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Characteristics of Pentachlorophenolate Degradation in Aqueous Solution by Means of Ultrasound

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■ This work describes the sonochemical degradation at 530 kHz of pentachlorophenolate (PCP) in aqueous solutions saturated with different gases: air, oxygen, and argon. The main features of the sonochemical transformation are as follows: fast cleavage of the carbon-chlorine bond releasing Cl^- , mineralization of PCP to CO_2 when the solution is saturated with air or oxygen, CO production if argon is the saturating gas, nitrite and nitrate formation when the reaction is conducted with aerated solutions. It has also been shown that PCP disappearance is followed by a decrease in the toxicity of the medium for the green algae *Scenedesmus subspicatus*.

Introduction

Ultrasonic waves in a liquid induce the formation of cavitation bubbles. Submitted to an oscillating pressure field, cavities filled with vapor and dissolved gas(es) pulsate, grow, and implode violently when they reach a critical resonant size (1, 2). The collapse of a bubble occurs in such a short period of time [less than the compression cycle (3, 4)] that the temperature inside the bubble reaches thousands of degrees (K) and the pressure several hundreds bars (5–7). Under these extreme conditions, molecules vaporized in the bubble as well as compounds present in the surrounding condensed layer undergo reactions comparable to those found in high-temperature combustions (8–13).

It has been proved that sonication of water saturated with argon produces its sonolysis into $\cdot\text{OH}$ and $\cdot\text{H}$ radicals (eq 1). When oxygen is the saturating gas, sonication leads to O (eq 2) and $\cdot\text{OOH}$ is obtained at the expenses of $\cdot\text{H}$ (eq 3) (14–17). These reactive species are available in the medium for reactions with compounds dissolved in solution (18).



Oxidative species from different sources are used to degrade toxic organic pollutants present in water. They are produced in different ways, among them, photolysis, radiolysis, hydrogen peroxide decomposition, and ozone reaction (19–26). Ultrasonication, which is able to provide such reactive intermediate, has shown some efficiency in the degradation of organic pollutants present in water (27–30). In this work, we have studied the ultrasonic wave effect on the degradation of pentachlorophenolate (PCP) at 530 kHz. At this frequency, oxidative processes induced by ultrasound give better yields in comparison with results obtained with the usual equipment operating at 20 kHz (31, 32).

PCP was chosen as a model because it belongs to the class of aromatic halides that have to be removed from

waste water. By itself, it is still a widely used compound for wood treatment and it exhibits a high toxicity (33–35).

Experimental Section

Ultrasonic irradiations were performed at $24 \pm 1^\circ\text{C}$. The reactor was made of a glazed titanate-lead zirconate disk transducer (diameter 4 cm) fixed at the bottom of a cylindrical tube (diameter 5 cm) and equipped with a thermostated jacket (27). Temperature was controlled with the help of a thermocouple immersed in the reacting medium. The system is operated at 530 kHz with a 20-W high-frequency electrical power source. Ultrasonic intensity determined by a calorimetric method (36) was 1.06 W/cm^2 .

PCP (0.5 M) was prepared as stock concentrated solution from equimolar pentachlorophenol (99%, Fluka) and NaOH. Experiments were performed at $\text{pH} = 7$ in 10^{-3} M phosphate buffer medium with 10^{-4} M PCP solutions. The irradiated volume (100 mL) was continuously bubbled with gas through a gas dispersion fritted disk at a 25 mL/min flow rate. The sonication was stopped at periodic intervals, the medium was analyzed for gases, ions, and PCP, and its toxicity was determined. For the detection and the analysis of gaseous products, the reactor was closed after 30-min saturation with gas and connected to a gas buret to ensure a constant pressure (1 atm).

Chloride, nitrite, and nitrate were determined with a ILC-1 Waters ion-liquid chromatograph on an IC-Pak anion column using a sodium borate-gluconate eluent. A Waters HPLC apparatus with a Spherisorb ODS2 (5 μm) column ($4.6 \times 250 \text{ mm}$) was used for PCP quantification. The eluent was a mixture of aqueous 10^{-3} M phosphoric acid and methanol in the volume ratio 25/75. Detection was made at 254 nm using a Model 440 absorbance detector.

Gas analysis was performed on a Delsi 330 chromatograph equipped with a Porapak Q, $2 \text{ m} \times 2 \text{ mm}$ i.d. column. Identification and quantification of the peaks was effected at 50°C by comparison with pure gas standards.

ESR measurements were made on a Varian E112 spectrometer operating in the 100-kHz X band.

Acute toxicity was evaluated with algal assay according to French standard methods (AFNOR T90/304). *Scenedesmus subspicatus* population was exposed for 5 days in a static subsystem to the series of samples from the aqueous degradation solutions of PCP. Two modifications were made to the procedure: the response of the population growth was measured in terms of changes in absorbance at 685 nm (maximum of absorbance) and the culture medium was a 1/10 Hoagland's solution, more suitable for our experiments. Results are expressed in percentages of a control population growth.

Results and Discussion

PCP Degradation in Aerated Solution. As shown in Figure 1, when PCP solution (10^{-4} M) under continuous air bubbling is submitted to ultrasound effects, the characteristic (248, 317 nm) absorption bands decrease and the treatment leads to a complex mixture of products. By

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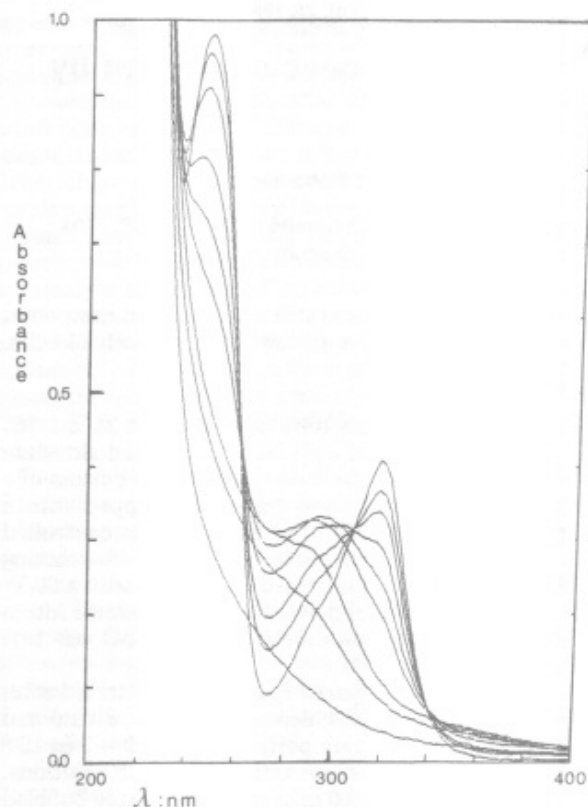


Figure 1. Change of absorption spectra during sonication at 530 kHz of aerated solution of PCP (pH = 7).

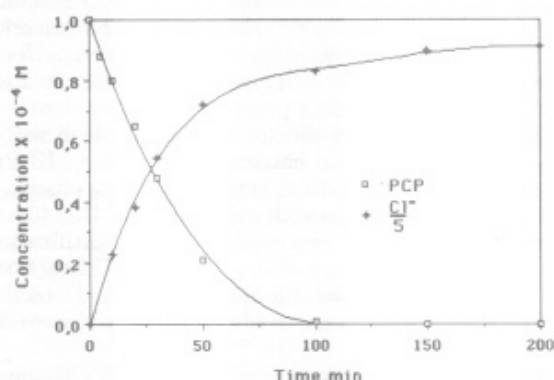


Figure 2. Kinetics of PCP disappearance and Cl^- formation during sonication of a continuously aerated PCP solution (10^{-4} M, pH = 7).

monitoring the PCP disappearance with HPLC, one can observe that its concentration becomes less than 10^{-6} M after 100-min sonication (Figure 2). Carbon-chlorine bonds are rapidly cleaved, and after 150-min sonication time, 90% of the chlorine is recovered in the solution as chloride ions.

PCP transformation in aerated solution occurs together with nitrite and nitrate formation, as expected from literature data (37) (Figure 3). From fundamental studies (18, 38–40) the following pathways that explain nitrogen behavior in sonochemical conditions has been proposed: nitrogen inside the cavitation bubble reacts at high temperature with hydroxyl radicals and oxygen atoms to give nitrous oxide and nitrogen oxide (eqs 4–6). Oxygen atoms can be produced by oxygen dissociation (eq 2) or hydroxyl radical reaction (eq 7) (17). N_2O is unstable under the high-temperature conditions of the cavitation bubble and may be further transformed to NO (eq 8). NO is then oxidized to nitrite and nitrate, NO_2^- giving NO_3^- via its

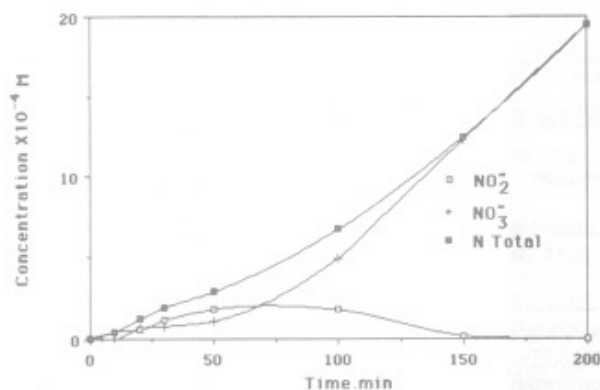


Figure 3. NO_2^- , NO_3^- , and $\text{NO}_2^- + \text{NO}_3^-$ formation during the sonication of a continuously aerated PCP solution (10^{-4} M, pH = 7).

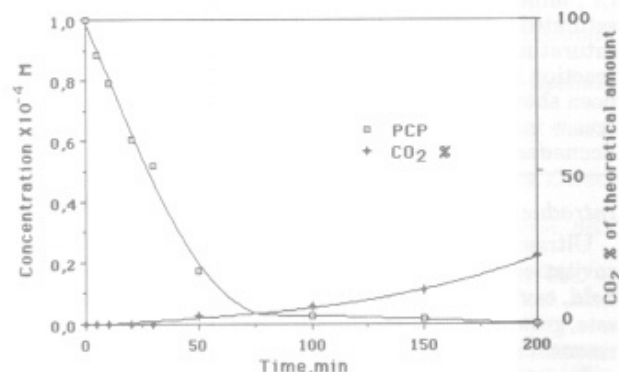


Figure 4. Kinetics of PCP disappearance and CO_2 formation during sonication of a PCP solution (10^{-4} M, pH = 7) previously saturated with air.

oxidation with hydrogen peroxide, a product of water sonolysis (eq 9).



Carbon dioxide is a product of PCP degradation. The CO_2 production can be shown under different experimental conditions. After saturation with air, the reactor is connected to a gas buret and the gas evolution analyzed by periodical withdrawal of the gaseous atmosphere. CO_2 is the only gas detected. Its first detection is after 50 min of reaction, and its yield reaches 22% of the theoretical amount after 200 min (Figure 4). It must be noted that in this experiment, in comparison with the results presented in Figure 2, it is difficult to degrade the residual amount of PCP from the solution. This observation points out an important phenomenon that occurs when sonication is run in a closed system. CO_2 is a product of the PCP degradation, and it has long been recognized as an inhibitor for sonochemical reactions (13). So an incomplete removal of this gas in the medium due to the absence of bubbling will slow down the degradation processes.

PCP Degradation in Solutions Saturated with Argon or Oxygen. Sonochemical reactions are strongly affected by ambient gas because the temperature inside the collapsing bubble is in close relationship with the polytropic ratio (C_p/C_v) and the thermal conductivity of the

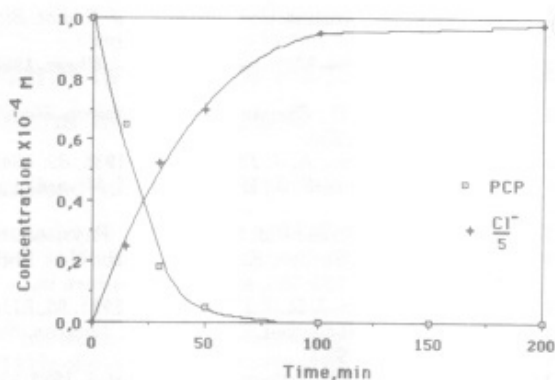


Figure 5. Kinetics of PCP disappearance and Cl^- formation during sonication of a PCP solution (10^{-4} M) continuously bubbled with oxygen at pH = 7.

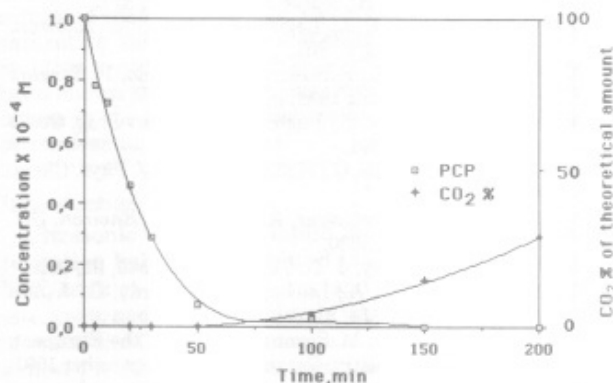


Figure 6. Kinetics of PCP disappearance and CO_2 formation during sonication of a PCP solution (10^{-4} M, pH = 7) previously saturated with oxygen.

gas (1, 7). In addition, and as noted above, the reactions with gases like O_2 , N_2 , and CO_2 are directly affected by the high temperature reached during the collapse of the bubble. In some cases they are able to undergo reactions with the products of water sonolysis. As a consequence, reactive species available for PCP degradation and their rate of production will depend on the nature of the gas.

By means of spin-trapping reagents in ESR experiments, Riesz et al. (14, 15) found (at 20 kHz and 1 MHz ultrasonic frequencies) that radicals which escape into the solution are $\cdot\text{OH}$ and $\cdot\text{H}$ when argon is the saturating gas but only $\cdot\text{OH}$ is evidenced with oxygen. In the same way we have seen that at 530 kHz both $\cdot\text{OH}$ and $\cdot\text{H}$ are trapped by 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) in an argon atmosphere and only the $\cdot\text{OH}$ radical adduct is observed under oxygen. In this latter case, $\cdot\text{H}$ does not escape into the medium because it reacts with O_2 in the bubble or in the layer surrounding the bubble (16) (eqs 3 and 10).



Degradation of PCP occurs rapidly when the solution is flushed with oxygen, and Cl^- is recovered in high yield (98%) (Figure 5). Without gas bubbling in a closed system, it should be noted, as previously seen, that degradation efficiency is lowered. Reaction releases CO_2 in 29% of the theoretical yield (Figure 6).

Under argon bubbling, the degradation is faster than under air or oxygen; no PCP is detected after 50-min sonication (Figure 7). Without bubbling it is difficult to bring the reaction to completion, and if CO_2 is the first gas evolved, it is rapidly substituted by CO (Figure 8). This result agrees with literature data, where it has been reported that degradation under argon of organic compounds

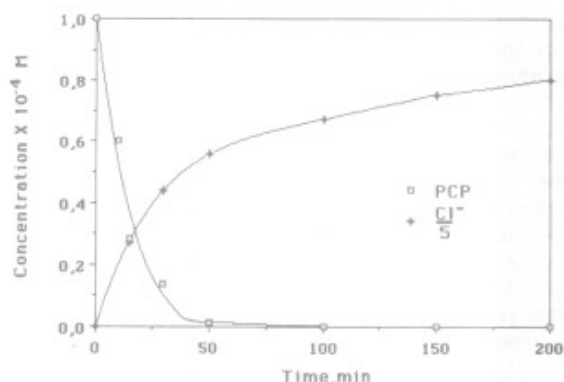


Figure 7. Kinetics of PCP disappearance and Cl^- formation during sonication of a PCP solution (10^{-4} M) continuously bubbled with argon at pH = 7.

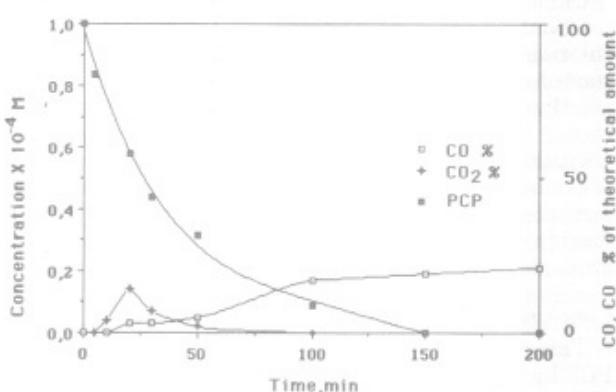


Figure 8. Kinetics of PCP disappearance and CO_2 and CO formation during sonication of a PCP solution (10^{-4} M, pH = 7) previously saturated with argon.

Table I. Growth Inhibition of *Scenedesmus subspicatus* versus Sonochemically Degraded 10^{-4} M PCP Solution Saturated with Different Gases*

time, min	air	toxicity, %	
		oxygen	argon
0	100	100	100
5	100	100	100
10	100	100	100
20	100	100	100
30	100	94	62
50	100	53	31
100	15	31	12
150	10	17	12
200	9	8	11

*Results are expressed as percentage of a control.

leads mainly to CO (43). It has also been demonstrated that CO is produced when water is sonicated under an atmosphere of argon that contains CO_2 (39). From these experiments it was postulated that, because of the high temperature inside the cavitation bubble, CO_2 is transformed to CO as observed in high-temperature chemistry (eqs 11 and 12) (44).



Acute Toxicity of the Solutions. The toxicity of solutions flushed with air, oxygen, and argon was checked by mean of a test conducted with the green algae *Scenedesmus subspicatus*. Results are reported in Table I. According to the PCP degradation, the decrease of toxicity

appears more rapidly for an argon atmosphere than for air or oxygen. There is no increase due to newly formed degradation products as seen with ozone treatment (45). The weak toxicity observed after 200-min irradiation may result from residual PCP because EC_{50} growth for *Scenedesmus* species ranges from 3×10^{-7} to 7.5×10^{-6} M (46). Other chlorophenols expected during the course of the reaction may be also responsible for this remaining toxicity.

Sonoreaction Location. The central phenomenon of sonochemistry in homogeneous media is cavitation. Consequently a sonochemical reaction is a highly heterogeneous reaction in which reactive species and heat are produced from a well-defined reactor, "the bubble of cavitation". Depending on their physical properties and concentrations, molecules present in the medium will be "burned" in, be close to the bubble or will undergo radical reactions.

Our results are consistent with the scheme of radical reactions occurring most probably in the solution because chloride appears very soon after the sonication has been started and CO_2 evolution appears after a lag time. If the reaction takes place inside the bubble, these compounds should be produced together from the beginning of the reaction. On the other hand, because they are products of combustion reactions, gaseous derivatives like acetylene, methane, and ethane should be formed along with carbon dioxide. Such results are obtained from the sonication of aromatic compounds (47, 48).

Conclusion

This work provides information on the destruction of PCP by the use of ultrasonic waves. Several characteristics of the sonochemical treatment have been pointed out, such as the involvement of the saturating gas and the experimental conditions. Our results demonstrate that the application of this technique can be envisaged as a way to treat toxic wastes present in water because it mineralizes organic derivatives, offering thus an alternative solution competing with other methods.

Registry No. CO_2 , 124-38-9; Ar, 7440-37-1; O_2 , 7782-44-7; CO, 630-08-0.

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