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Ultrasound and Environment: Sonochemical Destruction of Chloroaromatic Derivatives

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Propagation of an ultrasonic wave in a water generates the cavitation bubbles, which behaving like microreactors are the center of a high-energy phenomenon leading to destruction of organic pollutants. In this work, a comparative study conducted with chlorobenzene and 4-chlorophenol as models for hydrophobic and hydrophilic substrates, respectively, clearly shows the two sites where the sonochemical reactions can occur. As ultrasonic frequency may alter noticeably the reaction rates, the experiments were conducted at 20 and 500 kHz. The dechlorination yields were found to be higher with the 500-kHz ultrasonic source than with the common 20-kHz probe. For chlorobenzene (ClBz), the reaction proceeds expeditiously, chlorine is quantitatively recovered as chloride ions, and 44% of the carbon atoms are recovered as CO and CO_2. The rate of disappearance of starting material, Cl^- release, and intermediate and final products provide some evidence of a reaction occurring thermally inside the cavitation bubble. 4-Chlorophenol (4-ClPh) degradation occurs at a lower rate. Cl^- release and formation of hydroxylated intermediates are evidence of a two-step reaction involving the $^{\bullet}OH$ radical outside the cavitation bubble. The consequences are important for water containing both 4-ClPh (0.5 mM) and ClBz (0.5 mM). ClBz degrades first; 4-ClPh transformation starts only when ClBz concentration reaches a low level (0.02 mM). The sonochemical treatment appears to be particularly efficient for the destruction of volatile chloroaromatic hydrocarbons (1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,3,5-trichlorobenzene, 1-chloronaphthalene).

Introduction

Since 1990, there has been an increase of interest in the use of ultrasound to destroy organic contaminants present in water, and the scaleup of the corresponding technology is currently under development (*1−3*).

The center of the sonochemical activity is the cavitation bubble which, during pulsation and/or collapse, is the site of high-energy phenomenon (*4−7*). The nature of these phenomena is not clearly defined, but depending on physical and chemical characteristics of the substrate, sonochemical products are identical to those obtained under pyrolytic or radiolytic conditions (*8−10*).

It can be schematically stated that compounds with a high vapor pressure can enter the bubble where they undergo thermolytic reactions (*11, 12*). On the other hand, hydrophilic compounds are much less prone to volatilization and undergo preferential hydroxylation reactions out of the bubble either in the limit layer or in the bulk solution. The hydroxylating agent, the $^{\bullet}OH$ radical itself, is generated according to eq 1 by water sonolysis (*13, 14*):

$$H_2O \rightarrow H^{\bullet} + {}^{\bullet}OH \qquad (1)$$

Successful results were obtained for the destruction of aliphatic and aromatic compounds (*15−17*), but in most cases, little information is available concerning the products resulting from a sonochemical treatment. This is the case for chloroaromatics, which degrade and release chloride ion upon ultrasonic treatment (*18−23*). In any case, no satisfactory connection exists between the degradation rate and the chloride ion mass balance, and little is known about the fate of the aromatic ring itself.

To bring more details on the sonochemical destruction of chlorinated phenyl compounds, this work will focus on the chlorobenzene degradation at 20 and 500 kHz. Findings will be compared with those obtained from experiments run with 4-chlorophenol. Complementary results obtained with diverse aromatic halides (1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,3,5-trichlorobenzene, 1-chloronaphthalene) are also reported in this paper.

Experimental Section

Reactions were conducted in deionized water equilibrated with air using the 20 and 500 kHz equipments previously described (*24*). The radiating surface is the same at both frequencies: 4.9 cm^2. The ultrasonic power dissipated in the medium (30 W) was estimated calorimetricaly (*25*). Reagent grade compounds were used as received and were dissolved upon stirring (15 h).

To avoid the problems resulting from the high vapor pressure of chlorobenzene, the headspace of the reactor is small (100 mL) and connected to a gas buret to ensure a constant pressure. The initial concentrations and temporal evolution were determined by high-performance liquid chromatography using a Waters equipment (model 600 pump, absorbance detector 486). Separations were achieved on a Spherisorb column (250 mm × 4.6 mm, 5 μm, ODS2) with CH_3CN/H_2O mixtures: chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1-chloronaphthalene (CH_3CN/H_2O: 80/20); chlorophenol, (CH_3CN/H_2O: 60/40). Calibration curves were drawn using standard solutions in methanol.

Chloride ion was determined with a ILC-1 Waters ion-liquid chromatograph equipped with an Alltech Universal Anion column, using a benzoate eluent (10^{-3} M) adjusted at pH = 6 with LiOH. Hydrogen peroxide concentration was determined iodometrically (*26*).

Gaseous products were separated isothermally at 40 °C with a Hewlett-Packard (HP 6890) gas chromatograph equipped with a flame ionization detector and a Poraplot Q column (10 m × 530 μm). Identification and characterization of the peaks were effected by comparison with gas standards.

Results and Discussion

Ultrasonic irradiation of an air-equilibrated water solution of chlorobenzene (250 mL, 5×10^{-4} M) leads to the disappearance of the aromatic halide with quantitative formation of chloride (Figure 1). As it was generally observed, the rate of the reaction is higher at 500 kHz than at 20 kHz

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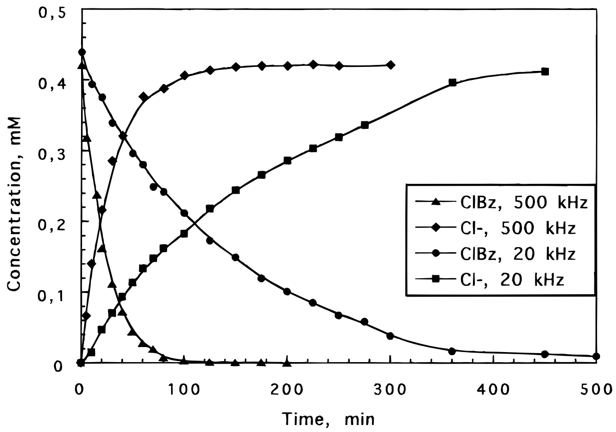


FIGURE 1. ClBz and Cl^- concentration evolution with ultrasonic treatment time (volume: 250 mL, ultrasonic power: 30 W, temperature: 20 °C).

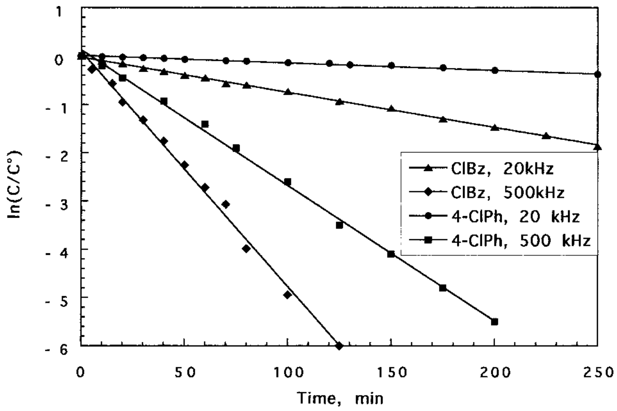


FIGURE 2. First-order plot of 4-ClPh and ClBz decay at 20 and 500 kHz. Ultrasonic power: 30 W.

for the same ultrasonic power (*24, 27, 28*). Our experimental data give for the initial rate at 20 kHz of 2.5 μM min^{-1} and of 11.2 μM min^{-1} at 500 kHz. In both cases, degradation follows a pseudo-first-order kinetic law (Figure 2). The rate constants were determined from the slope of ln $[C/C_0]$ versus time plot: $k_{20\ \mathrm{kHz}} = 1.2 \times 10^{-4}$ s^{-1}; $k_{500\ \mathrm{kHz}} = 8.1 \times 10^{-4}$ s^{-1}. In agreement with previous investigations, the ultrasonic treatment leads to the cleavage of the carbon chlorine bond, but in this work, we point out the quantitative mineralization of the halogen. During the course of the reaction, trace amounts ($<10^{-6}$ M) of phenol and 4-chlorophenol were detected. These compounds appear to be minor products of the reaction, which provides mainly gaseous compounds (Figure 3).

An evolution of carbon monoxide and acetylene follows the chlorobenzene disappearance. These clearly are the first kinetically stable products of the sonochemical destruction, with carbon dioxide appearing only in a second step. CO constitutes the first stable product on the multistep thermal degradation pathway, and acetylene should be formed by a thermolytic ring cleavage. The end of the gas evolution is concomitant to the end point of the chlorobenzene degradation, 44% of the carbon being recuperated. Afterward, no more gas is produced, but the CO_2 proportion increases to the expenses of CO and C_2H_2.

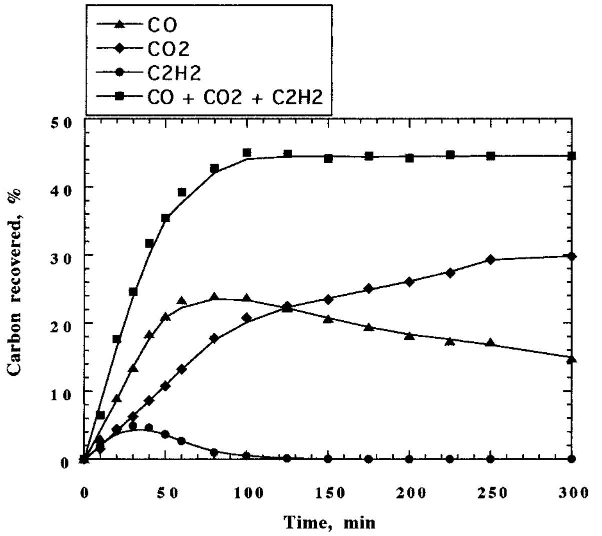


FIGURE 3. C_2H_2, CO, and CO_2 formation during ClBz ultrasonic treatment at 500 kHz (volume: 250 mL, ultrasonic power: 30 W, temperature: 20 °C).

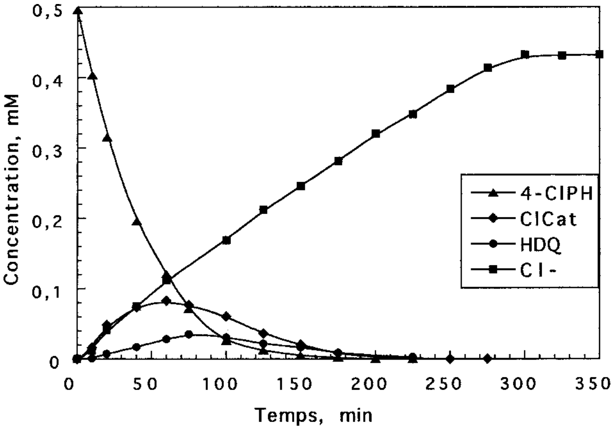
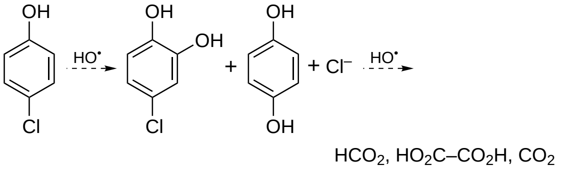
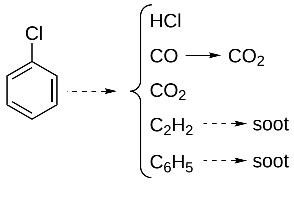


FIGURE 4. 4-ClPh, 4-chlorocatechol, hydroquinone, and Cl^- concentration evolution with ultrasonic treatment time (volume: 250 mL, ultrasonic power: 30 W, temperature: 20 °C).

SCHEME 1



SCHEME 2



Comparison of the behavior of chlorobenzene to that of 4-chlorophenol under the same experimental conditions provides another set of data (Figure 4). If the reaction follows the same pseudo-first-order kinetic law ($k_{20\ \mathrm{kHz}} = 0.26 \times 10^{-4}$ s^{-1}, $k_{500\ \mathrm{kHz}} = 4.85 \times 10^{-4}$ s^{-1}) (Figure 2), it proceeds at a slower rate, and the Cl^- release does not match the 4-chlorophenol decay. Hydroxylated intermediates including hydroquinone and 4-chlorocatechol are detected in higher yield. The final products (formic acid, oxalic acid and carbon dioxide) are found only in small amounts (15% of the initial carbon being recovered after 500 min).

Taking into account the reaction intermediates and final products, the sonochemical degradation of 4-chlorophenol

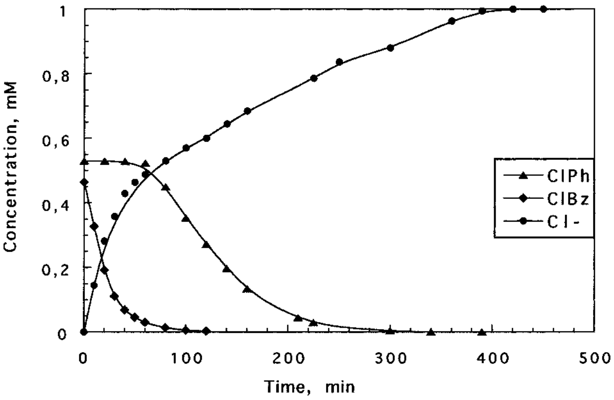


FIGURE 5. 4-ClPh, ClBz, and Cl$^-$ evolution with time. Simultaneous treatment of ClBz (0.5 mM) and 4-ClPh (0.5 mM) at 500 kHz.

TABLE 1. Initial Concentration and Chloride Yield after 150-min Irradiation for Degradation of Chloroaromatics[a]

chloroaromatic	concn (mM)	yield of Cl$^-$ (%)
1,2-dichlorobenzene	0.4	90
1,3-dichlorobenzene	0.05	89
1,4-dichlorobenzene	0.2	95
1,3,5-trichlorobenzene	0.02	95
1-chloronaphthalene	0.04	98

[a] Volume treated, 250 mL; ultrasonic power, 30 W; electric power, 50 W; frequency, 500 kHz.

at this concentration can be characterized as a stepwise reaction that is initiated by the collapse of the bubble. First step (eq 1) leads to the formation of hydroxyl radicals in the cavitation bubble. $^\bullet$OH radicals are then dispersed and react with organic substrate in the liquid layer surrounding the cavity (Scheme 1). The evolution of the starting compound, the nature of the intermediates, and the end products formation is consistent with a chemistry involving formation and reaction of $^\bullet$OH radical. Such a description agrees with similar schemes proposed earlier by Sehgal, Riesz, Serpone, Hoffmann for hydrophilic compounds (*13, 17, 29, 30*).

Chlorobenzene is found to behave differently. The chloride ion evolution, the low level of hydroxylated intermediates, the formation of gaseous products (CO_2, CO, C_2H_2) are elements that all suggest a preferential thermal degradation inside the cavitation bubble (Scheme 2). This is consistent with the first-order pyrolysis model proposed by De Vissher et al. for monocyclic aromatic compounds (*31*). In addition, products characteristic of the reaction (carbon monoxide, carbon dioxide, acetylene, HCl) are gases obtained experimentally in gas-phase flameless oxidation of chlorobenzene (*32, 33*).

A total carbon mass balance was not obtained, but some brown carboneous particles can be separated by filtration from the reaction mixture. This is consistent with soot formation under pyrolytic conditions. Soot can be formed through phenyl radical combination or C_2H_2 reactions at high temperature as evidence by Hart et al (*34*).

The consequences of the existence of these two different pathways are of importance for the treatment of a wastewater containing these two kinds of pollutants. Figure 5 presents the double sequence of the degradation of a medium containing both 4-chlorophenol and chlorobenzene. In the first stage, chlorobenzene degrades, with the transformation of 4-chlorophenol starting only when the concentration of the chlorinated hydrocarbon is less than 0.02 mM. This result shows clearly that the presence of compound with a high vapor pressure (Henry's law constant for chlorobenzene = 3.77×10^{-3} atm m^3 mol^{-1}) hinders efficiently the degradation of less volatile solute (Henry's law constant for 4-chlorophenol = 2.4×10^{-3} atm m^3 mol^{-1}) (*35*), but this inhibition must not to be considered as an inhibition of cavitation. In the bubble, the chlorobenzene degradation takes the place of the $^\bullet$OH formation according to eq 1.

Several chloroaromatic hydrocarbons were submitted to sonochemical degradation to check the possible extensions of the technique (Table 1). In the case of the compounds tested, the determination of the chloride concentration and the evolution of starting material concentration indicate that a complete destruction is achieved in 150 min and then the effectiveness of the method is demonstrated.

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