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The Kinetics of the Sonochemical Process for the Destruction of Aliphatic and Aromatic Hydrocarbons

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Abstract–The sonochemical destruction of volatile organic compounds in aqueous solution has been investigated by using TCE (trichloroethylene), PCE (tetrachloroethylene), benzene, and toluene as model compounds. The substrate's destruction was observed to be decreased at a pseudo first-order rate, and the rate of TCE decay ($k_0=1.7\times10^{-3}\ s^{-1}$) was the greatest when the initial concentration of TCE was 380 μM. The effect of initial concentrations of TCE (ranging from $[TCE]_0$=8.5-424 μM) on the overall decomposition rate of TCE, $k_{0,TCE}$ was investigated. The k_0 value decreases with the increase of $[TCE]_0$ to the level of 200 μM. But, the stays constant increasing the $[TCE]_0$ further. The effect of bicarbonate on TCE decomposition at low concentrations was investigated. The bicarbonate affects TCE decomposition insignificantly in the spiked bicarbonate range of 1 to 10 mM. The sonolytic rate of degradation of TCE appears to be enhanced by the presence of ozone, and the enhancement degree was quite significant at low concentrations of substrate. A kinetic model study was attempted to elucidate the specific reaction sites of the tested compounds and the major contribution of destruction route (OH• reaction or pyrolysis reaction) depending on the various conditions.

Key words: Cavitation, OH•, Ozonation, Pyrolysis, Sonochemical

INTRODUCTION

Water contamination by hazardous waste chemicals is now a matter of international concern. There has been a continuous search for innovative technologies to solve this problem. Advanced oxidation technologies are useful in the oxidative degradation of pollutants for the treatment of hazardous waste water. These processes include ultraviolet irradiation with hydrogen peroxide [Glaze, 1995], TiO_2 assisted photocatalytic degradation [Choi and Hoffmann, 1996], ultraviolet irradiation with ozone [Glaze et al., 1987], and ultrasonic irradiation [Hua and Hoffmann, 1996; Mason, 1990, 1991; Masschelein et al., 1997; Hua et al., 1995a, b; Serpone et al., 1994; Kotronarou et al., 1991, 1992; Barbier and Petrier, 1996]. For many years, ultrasound has been used to induce or enhance chemical reactivity [Mason, 1991], but it is only in recent years that a keen interest in sonochemistry has arisen.

Acoustic waves are mechanical oscillations propagated through an elastic medium. At high intensities, ultrasound propagates through an aqueous medium producing cavitation in liquids. Cavitation is due to the formation and growth of microbubbles during rarefaction phase of the acoustic wave and their subsequent violent collapse during compression cycle of the wave. There are two important effects of cavitation, and sonochemical reactions could be categorized as 1) pyrolysis reaction [Song and Hyun, 1999; Kim, 1996] involving thermal decomposition of solvent, solute, or gases present in solution as a result of the high pressures and temperatures upon bubble collapse, which is similar to thermolysis in the incineration process, and 2) radical reactions which occur in three distinct regions--within the hot bubble cavity, at the interface between the bubble and bulk liquid, and in the bulk media.

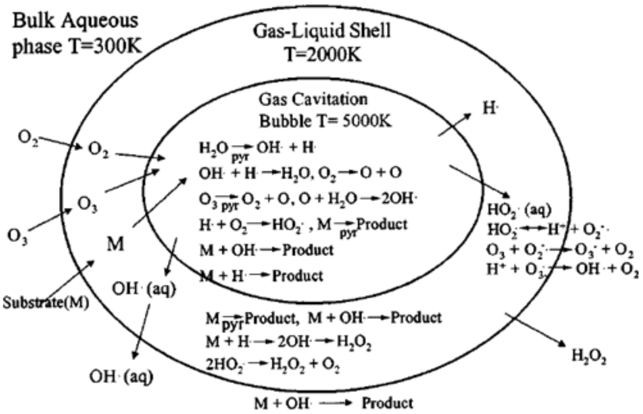

Fig. 1. Schematic diagram of the three regions of sonochemical reactions [Kotronarou, 1992; Kang and Hoffmann, 1998].

Fig. 1 shows a schematic diagram of those three regions of reaction sites with relevant sonochemical reactions. The diagram was originally proposed by Kotronarou [1992], but we modified with several other reactions, which might take place under the presence of ozone. The cavitation bubble contains vapor from the solvent, or any volatile solute present in water, or other gases if present in solvent. On collapse, the vapor is subjected to the enormous increases in both temperature and pressure [Mason, 1990]. Under such extreme conditions the solvent and/or gas molecules undergo homolytic bond breakage to generate reactive species, e.g., radicals. Thus when water is sonicated H• and OH• are produced, which then undergo a series of radical reactions.

$$H_2O \xrightarrow{)))} OH\bullet + H\bullet \tag{1}$$

If O_2 is present in the vapor phase of the bubble, O_2 scavenges H• as given by following reaction:

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$$H\bullet + O_2 \rightarrow HO_2\bullet \tag{2}$$

O_2 can also undergo thermolysis producing excited oxygen atom as follows:

$$O_2 \xrightarrow{\Delta} O + O \tag{3}$$

The oxygen atom is reactive species to produce OH• as follows:

$$O + H_2O \rightarrow 2OH\bullet \tag{4}$$

If ozone is involved, ozone may enhance OH radical production by the thermal decomposition process of ozone as given by following reaction:

$$O_3 \rightarrow O_2 + O \tag{5}$$

If substrate M is volatile and hydrophobic, it will flux into a cavitation bubble and be decomposed by the simultaneous reactions of pyrolysis and OH• reaction as follows:

$$M \rightarrow \text{product} \tag{6}$$

$$OH\bullet + M \rightarrow \text{product} \tag{7}$$

OH• can recombine to form hydrogen peroxide.

$$OH\bullet + OH\bullet \rightarrow H_2O_2 \tag{8}$$

The interface between the bubble and the bulk liquid is a region where surface-active reagents may accumulate or where radical species produced in the cavity will take place. The OH• which is produced in the hot vapor may react there with solute or diffuse into surrounding liquid phase. Temperatures on the order of 2,000 K have been estimated at the gas-liquid shell [Mason, 1990]. Therefore, in the interfacial region, pyrolysis reaction is still an important reaction pathway along with OH• for the decomposition of chemical substrates. OH• may diffuse out of bubble, or it may eject out upon bubble collapse. At bulk phase, the temperature is not high. Consequently, only OH• is expected to take place removing chemical substrate. Relative importance of reactions and reaction zone depends on the characteristics of chemical substrates (i.e., volatility) or the presence of dissolved gas. For example, if the substrate is non-volatile, OH• in the bulk phase is the major decomposition route.

In this paper we present kinetic data for the sonolytic degradation of selected VOCs in aqueous media. The kinetic model of sonochemical reactions with destruction mechanism of those selected compounds under various conditions is to be emphasized.

EXPERIMENTAL METHODS

Trichloroethylene (Aldrich, 99%), Tetrachloroethylene (Aldrich, 99.9%), benzene (Wako, 99.7%), and toluene (Aldrich, 99.9%) were used as received. All solutions were made in deionized water (R= 18 mΩ) with initial concentrations ranging from 8.5-424 μM. Ultrasonic irradiation in solutions was conducted with a Branson VCX-400 sonifier operating at 20 kHz as shown in Fig. 2. Reactions were performed in a 250 mL or 1 L of reactor under a constant temperature (24±2 °C) by circulating the cooling water.

The ultrasonic power delivered in aqueous phase was estimated by calorimetric method. The measured values of delivered energy into the 250 mL of reaction volume were 90 Watts, i.e., 360 Watts/L.

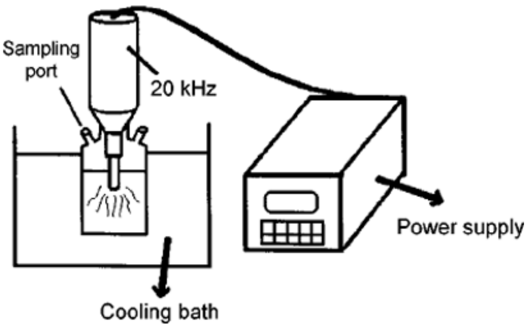

Fig. 2. Ultrasonic irradiation set-up.

To investigate the enhancement destruction rate of substrate, two kinds of ultrasound runs were made: ultrasound run and ultrasound combined with ozone run. For the case of the latter run, ozone was dosed initially and the aqueous ozone concentrations were continuously analyzed by a spectrophotometric method using indigo. The absorbance of indigo was measured by HPLC-UV detector at a wavelength of 600 nm. The concentration of H_2O_2 generated during ultrasound irradiation procedure was analyzed by cobalt method [Masschelein et al., 1997]. For quantitative determination of solute, samples were concentrated by SPME (Solid Phase Micro Extraction) followed by gas chromatograph with FID detection using a capillary column (CDP-10). Chloride ion determinations were carried out by ion chromatography, IC, with conductivity detection.

RESULTS AND DISCUSSION

1. Comparison of VOC Destruction Rates

Sonochemical destruction rates of TCE, PCE, benzene, and toluene were observed and compared as shown in Fig. 3. Without sonication, a blank run was performed to see the portion of the vaporized amount of those compounds. The volatilized loss was found to be less than 5%, which is negligibly small to account for the kinetic consideration. At 0.3-0.64 mM of initial concentration, the destruction pattern of substrate with ultrasound energy input of 360 Watts/L shows apparent first-order kinetics. Table 1 lists values of the rate constants for reaction of OH• with model substrates and also compares the measured values of apparent first-order rate constant, k_o.

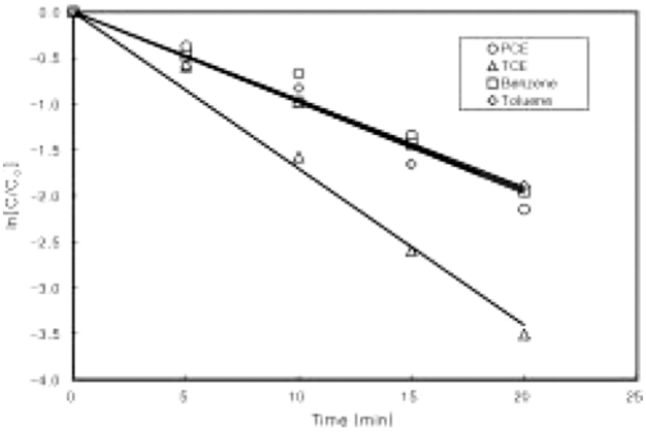

Fig. 3. First-order plot for VOCs.

Table 1. Comparison of the rate constants for the reaction of substrate with OH•, apparent first-order rate constant, and Henry's constant for the tested model compounds

Compound	$k_{M,OH}$ ($M^{-1}s^{-1}$)	Henry's constants (mg/m^3)/(mg/m^3)	k_o (s^{-1})
TCE	4.0×10^9	0.46	3.0×10^{-3}
PCE	2.3×10^9	0.96	1.7×10^{-3}
Benzene	7.8×10^9	0.19	1.6×10^{-3}
Toluene	6.8×10^9	0.24	1.6×10^{-3}

Of those compounds, sonochemical destruction rate of TCE decay was the greatest ($k_{o,TCE}=3.0\times10^{-3}$ s^{-1}), while the rate of other substrates decomposed rather slowly at a similar rate (1.6-1.7×10^{-3} s^{-1}). However, it is worthwhile to note that the second-order rate constants[16] for the reaction of benzene and toluene with OH•, $k_{benzene,OH}$, $k_{toluene,OH}$, are greater than $k_{TCE,OH}$.

The result of this study indirectly proved that OH• reaction is not the major decomposition route for those tested compounds, but the pyrolysis in the cavity or in the interfacial region may be the more predominant destruction pathway. The most favorable site for the pyrolysis reaction is inside of the bubble due to the highest temperature. The availability of pyrolysis reaction in the bubble may be significantly associated with substrate transport from the bulk phase into the gaseous bubble. Therefore, the lower rate of benzene and toluene even with high value of $k_{M,OH}$ may be explained with the lower flux rate from aqueous bulk phase to the inside of the bubble. The magnitude of Henrys constant (H_M) values listed in Table 1 might be strongly associated with the solute transfer rate from the bulk media to the cavity. The Henry's constant values of benzene and toluene, $H_{benzene}$, $H_{toluene}$, are about half of the H_{TCE}.

Comparing Henry's constant of TCE with PCE, H_{PCE} is two times greater that H_{TCE}, implying higher mass transport of PCE into the bubble and more favorable condition of PCE for pyrolysis. As of now, it would be wise to state that the sonochemical decomposition rate depends on the relative importance of pyrolysis and OH• reaction. Also, we should note that the volatility of substrates determines the reaction regions that occur during the cavitation process.

2. Effect of Initial Concentration of Substrate

The effect of initial concentrations of TCE ($[TCE]_o=8.5$-420 μM) on the pseudo first-order rate of TCE was investigated. Fig. 4 shows the results of k_o vs initial concentration of TCE. The k_o value was the largest at the lowest concentration of $[TCE]_o$, but k_o value decreases with the increase of initial concentration to the level of 200 μM, but the rate stays constant increasing $[TCE]_o$ further.

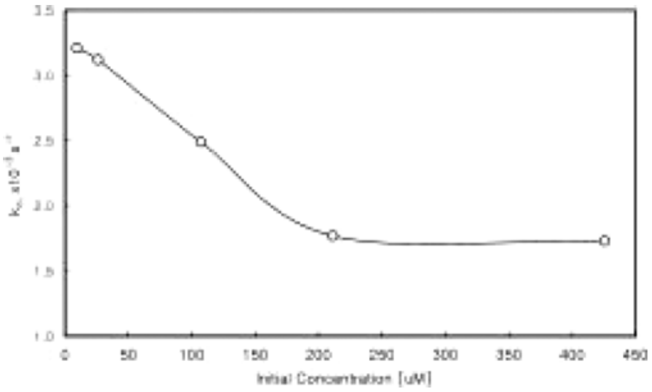

Fig. 4. The effect of initial concentration on the TCE degradation rate.

The effect of initial concentrations on k_o can be explained by the kinetic model as described below:

In this cavitation process, the decay of substrate M will be due to the reaction with OH• and pyrolysis pathway given by Eq. (9) and (10):

$$\left\{-\frac{d[M]}{dt}\right\}_{pyr}=k_{pyr}[M] \tag{9}$$

$$\left\{-\frac{d[M]}{dt}\right\}_{OH}=k_{M,OH}[M][OH\bullet] \tag{10}$$

Thus, the overall decomposition rate of M is

$$-\frac{d[M]}{dt}=(k_{pyr}+k_{M/OH}[OH\bullet])[M] \tag{11}$$

where k_{pyr} is the rate constant for pyrolysis, $k_{M,OH}$ is the second order rate constant for the reaction of OH• with M, [OH•] the steady state concentration of OH•, and k_o is the apparent first-order rate constant given by

$$k_o=k_{pyr}+k_{M,OH}[OH\bullet] \tag{12}$$

The major reactions occurring in the cavity are as follows:

$$H_2O\underset{k_1}{\overset{)))}{\rightarrow}}H\bullet+OH\bullet$$

$$OH\bullet+OH\bullet\underset{k_2}{\rightarrow}H_2O_2$$

$$M'+OH\bullet\underset{k_3}{\rightarrow}\text{Products}$$

$$H\bullet+OH\bullet\underset{k_4}{\rightarrow}H_2O$$

where M' is the transferred solute in the cavity given by

$$[M']=\eta[M]$$

where η is the transfer efficiency of substrate from bulk phase to the gaseous bubble.

Using the steady-state approximation for the radicals, the following equation for the steady state concentration of OH• may be derived:

$$[OH\bullet]=\frac{k_1P}{k_2[OH\bullet]+k_3\eta[M]+k_4[H\bullet]} \tag{13}$$

where P denotes ultrasound power. Under the condition that substrate is highly volatile and k_3 is large, the term $k_3\eta[M]$ will be much greater than the term ($k_2[OH\bullet]+k_4[H\bullet]$). Then k_o becomes

$$k_o=k_{pyr}+k_{M,OH}\frac{k_1P}{k_3\eta[M]}=k_{pyr}+k_{o,OH} \tag{14}$$

From this equation, we may elucidate our observation on the k_o vs initial concentration of TCE. That is, if [M] is large, the second term in Eq. (14) becomes less important and pyrolysis is the predominant destruction pathway. Whereas at low initial concentrations of sub-

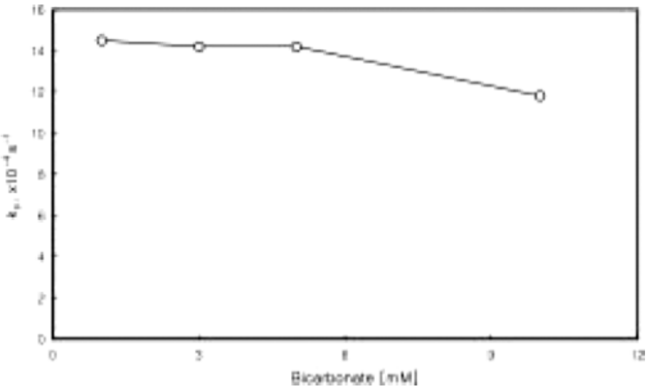

Fig. 5. Effect of bicarbonate for TCE removal.

strate, the term $k_{M, OH}(k_1P/k_3\eta[M])$ becomes more significant than k_{pyr}, meaning that OH radicals reactions are likely to predominate. However, we should note that the pyrolysis reactions always take place either at high or low concentrations of substrates, and the rate seems to be constant with respect to [M].

3. Effect of Bicarbonate

The effect of bicarbonate on TCE decomposition at low concentrations was investigated. Bicarbonate is a major inorganic OH• scavenger present in natural water and it may compete with organic matter for reaction with OH•. In our experiment, the bicarbonate affects TCE decomposition insignificantly in the spiked bicarbonate range of 1 to 10 mM. This result also proved that the major decomposition route of TCE is the pyrolysis pathway occurring in the interfacial region or cavity, not by the OH• reaction.

4. Enhancement Effect of Ozonation

The effect of ozonation on the sonolytic degradation of PCE was examined. The water containing 30 μM of initial concentration PCE was sonicated and aerated either with ozone or without ozonation. For the ultrasound/ozone system, ozone was dosed continuously at a rate of 0.5 mg/min. Fig. 5 compares the two runs of the ultrasound alone and the ultrasound/ozone system. The result shows that PCE decomposition rate was enhanced combining ultrasound and ozone even if the direct reaction rate of PCE with ozone molecule is quite low ($k_{O3, PCE}$<0.1 M^{-1}s^{-1}) [Buxton et al., 1988]. It is interesting to note that during the initial period of sonication, the oxidation with ozone did not exhibit any enhanced degradation, whereas the enhancement rate was observed at low concentrations of substrate. As previously proposed, presence of ozone in the sonicated solution will produce more OH• in the cavity enhancing the destruction rate of substrate. However, as previously described in the kinetic model, the relative importance of the destruction route between the OH• and pyrolysis depends on the concentration of target compounds. The results presented in Fig. 6 sufficiently demonstrate the enhancement effect of ozone on the oxidation rate of substrate.

5. Ozone Decomposition Kinetics by US

Kinetics of ozone decomposition by ultrasound was studied in a static configuration. The pH of the solution was adjusted down to pH=4.6, where the ozone self-decomposition is suppressed. The ozone gas was bubbled in the solution until the desired residual ozone was reached (target initial ozone concentration was 2.5 mg/L). For the ozone-ultrasound run, aqueous solution was sonicated and ozone samples was continuously analyzed by a spectrophotometric method

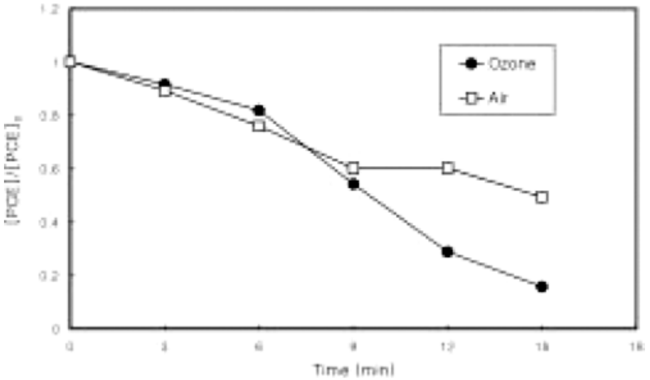

Fig. 6. The effect of ozonation on the sonolytic degradation of PCE.

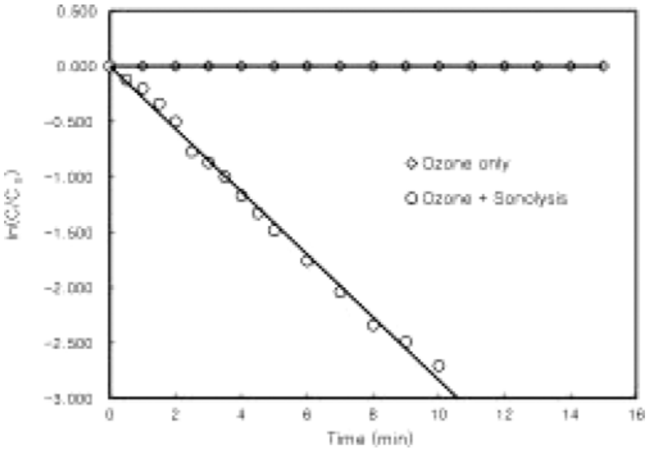

Fig. 7. Ozone decomposition kinetics with or without ultrasound.

using indigo with HPLC-UV detector. The ozone decomposition kinetic data with or without ultrasound was illustrated in Fig. 6. The ozone decomposition kinetics with ultrasound was first order with a rate constant, k_o=4.7×10^{-3} s^{-1}. When the solution was sonicated, ozone disappeared rapidly and more peroxide was generated than when the solution was saturated only with oxygen (Fig. 8). The increased efficiency of peroxide production may due to more OH• production inside of cavitation bubble leading to more favorable conditions for OH•-OH• combination reaction to form hydrogen peroxide.

6. Yield of Mineralization

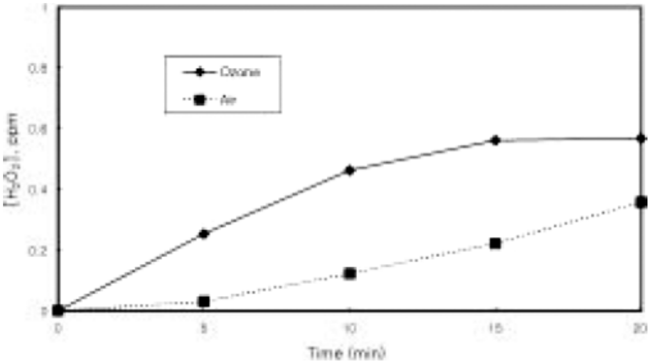

Fig. 8. Effect of ozonation on hydrogen peroxide formation.

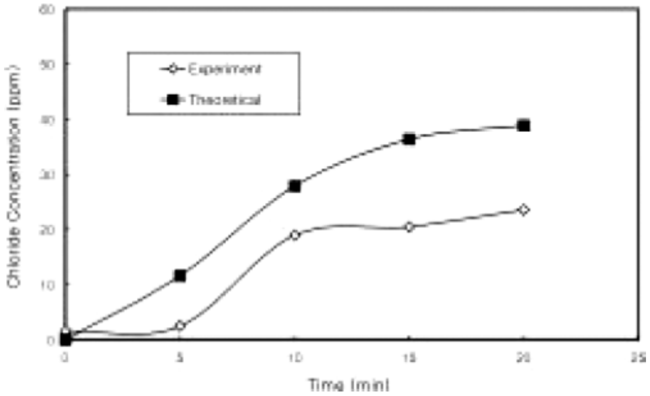

Fig. 9. Chlorine mass balance during ultrasound irradiation.

The formation of by-products from ultrasound irradiation is not the primary subject of this paper. However, some runs were made in an attempt to determine the yield of chloride ions from the oxidation of TCE. Two sets of samples were drawn from the reactor during an oxidation run with initial TCE concentration of 380 µM. One set of sample was analyzed for TCE, the other set for chloride ion with ion chromatography. The data, plotted in Fig. 9, show the chlorine mass balance after sonolysis. The formation of chloride ion from the oxidation of TCE is not quantitative, implying that there may be many by-products formed. According to Orzechowska et al. [1995], chloride ions were formed for the most part and a little $HCOO^-$ (formate ion) was produced. On the other hand, Glaze et al. [1993] reported that TCAA (trichloroacetic acid), TCAAD (trichloro acetaldehyde) etc. were formed by the reaction of TCE with hydroxyl radical. Accordingly, more studies on the intermediates and breakdown mechanism of VOCs are being explored.

CONCLUSIONS

The experimental studies described in this work suggest the following conclusions with respect to the application of ultrasound process for treatment of TCE, PCE, benzene, and toluene in aqueous media:

1. The substrate's destruction was observed to decreased at a pseudo first-order rate under the conditions used in our experimentation.
2. Of those tested compounds, the rate of TCE decay was the greatest even though $k_{benzene, OH}$ is greater than $k_{TCE, OH}$. This result indirectly proved that OH• reaction is not the major decomposition route for those tested compounds, but the pyrolysis in the cavity or in the interfacial region may be the more predominant destruction pathway.
3. The initial concentration level affects the sonolytic destruction rate of substrate and determines the relative importance of the destruction pathways, pyrolysis and OH• reaction. Pyrolysis was found to be the predominant pathway at high solute concentrations, whereas OH• reaction is likely to predominate at low initial concentrations of substrate.
4. The bicarbonate affects TCE decomposition insignificantly since the major decomposition route of TCE is the pyrolysis pathway occurring in the interfacial region or cavity.
5. The degradation of PCE by ultrasound was enhanced coupling with ozonation process. The enhancement rate was significant at low concentrations of substrate.
6. A careful study of by-product was not a part of this work. However, a run was made in an attempt to determine the yield of chloride ions from the sonochemical reaction of TCE. The chlorine mass balance after sonolysis was determined to be <60%.

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