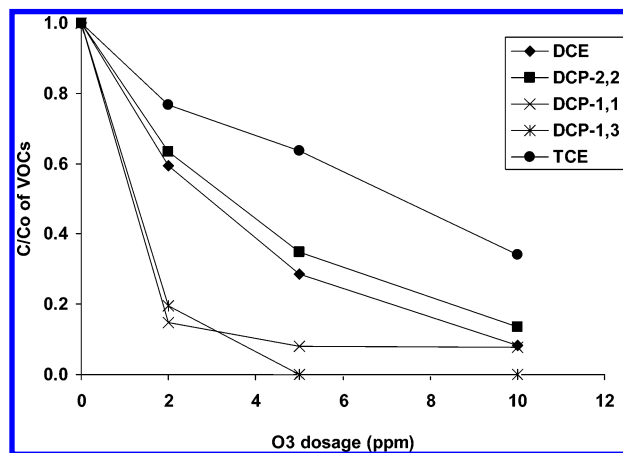


FIGURE 4. Removal of aliphatic VOCs as a function of applied ozone dose by O_3/H_2O_2 AOP. pH = 8.2, $[H_2O_2]_0 = 0.1$ mM, $[DCE]_0 = 103$ nM, $[DCP-2,2]_0 = 98$ nM, $[DCP-1,1]_0 = 101$ nM, $[DCP-1,3]_0 = 114$ nM, and $[TCE]_0 = 152$ nM.

during the ozonation experiments. Their removal rates vary at 40 min reaction time and are in the order 1,1-dichloropropane (87%) > 1,3-dichloropropane (81%) > 1,1-dichloroethane (33%) > 2,2-dichloropropane (28%) > 1,1,2,2-tetrachloroethane (26%). The difference between the chemical decay rates of the two groups of VOCs is expected because aromatic compounds are more reactive toward ozone and OH radicals than the halogenated aliphatic compounds are due to the unsaturation of the benzene ring. Explanations of the order of removal efficiency are discussed later when rate constants for both direct ozone reactions and indirect radical reactions are evaluated.

When the O_3/H_2O_2 AOP process is applied to aliphatic VOCs for further chemical removal, all but 1,3-dichloropropane fail to be completely removed, even at a high ozone dose of 10 mg/L (see Figure 4), indicating that ozonation and O_3/H_2O_2 AOP processes are not effective for the removal of aliphatic VOCs (except for 1,3-dichloropropane) from drinking water.

Determination of Rate Constants with O_3 and OH Radicals. *Aromatic VOC.* Rates of direct reactions for aromatic VOCs ($k_{O_3,M}$) (Table 1) vary over 3 orders of magnitude. $k_{O_3,M}$ values measured by the ozone consumption method and the solute consumption method agree well for 1,2,4-trimethylbenzene and *p*-cymene, but they differ significantly for bromobenzene. The difference may be due to some additional transformations of solutes by secondary radicals (but not OH radicals because they are quenched by tertiary butanol); however, the interfering reactions are less significant when the direct ozone reactions become faster. The implication is that the ozone consumption method is more accurate than the solute consumption method, especially when $k_{O_3,M}$ is small. However, when only the solute consumption method is possible (e.g., chemicals with low solubility), only an upper limit of $k_{O_3,M}$ is obtained for slow ozone reactions. $k_{OH,M}$ values obtained in the ozonation experiments (calculated using the R_{ct} model proposed by Elovitz and von Gunten (9)) agree well with the $k_{OH,M}$ obtained in UV/ H_2O_2 experiments, which is a strong support of the R_{ct} model. Please refer to the Supporting Information for detailed calculations.

The measured $k_{O_3,M}$ values of aromatic VOCs are in the order 1,2,4-trimethylbenzene > *p*-cymene > bromobenzene. This order is the same as in the previous ozonation experiments and can be explained by the linear free energy relationship (LFER) using the $\rho\sigma$ -eq, in which the logarithm of the rate constants of chemical reactions can be expressed by a linear relationship with the substituent constant (σ) of the substituent groups on the aromatic ring (4). Hoigne and

Bader (4) have found a strong negative response (i.e., highly selective reactions) of the substitution groups on the reaction rates, indicating the electrophilic nature of the direct ozone reactions. Therefore, aromatic compounds with a higher delocalization of electrons may exhibit a higher reactivity toward ozone.

Both 1,2,4-trimethylbenzene and *p*-cymene have multiple alkyl substitution groups on the benzene rings (see structures in Table 1). Alkyl groups donate electrons to the benzene ring by hyperconjugation and, thus, increase the reactivity of the aromatic ring (σ is negative) (13). 1,2,4-Trimethylbenzene has three sites on the benzene ring substituted by methyl groups and, thus, provides a higher delocalization of electrons than *p*-cymene, which has only two sites substituted by alkyl groups on the benzene ring. Therefore, the rate of reaction is greater for 1,2,4-trimethylbenzene than for *p*-cymene. Conversely, bromobenzene has halogens that are electronegative, and the electron density on the aromatic ring is decreased by the inductive effect (13). Therefore, bromobenzene showed lowest reactivity among the three aromatic VOCs in its reaction with ozone.

However, the indirect OH reactions are fast and non-selective, demonstrated by high (on the order of 10^9) and similar $k_{OH,M}$ values (see Table 1). Therefore, the fast elimination of aromatic VOCs in the ozonation reaction is mainly attributed to the fast indirect OH reactions, whereas the order of elimination is caused by the selectivity of the direct ozone reactions.

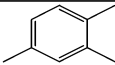
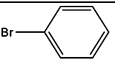
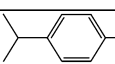
Aliphatic VOCs. The aliphatic VOCs on the CCL are not easily degraded by ozone because of their multiple chlorine substitutions and their lack of unsaturated bonds. $k_{O_3,M}$ was not obtained because the rate constants of these compounds are too small ($<10^{-2} \sim 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) to be accurately measured (3). $k_{OH,M}$ values measured by ozonation (ozone alone), O_3/H_2O_2 AOP, and UV/ H_2O_2 AOP are generally in excellent agreement (see Table 2). This indicates that reaction with the OH radical is the dominant mechanism for these processes.

The $k_{OH,M}$ for aliphatic VOCs is considerably lower (1–2 orders of magnitude) than that of the aromatic VOCs. Because of the extremely low rate of direct ozone reactions of these chemicals, the indirect OH radical reactions are expected to play a major role in the oxidation of these chemicals. The OH radicals react with organic matter by either adding to a C=C double bond or by abstracting a carbon-bound H atom (14). Generally, the addition to double bonds is faster than the H abstraction reaction. Since none of the aliphatic VOCs in this study has a C=C bond, the only mode of reaction for these compounds with OH radicals is H-atom abstraction. A previous study showed that although the OH radical is relatively nonselective toward C–H bonds, it is least reactive with aliphatic polyhalogenated compounds (6).

The $k_{OH,M}$ values for aliphatic VOCs are in the order 1,1-dichloropropane > 1,3-dichloropropane > 1,1-dichloroethane > 2,2-dichloropropane > 1,1,2,2-tetrachloroethane. The most chlorinated VOC (1,1,2,2-tetrachloroethane) showed the lowest reactivity during ozonation. Several other researchers using various methods for generating OH radicals also noted decreasing rates of reaction of aliphatic halogenated compounds with increasing halogenation (6, 14–17). This is thought to be due to the higher potential for H abstraction reactions when more H atoms are available (15).

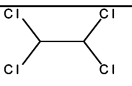
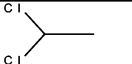
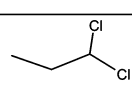
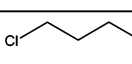
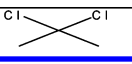
Despite of the relative nonselectivity and the diffusion-controlled reaction rate, there is some degree of selectivity of the OH radical reaction, as demonstrated by different reaction rates of the aliphatic VOCs. The selectivity can be attributed to the stability of the intermediates (e.g., the carbon-centered free radicals) or the amount of bond dissociation energy of bonds making or breaking. The more

TABLE 1. Second-Order Reaction Rate Constants $k_{O_3,M}$ and $k_{OH,M}$ for Aromatic VOCs. (unit = $M^{-1} s^{-1}$)

Chemical Names	Structures	$k_{O_3,M}^{a,c}$ (O ₃ Consump)	$k_{O_3,M}^{b,e}$ (Solute Consump)	$k_{OH,M}^c$ (Ozonation)	$k_{OH,M}^{d,e}$ (UV/H ₂ O ₂)
1,2,4-Trimethylbenzene		304	238±17	6.2 × 10 ⁹ (ref) ^f	
Bromobenzene		0.16±0.04	9.8±1.6	5.3×10 ⁹ (4.4-9)×10 ⁹ ^f	(5.9±0.4)×10 ⁹
p-isopropyl-toluene (p-cymene)		47±13	48±0.3	6.6 × 10 ⁹	(5.6±0.3)×10 ⁹

^a $k_{O_3,M}$ measured by ozone-consumption method. ^b $k_{O_3,M}$ measured by solute-consumption method. ^c $k_{OH,M}$ measured in ozonation experiments. ^d $k_{OH,M}$ measured in UV/H₂O₂ experiments. ^e Mean ± 1.96 × (standard error) indicating 95% confidence level. Two experiments were performed where the standard errors were reported. ^f Values from (5).

TABLE 2. Second-order Rate Constants for Indirect OH Radical Reactions ($k_{OH,M}$) for aliphatic VOCs. (unit = $M^{-1} s^{-1}$)

Chemical Names	Structures	O ₃ alone (× 10 ⁸) ^b	O ₃ /H ₂ O ₂ (× 10 ⁸)	UV/H ₂ O ₂ (× 10 ⁸) ^b
1,1,2,2-Tetrachloro-ethane		0.52 ± 0.02	0.55	1.4 ^a
1,1-Dichloro-ethane		1.3 (reference compound) ^c		
1,1-Dichloro-propane		5.5 ± 1.0	4.77	5.8 ± 1.3
1,3-Dichloro-propane		4.45 ± 0.69	4.07	4.6 ± 1.3
2,2-Dichloro-propane		1.09 ± 0.03	1.06	0.92 ± 0.74

^a $k_{OH,M}$ determined only from 50 mg/L H₂O₂ data because not enough reaction was observed with 25 mg/L H₂O₂. ^b Mean ± 1.96 × (standard error) indicating 95% confidence level. Two experiments were performed where the standard errors were reported. ^c Values from (5).

TABLE 3. Carbon-Centered Intermediates for Aliphatic VOCs

aliphatic VOCs	secondary radicals	primary radicals	primary radicals with Cl group
1,1-dichloropropane	CHCl ₂ (·CH)CH ₃ [2] ^a	CHCl ₂ CH ₂ (·CH ₂) [3]	(·CCl ₂)CH ₂ CH ₃ [1]
1,3-dichloropropane	CH ₂ Cl(·CH)CH ₂ Cl [2]		CH ₂ ClCH(·CHCl) [4]
2,2-dichloropropane		CH ₃ CCl ₂ (·CH ₂) [6]	
1,1-dichloroethane		CHCl ₂ (·CH ₂) [3]	CH ₃ (·CCl ₂) [1]
1,1,2,2-tetrachloroethane			CHCl ₂ (·CCl ₂) [2]

^a Numbers in the brackets indicate number of possible free radicals at this carbon center through H-atom abstraction reactions.

stable intermediate is due to the lower energy it needs for bond breaking. The stabilities of alkyl radicals are in the order tertiary > secondary > primary > methyl. Alkyl radicals have odd electrons and, thus, are electron-deficient. Electron-releasing alkyl groups attached to a carbon can provide a stabilization effect, and the more alkyl groups that are attached to this carbon, the more stable the radical is. On the other hand, the presence of an electron-withdrawing Cl group attached or adjacent to the carbon can destabilize the radical intermediate (13).

1,1-Dichloropropane, 1,3-dichloropropane, and 2,2-dichloropropane are isomers that have exactly the same number of C, H and Cl atoms; however, depending on the different Cl positions on the carbon chain, the stabilities of carbon-centered radical intermediates (see Table 3) are different, and thus, the rates of relevant radical reactions

differ. Both 1,1-dichloropropane and 1,3-dichloropropane can form two secondary carbon-centered free radicals, whereas 1,1-dichloropropane can form 3 more stable primary radicals (without a Cl group attached) than 1,3-dichloropropane. Therefore, 1,1-dichloropropane showed slightly higher reactivity in ozonation than 1,3-dichloropropane. On the other hand, 2,2-dichloropropane cannot form any secondary carbon radicals, and the six primary radicals it formed are all destabilized by the two Cl groups on the adjacent carbon. Therefore, 2,2-dichloropropane is significantly less reactive than the other two dichloropropane isomers.

Both 1,1-dichloroethane and 1,1,2,2-tetrachloroethane are chlorinated ethanes. The lower reactivity of 1,1,2,2-tetrachloroethane is caused by its high levels of chlorination, as well as its highly destabilized (by multiple adjacent Cl groups)

carbon-centered radical intermediates. It is generally difficult to compare the rates of chemicals with different carbon numbers; however, 1,1-dichloroethane and 2,2-dichloropropane can form similar carbon-centered intermediates. That fact that 2,2-dichloropropane is less reactive may be caused by the steric hindrance of the more bulky CH₃ group than the single H atom for 1,1-dichloroethane on the adjacent C of the primary radical intermediate.

Ozonation Byproducts. No ozonation byproducts were observed by purge-and-trap GC/MS, indicating that the VOC ozonation byproducts are not volatile. The reaction byproducts of the oxidation of aromatic compounds and chlorinated alkanes with ozone are not well-studied in the literature (18). The major product of benzene with the OH radical is phenol (19), and the major products of chlorobenzene under O₃/H₂O₂ AOP conditions are 2-chlorophenol and 4-chlorophenol (20), both indicating that the OH attack takes place on the C–H bond through H abstraction. Therefore, the major ozonation product for bromobenzene is expected to be bromophenol. Elevated bromide (Br[−]) concentration (from 0 to 777 μg/L) was observed during bromobenzene ozonation at an initial bromobenzene concentration of 65 μM and an initial ozone concentration of 2 mg/L. Subsequent bromate formation is very likely and may cause ozonation and O₃/H₂O₂ AOP unsuitable for bromobenzene, even though it is kinetically favorable. In the case of 1,2,4-trimethylbenzene and *p*-cymene, alternative OH attacks may also occur on the C–H bond on the methyl and *tert*-butyl groups in addition to those on the benzene rings.

For the volatile VOCs (chlorinated alkanes), the primary byproducts with OH radicals are expected to be alcohols through H abstraction mechanism. All of these byproducts are relatively polar and nonvolatile and, therefore, cannot be detected by P&T GC/MS. Byproducts may be ozone-reactive and are further oxidized.

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Supporting Information Available

Additional data and explanations for the calculation of $k_{O_3,M}$ and $k_{OH,M}$ values in Tables 1 and 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) U.S. Environmental Protection Agency. Announcement of the Drinking Water Contaminant Candidate List. *Fed. Regist.* **1998**, 63 (40), 10273.
- (2) U.S. Environmental Protection Agency. Drinking Water Contaminant Candidate List 2; Final Notice. *Fed. Regist.* **2005**, 70 (38), 9071–9077.
- (3) Yao, C. C. D.; Haag, R. W. Rate constants for direct reactions of ozone with several drinking water contaminants. *Water Res.* **1991**, 25, 761–773.
- (4) Hoigné, J.; Bader, H. Rate constants of reactions of ozone with organic and inorganic compounds in water. I. Nondissociating organic compounds. *Water Res.* **1983**, 17, 173–183.
- (5) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, W. P. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, 17, 513–886. Internet: <http://allen.rad.nd.edu> or <http://kinetics.nist.gov/solution/index.php>.
- (6) Haag, W. R.; Yao, C. C. D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ. Sci. Technol.* **1992**, 26, 1005–1013.
- (7) Hoigné, J.; Bader, H. Ozonation of water: oxidation-competition values of different types of waters in Switzerland. *Ozone Sci. Eng.* **1979**, 1, 357–372.
- (8) Hoigné, J.; Bader, H. Characterization of water quality criteria for ozonation processes. Part II: lifetime of added ozone. *Ozone Sci. Eng.* **1994**, 16, 121–134.
- (9) Elovitz, M. S.; von Gunten, U. Hydroxyl radical/ozone ratios during ozonation processes. I. The R_{Cl} concept. *Ozone Sci. Eng.* **1999**, 21, 239–260.
- (10) Liu, W.; Andrews, S. A.; Bolton, J. R.; Linden, K. G.; Sharpless, C. M.; Stefan, M. I. Comparison of disinfection byproduct (DBP) formation from different UV technologies at the bench-scale. *Water Sci. Technol.: Water Suppl.* **2002**, 2 (5/6), 515–521.
- (11) Sharpless, C. M.; Linden, K. G. Experimental and model comparisons of low- and medium-pressure Hg lamps for the direct and H₂O₂-assisted UV photodegradation of *N*-nitrosodimethylamine in drinking water. *Environ. Sci. Technol.* **2003**, 37, 1933–1940.
- (12) Bader, H.; Hoigné, J. Determination of ozone in water by the indigo method. *Water Res.* **1981**, 15, 449–456.
- (13) Solomons, T. W. G. *Organic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1996.
- (14) von Sontaag, C.; Dowideit, C. P.; Fang, X.; Mertens, R.; Pan, X.; Schuchmann, M. N.; Schuchmann, H.-P. The fate of peroxy radicals in aqueous solution. *Water Sci. Technol.* **1997**, 35 (4), 9–15.
- (15) Shen, Y.-S.; Young, K. Treatment of gas-phase volatile organic compounds (VOCs) by the UV/O₃ process. *Chemosphere* **1999**, 38 (8), 1855–1866.
- (16) Nelson, L.; Shanahan, I.; Sidebottom, H. W.; Treacy, J.; Nielsen, O. J. Kinetics and mechanism for the oxidation of 1,1,1-trichloroethane. *Int. J. Chem. Kinet.* **1990**, 22 (6), 577–590.
- (17) Paillard, H.; Brunet, R.; Dore, M. Optimal conditions for applying an ozone–hydrogen peroxide oxidation system. *Water Res.* **1988**, 22 (1), 91–103.
- (18) von Gunten, U. Ozonation of drinking water: Part I. Oxidation kinetics and product formation [Review]. *Water Res.* **2003**, 37 (7), 1443–1467.
- (19) Pan, X.-M.; Schuchmann, M. N.; von Sontaag, C. Oxidation of benzene by the OH radical – a product and pulse-radiolysis study in oxygenated aqueous solutions. *J. Chem. Soc., Perkin. Trans.* **1993**, 2, 289–297.
- (20) Cortes, S.; Ormad, P.; Puig, A.; Ovalleiro, J. L. Study of the advanced oxidation processes of chlorobenzenes in water. *Ozone Sci. Eng.* **1996**, 18 (4), 291–298.

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