# Kinetics and Mechanism of the Sonolytic Degradation of CCI<sub>4</sub>: Intermediates and Byproducts

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The sonolytic degradation of aqueous carbon tetrachloride is investigated at a sound frequency of 20 kHz and 135 W (112.5 W cm<sup>-2</sup>) of power. The observed first-order degradation rate constant in an Arsaturated solution is  $3.3 \times 10^{-3} \text{ s}^{-1}$  when the initial CCl<sub>4</sub> concentration,  $[CCl_4]_{i}$ , is 1.95  $\times$  10<sup>-4</sup> mol L<sup>-1</sup> and increases slightly to  $3.9 \times 10^{-3} \text{ s}^{-1}$  when  $[CCl_4]_i =$  $1.95 \times 10^{-5}$  mol L<sup>-1</sup>. Low concentrations ( $10^{-8}-10^{-7}$ mol L<sup>-1</sup>) of the organic byproducts, hexachloroethane and tetrachloroethylene, are detected, as well as the inorganic products chloride ion and hypochlorous acid. The chlorine mass balance after sonolysis is determined to be >70%. The reactive intermediate, dichlorocarbene, is identified and guantified by means of trapping with 2,3-dimethyl-2-butene. The presence of ozone in the sonicated solution does not significantly effect the rate of degradation of carbon tetrachloride; however, O<sub>3</sub> inhibits the accumulation of hexachloroethane and tetrachloroethylene. Ultrasonic irradiation of an aqueous mixture of p-nitrophenol (p-NP) and carbon tetrachloride results in the acceleration of the sonochemical degradation of p-NP. The sonolytic rate of degradation of *p*-NP appears to be enhanced by the presence of hypochlorous acid, which results from the sonolysis of CCl<sub>4</sub>.

## Introduction

Carbon tetrachloride contamination in the environment is widespread due to its refractory nature and its large-scale production. Under ambient conditions, CCl<sub>4</sub> does not degrade readily (1, 2). However, CCl<sub>4</sub> is reduced by H<sub>2</sub>S in the presence of mineral surfaces (3, 4) and over cobalt catalysts (5). CCl<sub>4</sub> is unreactive toward the hydroxyl radical (half-life > 330 years) (6) but degrades via direct photolysis in the stratosphere (7, 8) where it is thought to play a minor role in the depletion of stratospheric ozone (9, 10). The persistence of CCl<sub>4</sub> in the environment is of concern because of its short-term and chronic human health effects and because it is a suspected human carcinogen and an Environmental Protection Agency (EPA) priority pollutant (11). The mechanisms of  $CCl_4$  toxicity (12–17), its physical properties, and its environmental fate (18, 19) have been studied.

\* Corresponding author telephone: (818) 395-4391; fax: (818) 395-3170; e-mail address: mrh@cco.caltech.edu. Numerous methods have been applied to the degradation of gas-phase CCl<sub>4</sub> such as catalytic decomposition over mixed metal oxide/porous carbon catalysts (20), incineration (21, 22), reduction over metallic iron (23), and decomposition with electron-beam plasmas (24, 25). The treatment of aqueous-phase CCl<sub>4</sub> has been explored using anaerobic activated carbon reactors (26), UV photolysis (27), and high-pressure (20 MPa) liquid water hydrolysis (28).

Ultrasonic irradiation of aqueous solutions of halogenated hydrocarbons, including chlorofluorocarbons (29) and  $CCl_4$  (30-34) has been reported. The extreme temperatures and pressures generated during cavitation result in solute thermolysis as well as the formation of hydroxyl radical and hydrogen peroxide (35, 36). The decomposition of aqueous CCl<sub>4</sub> during sonication was reported by Weissler et al. (37) and Griffing (38). CCl<sub>4</sub> sonolysis was also shown to result in enhanced sonoluminescence (39, 40). The sonolysis of CCl<sub>4</sub> in the presence of iodide (41), magnesium chloride (42), and di-n-butyl sulfides (43) has also been examined. The results of these studies indicate that the decomposition of CCl<sub>4</sub> during ultrasonic irradation is significant, with first-order rate constants ranging from  $10^{-2}$ to  $10^{-3}$  s<sup>-1</sup>. The effect of reaction variables such as initial concentration, steady-state temperature, and power intensity has been investigated. However, quantitative data on byproduct analysis and intermediate formation is lacking.

In this paper, we examine the kinetics and mechanism of the ultrasonic irradiation of  $CCl_4$  in aqueous solution with a particular focus on the  $Cl^-$  balance, reaction intermediates, and reaction byproducts. The effects of ozone and *p*-nitrophenol on  $CCl_4$  degradation are also explored.

# **Experimental Methods**

High-purity carbon tetrachloride (calibration standard; Supelco, Bellefonte, PA), hexachloroethane (98%; Aldrich, Milwaukee, WI), tetrachloroethylene (99.9%; Sigma-Aldrich, St. Louis, MO, and Milwaukee, WI), 2,3-dimethlybutene (Aldrich), p-nitrophenol (p-NP; Aldrich, 98%), 5,5',7-indigotrisulfonic acid (Sigma Chemical Co.), and pentane (Omnisolv grade, EM Science, Gibbstown, NJ) were used as received. All aqueous solutions were made in water purified with a MilliQ UV Plus system ( $R = 18.2 \text{ m}\Omega$ ). Reproducible concentrations of CCl<sub>4</sub> in water were obtained by adding a specific volume of the solute into a vial filled with Ar-saturated water and sealing the vial with zero headspace. The vial was then shaken at  $\sim$ 285 rpm at room temperature for 12 h to achieve complete dissolution. The solutions were then diluted in Ar-saturated water to the appropriate concentration and adjusted to pH 11.8 with NaOH. Buffers were not used to control the pH because many buffers (e.g., carbonate or bicarbonate) are effective radical scavengers (44) and would interfere with degradation of the target solute. Saturated solutions were made by stirring excess CCl<sub>4</sub> with Ar-saturated water.

Sonications at 20 kHz were done with a VCX-400 Vibracell (Sonics and Materials, Inc., Danbury, CT) operated at 30% power amplitude and an average output of 135 W as measured with a built-in wattmeter. The titanium tip of



FIGURE 1. Schematic diagram of a gas-tight glass reactor cell with a Teflon collar for attachment to stainless steel sonication probe.

the probe was polished and the transducer tuned before every use to give a minimal power ouptut when vibrating in air. A 95-mL aliquot of solution was transferred into a water-jacketed glass cell, which was closed to the atmosphere (total volume, 110 mL). The bottom of the glass reactor (Figure 1) had a 1-cm indentation in the center for reflection of the sound waves and for even distribution of the cavitation bubbles in the solution. The reactor was made air-tight with two O-ring seals in the threaded Teflon collar connecting the glass cell to the stainless steel probe. In addition, sampling ports were sealed with Teflon valves and covered with rubber septa. Cooling water was circulated through the system by a Haake A80 cooler/recirculator in order to maintain a constant temperature. Aliquots (1.0 mL) were withdrawn with a Hamilton syringe and mixed with 0.5 mL of pentane. A  $0.5-\mu$ L sample of the pentane extract was then analyzed with an HP 5880A gas chromatograph-electron capture detector (GC-ECD) operated in the splitless mode and equipped with an HP-5 column (cross-linked 5% phenyl methyl siloxane, 25 m  $\times$  0.32 mm  $\times$  1.05  $\mu$ m film thickness). The instrument was calibrated with standard solutions of carbon tetrachloride, hexachloroethane, and tetrachloroethylene in pentane. Ion-selective electrodes were used to quantify chloride ion and hypochlorous acid (Orion, Models 96-17B and 97-70).

All experiments with ozone were performed with an Orec Model V10–0 Ozonator (Ozone Research and Equipment Corp., Phoenix, AZ) operated at 9 psi and a flow rate of 4.5 L min<sup>-1</sup>. Water was placed in a gas dispersion bottle and bubbled with ozone at a flow rate of 20 mL min<sup>-1</sup>. Ozonesaturated water was used to dilute 140 mL of an Ar-saturated CCl<sub>4</sub> solution to 250 mL. Any residual ozone in the aliquots withdrawn during sonication was quenched by adding 200  $\mu$ L of 1-mmol solution of 5,5',7-indigotrisulfonic acid (Indigo Blue), following standard procedures (45). Pentane extracts were analyzed as described above.

Intermediates were trapped by sonicating a CCl<sub>4</sub> solution in the presence of 2,3-dimethyl-2-butene and Ar. Sample



FIGURE 2. Variation of the degradation rate constant with initial carbon tetrachloride concentration.

volume and extraction methods were the same as above. The detection of the 1,1-dichloro-2,2,3,3-tetramethylcyclopropane was achieved with a Hewlett-Packard 5890 Series II gas chromatograph (HP-5 column,  $3-\mu$ L injection volume, He carrier gas) connected to a Hewlett-Packard 5972 Series mass selective detector operated in the singleion mode. A characteristic peak at 131 amu was used for quantification. Confirmation of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane was obtained by comparing the mass spectrum of the sonicated sample to the spectrum of the authentic compound.

Sonication of 100  $\mu$ M *p*-NP in a solution saturated with CCl<sub>4</sub> and Ar was performed in an identical fashion as described above. Quantification of the *p*-NP was achieved with a Hewlett-Packard 8452a UV/visible spectrophotometer as described previously (*46, 47*).

#### Results

A solution of  $CCl_4$  was stirred and maintained at 25 °C, and liquid samples were sequentially withdrawn and analyzed. None of the dissolved  $CCl_4$  appeared to be lost from the solution over a period of 90 min. Thus, even with a small headspace in the reactor, loss of  $CCl_4$  due to volatization during sonolysis is negligible.

A first-order plot of [CCl<sub>4</sub>] vs time during sonolysis of an Ar-saturated solution is shown in Figure 2. At two different initial concentrations, 195 and 19.5  $\mu$ M, the reaction exhibits apparent first-order kinetics for ~4 half-lives. The first-order rate constant did not differ significantly over this concentration range; it was slightly higher [(3.9 ± 0.19) × 10<sup>-3</sup> s<sup>-1</sup>] when the initial concentration was 19.5  $\mu$ M than at 195  $\mu$ M [(3.3 ± 0.23) × 10<sup>-3</sup> s<sup>-1</sup>]. In both cases, the concentration of carbon tetrachloride was reduced by 90% within 12 min of sonication.

A mass balance of chlorine atoms during CCl<sub>4</sub> sonolysis was determined as follows:

## TABLE 1 Final Distribution of Chlorine Atoms in a Sonicated Solution of CCl<sub>4</sub> after 90 min of Sonolysis





Sonication time, [min]

FIGURE 3. Concentration of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane as a function of sonication time.

chlorine atom yield =  

$$\frac{[Cl^{-}] + [HOCl] + 4[C_2Cl_4] + 6[C_2Cl_6] + 4[CCl_4]_f}{4([CCl_4]_i - [CCl_4]_f)} (1)$$

Table 1 lists values for the observed byproducts after ultrasonic irradiation. A typical chlorine balance was > 70% with Cl<sup>-</sup> found to be the dominant product. Hexachloroethane and tetrachloroethylene are the only organic byproducts detected and are not present when the initial CCl<sub>4</sub> concentration is low (19.5  $\mu$ M). Thus, despite the known degassing effect (48) of ultrasound; in a closed system, volatile solutes re-enter the treated solution and the observed losses are due to chemical reaction and not to volatization.

The formation of the reactive intermediate, dichlorocarbene, was confirmed by utilizing the reaction

$$C(H_{3}C)_{2} = C(CH_{3})_{2} \xrightarrow{:CCl_{2}} H_{3}C \xrightarrow{Cl} CH_{3} (2)$$

to form 1,1,-dichloro-2,2,3,3-tetramethylcyclopropane. A peak concentration of 2.8  $\mu$ M was observed after 15 min of sonication, as shown in Figure 3. This concentration allows a lower limit to be placed on the dichlorocarbene concentration in solution during sonication. Figure 4 provides



FIGURE 4. (a) Mass spectrum of 100  $\mu$ M 1,1-dichloro-2,2,3,3-tetramethylcyclopropane. (b) Mass spectrum of an aliquot withdrawn after 15 min of sonication of an aqueous solution saturated with CCI<sub>4</sub>, 2,3-dimethyl-2-butene, and Ar.

## TABLE 2

# Abundances of Major Mass Fragments for Identification of Dichlorocarbene

sample	131	95	77
C <sub>7</sub> H <sub>12</sub> Cl <sub>2</sub> <sup>a</sup> sonicated sample <sup>b</sup>	70 912 978	23 696 398	35 948 544
<sup>a</sup> 100 µM 1,1-dichloro-2,2	,3,3-tetramethy	lcyclopropane	e. <sup>b</sup> Sonicatio

 $^a$  100  $\mu M$  1,1-dichloro-2,2,3,3-tetramethylcyclopropane.  $^b$  Sonication of an aqueous solution saturated with CCl4, C6H12, and Ar.

a comparison of the mass spectrum of an authentic sample of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane and that of the compound detected during the sonication of carbon tetrachloride. The chromatographic retention times of the peaks in each sample were in agreement to within 0.36 s. Furthermore, the correct distribution of abundances and ratios was observed for several characteristic fragments: 131, 95, and 77 amu. The representative abundances and mass fragments are summarized in Table 2.

In a separate set of experiments, the effect of ozone on the degradation kinetics of carbon tetrachloride was determined. Under ambient conditions, a solution of CCl<sub>4</sub> saturated with ozone did not exhibit an appreciable degradation after 90 min. Sonication of CCl<sub>4</sub> in the presence of a 56%:44% (v/v) Ar/O<sub>3</sub> mixture (Figure 5) does not result in enhanced degradation of CCl<sub>4</sub>. However, the formation of C<sub>2</sub>Cl<sub>4</sub> and C<sub>2</sub>Cl<sub>6</sub> was found to be strongly inhibited in ozone saturated solutions, as shown in Figure 6. The maximum concentrations of both byproducts were attained during the early stages of the reaction, regardless of the saturating gas mixture. However, the maximum concentration was substantially less in the presence of ozone.

The results presented in Figure 7 demonstrate the acceleration of p-NP degradation during sonolysis in a CCl<sub>4</sub>-saturated system. In the absence of ultrasonic irradiation, p-NP does not degrade in a saturated solution of CCl<sub>4</sub>. However, addition of CCl<sub>4</sub> during sonication of p-NP in an Ar-saturated, aqueous solution enhances the rate constant of p-NP degradation by a factor of 4.5 compared to sonication without CCl<sub>4</sub>. The accumulation of 4-nitrocat-



FIGURE 5. Effect of ozonolysis on the degradation of carbon tetrachloride during sonolysis.

echol, an aromatic degradation product, is minimized in the presence of CCl<sub>4</sub>.



#### Discussion

The observed kinetics and byproducts of the sonolysis of aqueous  $CCl_4$  will now be discussed in the context of the "hot-spot theory", a theory which proposes that the chemical effects of cavitation are due to the extremely high temperatures and pressures that result when a bubble implodes. Alternative viewpoints are reviewed by Margulis (49).

The weak influence of the initial concentration on the first-order rate constant for the sonolytic degradation of CCl<sub>4</sub> has also been observed by other investigators (34). In contrast, the degradation rate constant of p-NP is inversely correlated to its intitial concentration during sonication (47). CCl<sub>4</sub> appears to undergo pyrolysis in the gas-phase interior of the bubble as well as in the interfacial region, whereas *p*-NP reacts predominantly at the interface. The volume of the gas phase is estimated to be  ${\sim}2 \times 10^4$  larger than the volume of the interfacial region (50). Thus, more molecules of CCl<sub>4</sub> than *p*-NP can react during a single cavitation event. Table 3 lists the relevant properties of the two substrates. On the basis of its higher K<sub>OW</sub>, CCl<sub>4</sub> partitions more effectively to the hydrophobic (51, 52) cavitation bubble interface. Furthermore, with a higher vapor pressure and lower boiling point, a greater fraction of CCl<sub>4</sub> will react in the gas phase.

The reaction pathways of CCl<sub>4</sub> during sonolysis can be inferred from combustion and shock tube studies. The thermal dissociation of CCl<sub>4</sub> in an Ar gas phase is known to produce two chorine atoms for every molecule of CCl<sub>4</sub>; fission of the second chlorine is thought to occur at  $\sim 10\%$ 



FIGURE 6. Effect of ozonolysis on the accumulation of  $C_2CI_4$  and  $C_2CI_6$  in a sonicated solution of aqueous  $CCI_4$ .



FIGURE 7. Enhancement of *p*-NP sonolytic degradation by addition of CCI<sub>4</sub>.

of the rate of primary fission (53). The initial steps of  $CCl_4$  degradation during sonolysis appear to be as follows:

$$\operatorname{CCl}_4 \xrightarrow{\Delta} \operatorname{CCl}_3 + \operatorname{Cl}$$
 (3)

$$CCl_3 \rightarrow CCl_2 + Cl$$
 (4)

Formation of dichlorocarbene,  $:CCl_2$ , is also thought to occur by the simultaneous elimination of two chlorine atoms (54):

## TABLE 3 Selected Physical Properties of Carbon Tetrachloride and p-Nitrophenol<sup>a</sup>

compound	log K <sub>ow</sub>	vapor pressure, mmHg	boiling point, °C
CCI <sub>4</sub>	2.83	113.83	77
<i>p</i> -NP	1.91	10 <sup>-3</sup>	279 (dec)

<sup>a</sup> Data in this table were taken from refs 18, 88, and 89.

$$\operatorname{CCl}_4 \to :\operatorname{CCl}_2 + \operatorname{Cl}_2 \tag{5}$$

A third mechanism for dichlorocarbene formation is disproportionation of the trichloromethyl radical, which can be inferred from an analogous reaction between the trifluoromethyl radical and the hydrodifluoromethyl radical (55):

$$^{\bullet}CCl_{3} + ^{\bullet}CCl_{3} \rightarrow CCl_{4} + :CCl_{2}$$
(6)

All three pathways are possible at the hot center of the imploding bubble. The trichloromethyl radical can also couple to form hexachloroethane (*56*):

$$^{\bullet}\mathrm{CCl}_{3} + ^{\bullet}\mathrm{CCl}_{3} \to \mathrm{C}_{2}\mathrm{Cl}_{6} \tag{7}$$

The relative rate of disproportionation to that of combination depends on the radical species but is usually less than 1 (*57*). The recombination of the trichloromethyl radical in the gas phase has been studied, and at 298 K and 1 atm (in Ar), the rate constant of formation of hexachloroethane is  $\sim$ 1 order of magnitude less than the re-formation of CCl<sub>4</sub> (*58*).

In the presence of oxidizing species, the trichloromethyl radical can act as a scavenger of hydroxyl radical

$$^{\bullet}CCl_{3} + ^{\bullet}OH \rightarrow HOCCl_{3}$$
 (8)

or molecular oxygen (59)

$$^{\bullet}CCl_3 + O_2 \rightarrow ^{\bullet}O - OCCl_3 \tag{9}$$

The relative concentrations of trichloromethyl radical and hydroxyl radical in the gas phase of a cavitation bubble can be estimated by comparing the carbon–chlorine bond strength in carbon tetrachloride, 73 kcal mol<sup>-1</sup> (*60*), to the hydrogen–oxygen bond strength in a water molecule, 119 kcal mol<sup>-1</sup> (*61*). Thus, sufficient quantities of trichloromethyl radical are formed such that recombination and radical scavenging occur in parallel. At high trichloromethyl radical concentrations in an Ar atmosphere, self-reaction of two CCl<sub>3</sub> radicals appears to be a likely primary reaction. The relative concentrations of the precursor molecules CCl<sub>4</sub> and H<sub>2</sub>O are probably also important and can be estimated by comparing the boiling points (77 vs 100 °C).

Based on analogous gas-phase mechanims, the reactive intermediate HOCCl<sub>3</sub> appears to react rapidly to yield phosgene and other products as follows:

$$\text{HOCCl}_3 \rightarrow \text{HCl} + \text{COCl}_2$$
 (10)

$$\operatorname{COCl}_2 + \operatorname{H}_2 \operatorname{O} \rightarrow \operatorname{CO}_2 + \operatorname{HCl}$$
 (11)

$$O - OCCl_3 + H_2O \rightarrow COCl_2 + HOCl$$
 (12)

Phosgene hydrolyis in water is rapid (62) under ambient conditions, and the rate constant is positively correlated

with temperature (63). Thus, the hydrolysis of this intermediate can be enhanced by the occurrence of supercritical water (46) during cavitional bubble collapse:

$$COCl_2 + H_2O \rightarrow HCl + CO_2$$
(13)

The dichlorocarbene can couple to form tetrachloroethylene

$$2:CCl_2 \to C_2Cl_4 \tag{14}$$

or hydrolyze to carbon monoxide and hydrochloric acid:

$$:CCl_2 + H_2O \rightarrow CO + 2 HCl$$
(15)

Chlorine atoms can combine to form molecular chlorine, which hydrolyzes to hypochlorous acid and chloride ion:

$$2^{\bullet}Cl \rightarrow Cl_2 \xrightarrow{H_2O} HOCl + HCl$$
(16)

Chlorine atom recombination in the gas phase is a termolecular process (*57*). If molecular chlorine is the third body, then the recombination rate constant at 298 K is larger ( $k = 2.0 \times 10^{10} \text{ L}^2 \text{ mol}^{-1} \text{ s}^{-1}$ ) than when Ar is the third body ( $k = 4.4 \times 10^9 \text{ L}^2 \text{ mol}^{-1} \text{ s}^{-1}$ ) (*64*). Thus, during a cavitational event, the rate of molecular chlorine formation will vary as the relative ratio of molecular chlorine and Ar atoms varies.

The detection of dichlorocarbene in a sonicated, aqueous solution of CCl<sub>4</sub> confirms the validity of extrapolating gasphase reaction mechanisms to those occurring in the hottest regions of the cavitation bubble. Sonolysis of aqueous CCl<sub>4</sub> appears to include pathways similar to those occurring during sonolysis of pure CCl<sub>4</sub> and CHCl<sub>3</sub>. Spin-trapping studies (*65*) during ultrasonic irradation of pure CCl<sub>4</sub> indicated the formation of •Cl. The formation of a carbene intermediate was also postulated (*66*) during the sonication of CHCl<sub>3</sub>. The standard biphasic reaction (NaOH/CHCl<sub>3</sub>) for generating dichlorocarbene in the aqueous phase is enhanced by sonolysis (*67*), most likely due to enhanced mixing. Characterization of intermediates during sonolysis of aqueous CCl<sub>4</sub> may allow further insight into the mechanism by which CCl<sub>4</sub> enhances sonoluminescence.

The possible enhancement of sonolytic processes by the addition of ozone has been investigated in both chemical and biological systems (68-72). The use of ozone in conjunction with ultrasonic irradiation in this study demonstrates the efficacy of simultaneous treatment processes. The initial refractory compound, CCl<sub>4</sub>, is transformed into more reactive species via pyrolysis. Degradation byproducts such as C<sub>2</sub>Cl<sub>4</sub> can then be attacked by ozone. Various different reaction pathways can be enhanced in a single reactor by combining advanced treatment technologies.

Ozone can react directly with solute molecules and also decomposes in the gas phase to yield oxygen atoms and hydroxyl radical as follows (*68*):

$$O_3 \rightarrow O_2 + 0 \tag{17}$$

$$^{\bullet}\mathrm{O} + \mathrm{H}_{2}\mathrm{O} \rightarrow 2^{\bullet}\mathrm{OH}$$
 (18)

Aqueous ozone decomposition in solution is strongly influenced by pH and results in a variety of reactive species, including superoxide radical and hydrogen peroxide (73). These species may also react with both tetrachloroethylene and hexachloroethane concentrated at the cavitation bubble interface. Ozone and its decomposition products most likely accelerate the decomposition of  $C_2Cl_4$  (74–76) during sonolysis. Direct reaction of ozone with alkenes is facile (77):

Rearrangement of the molozonide to the ozonide and subsequent hydrolysis yields phosgene and hydrogen peroxide:

$$CI \xrightarrow{O} CI \xrightarrow$$

$$CI > C \xrightarrow{O} C \xrightarrow{CI} C_{CI} \xrightarrow{H_2O} 2 \xrightarrow{O} II + H_2O_2 \qquad (21)$$

$$CI \xrightarrow{C} CO_2 + 2HCI$$
(22)

Hydrolysis of phosgene to carbon dioxide and hydrochloric acid is the final step leading to mineralization.

On the other hand, the decomposition of hexachloroethane is not expected to be influenced by ozone. Thus, a lower concentration of hexachloroethane in an ozonesaturated, sonicated solution is observed because a greater fraction of the trichloromethyl radical is scavenged before it can couple to form hexachloroethane.

In the absence of ozone, hexachloroethane and tetrachloroethylene (78, 79) can react thermally. Because the C-C bond strength is  $145 \pm 5$  kcal mol<sup>-1</sup> (80) whereas the C-Cl bond strength is 93 kcal mol<sup>-1</sup> (81), the further degradation of hexachloroethane is probably dominated by thermal cleavage of a C-Cl bond. At pH 6.5, tetrachloroethylene reacts rapidly with hydroxyl radical ( $k = 2.8 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>) (44, 82).

Acceleration of *p*-NP degradation could occur in several different regions of the sonicated solution. The formation of hypochlorous acid is rapid during sonication of CCl<sub>4</sub>. This byproduct is highly oxidizing and most likely reacts directly with *p*-NP in the bulk solution. Micromolar concentrations of chloropicrin (CCl<sub>3</sub>NO<sub>2</sub>) are obtained when 3-nitrophenol is exposed to 200  $\mu$ M chlorine (*83*), while 2-nitrophenol and 2,4-dinitrophenol concentrations are reduced by 76 and 12%, respectively, during chlorination (*84*).

Reactions at the cavitation bubble interface may involve intermediates from the degradation of both molecules. For example, hydroquinone could react with dichlorocarbene in a fashion similar to 2,3-dimethyl-2-butene:



The results of this investigation suggest that sonolysis is a particularly suitable method for degrading volatile, hydrophobic molecules because these compounds are reactive in the largest region of the cavitation bubble (i.e., the gas phase). CCl<sub>4</sub> was significantly degraded during sonolysis: 90% reduction was observed after ~12 min, and 99% reduction occurred after ~90 min. The quick reduction of CCl<sub>4</sub> is important in scaleup operations because it allows for a shorter residence time when operating in a continuous-flow mode.

The reactive pathways of CCl<sub>4</sub> in a sonicated, aqueous solution are in agreement with those observed during sonolysis of the pure liquid. Furthermore, detection of dichlorocarbene during sonolysis is important for confirming the mechanism of the formation of tetrachloroethylene. The self-reaction of dichlorocarbene is a likely pathway for the formation of tetrachloroethylene. In addition, the selfcoupling reactions of dichlorocarbene and trichloromethyl radicals indicate that both species maybe present in excess of gas-phase oxidizing species, such as hydroxyl radical.

The weak correlation of the apparent first-order degradation rate constant with the initial concentration suggests that, despite the high concentration of CCl<sub>4</sub> in the interior of the imploding bubble, the final collapse temperature is not significantly reduced at higher solution concentrations. Furthermore, although ozone should also decrease the final collapse temperature because of its lower polytropic index ( $K_{O_3} = 1.2$  vs  $K_{Ar} = 1.66$ ), it does not appear to have a significant effect when mixed in the proportion used during this investigation. The influence of the nature of the saturating gas on the temperature at the center of a collapsed cavitation bubble is given by

$$T_{\max} = T_{o} \left\{ \frac{P_{m}(K-1)}{P} \right\} = T_{o} \left( \frac{R_{o}}{R_{\min}} \right)^{3(K-1)}$$
 (24)

where  $T_{\rm o}$  is the temperature of the bulk solution, *K* is the polytropic index of the cavity medium, *P* is the pressure in the bubble at its maximum size, and  $P_{\rm m}$  is the pressure in the bubble at the moment of transient collapse (*85, 86*). The effect on sonochemical degradation rates of variable Ar/O<sub>3</sub> mixtures should be similar to variations in Ar/O<sub>2</sub> mixtures, which results in a maximum rate of I<sup>-</sup> oxidation at a discrete mixture proportion, 70% Ar/30% O<sub>2</sub> (*87*).

Multicomponent wastestreams are a more realistic matrix to consider for practical treatment situations. The sonication of a mixture of CCl<sub>4</sub> and *p*-NP results in the enhancement of *p*-NP degradation and demonstrates that ultrasound is not limited to single-solute solutions. Because of the variety of reaction pathways and reactive regions that occur during cavitation, competition between different solutes is minimized. The effect of CCl<sub>4</sub> in a mixed wastestream is particularly interesting because it releases a residual oxidant, which can continue to attack other refractory molecules in solution, after the ultrasonic irradiation is halted.

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