Sonochemical Degradation of Phenol in Dilute Aqueous Solutions: Comparison of the Reaction Rates at 20 and 487 kHz

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The degradation of phenol in aqueous solution by means of ultrasound was performed at two frequencies: 20 and 487 kHz. Using the same acoustical power (30 W) determined by the calorimetric method, the treatment appears more efficient for the higher frequency. The initial rates were found to be dependent on the initial phenol concentration, reaching limit values $k_{20kHz} = 1.84 \times 10^{-6}$ M min^{-1}, and $k_{487kHz} = 11.6 \times 10^{-6}$ M min^{-1}. Identification of the first intermediates of the reaction (hydroquinone, catechol, benzoquinone) indicates that •OH is involved in the degradation pathways. Correlation with hydrogen peroxide formation in water saturated with air has shown that the rate of H_2O_2 formation is more elevated at 487 kHz ($k = 4.9 \times 10^{-6}$ M min^{-1}) than at 20 kHz ($k = 0.75 \times 10^{-6}$ M min^{-1}). It has been shown that the rate of sonochemical degradation is directly linked to the •OH availability in the solution. Using luminol as a probe to visualize the region where •OH radicals are produced, it was shown that there is a great difference between the ultrasonic field at the two frequencies.

Introduction

Propagation of an ultrasonic wave in liquid generates the formation of cavitation bubbles which can grow and implode under the periodic variations of the pressure field.[1−4] In water, implosion and fragmentation of the bubble which collapses are the center of high-energy phenomena; temperature, pressure, and electrical discharges giving rise to H_2O sonolysis with production of radical species (H•, •OH, HOO•) and direct destruction of solute.[5−17]

Ultrasound is then a source of radicals, especially the hydroxyl radical, •OH, the very strong and nonspecific oxidizing species which escapes out of the bubble and reacts rapidly with compounds in solution.[18−20]

In relationship with water treatment, there are several reports in the recent literature which describe the ultrasonic destruction of organic compounds in water.[21−31] Most of the work is performed with the help of the commercially available probe system working at 20 kHz,[32] but it has been demonstrated that for the same acoustical power the production rate of •OH is better at higher frequencies.[33−37]

In order to determine experimental conditions that could lead to the best reaction yields, we report a study of phenol degradation with two different ultrasound systems. One system operates at 20 kHz and uses a classical titanium horn. The other was built around a piezoelectric disc operating at 487 kHz.

Experimental Section

Materials. Phenol (Prolabo, 99%+), 3-aminophthalhydrazide (Lancaster, 98%), and other chemicals were used as received. 5,5-Dimethyl-1-pyrrolidine *N*-oxide (Aldrich, 97%) was distilled under vacuum.[37] Aqueous solutions were prepared by dissolving the compounds in deionized water.

Analytical Methods. Progress of the reactions was monitored by HPLC with a Waters Model 600E pump equipped with a 486 absorbance detector, using a Spherisorb 5 μm C18, ODS 2 column (250 × 4.6 mm). The intermediates of the ultrasonic degradation were identified by comparing their retention times with those of known standards. Eluent consisted of a CH_3CN/H_2O (35/65) mixture containing acetic acid (1%).

Gas chromatography analyses were performed on an Intersmat apparatus using a FID detector and a 2.5 m Porapak column.

Electron spin resonance (ESR) measurements were performed on a Varian E 112 spectrometer operating in the 100 kHz X band. A circulating system connects the sonochemical reactor to a quartz flat cell fixed in the cavity of the spectrometer.

Hydrogen peroxide concentrations have been determined iodometrically, using the method described by Kormann et al.[38] Aliquots of the irradiated water were added in the sample quartz cuvette of the spectrophotometer (Shimadzu, UV-2101 PC) containing the iodide reagent (potassium iodide, 0.1 M; ammonium molybdate, 10^{-4} M), and the absorbance was recorded versus time. With this procedure it was shown that there was no disturbance of the H_2O_2 determination by other products which may be formed during the sonochemical reaction (HNO_2, organic peroxides).

Photographs of the sonochemical-induced chemiluminescence of the 3-aminophthalhydrazide (luminol) were obtained from 10^{-3} M (pH = 10.5) luminol solution saturated with air. The camera was equipped with a 55 mm, *f*:1.8 lens and used Kodak films (1600 ASA). The exposure times range from 15 s to 1 min.

Apparatus. Reactions were performed at 25 °C in a cylindrical jacketed glass cell equipped with a Teflon holder,

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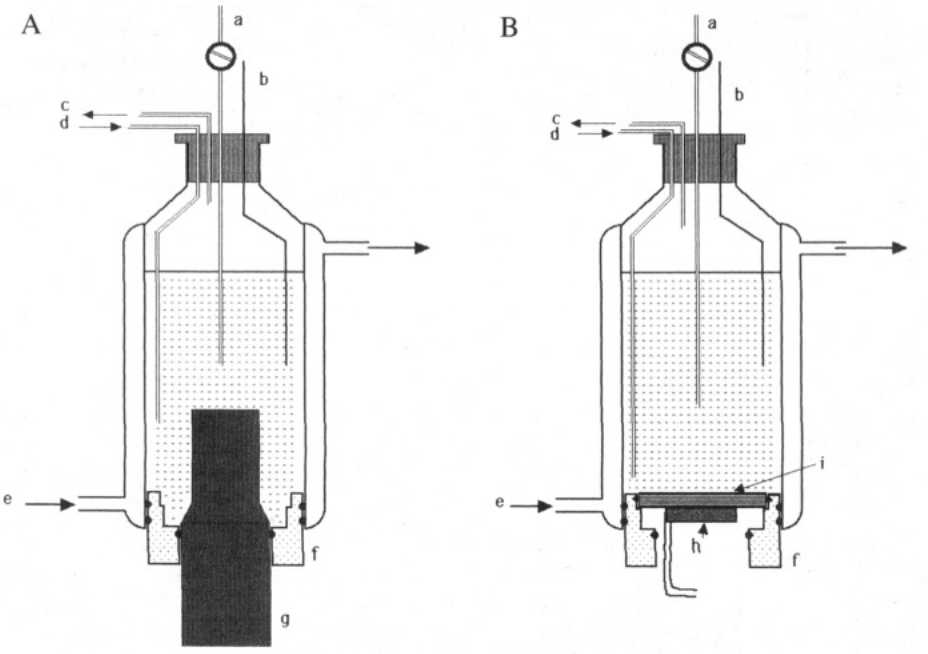


Figure 1. Schematic description of the ultrasonic setup: (A) 20 kHz equipment; (B) 487 kHz equipment; (a) sampling port; (b) thermocouple; (c) air outlet; (d) air inlet; (e) cooling fluid; (f) Teflon holder; (g) titanium probe; (h) ceramic transducer (diameter 2.5 cm); (i) stainless steel plate (diameter 5 cm). The reactor has an inner diameter of 6 cm.

which accepted the two different ultrasonic converters (Figure 1). The temperature was monitored with the help of a thermocouple immersed in the reacting medium. During the treatment, solutions were continuously sparged with air (30 mL/min). In all cases, 200 mL of solution were treated. For the detection and the analysis of gaseous products, the reactor was closed after 30 min saturation with air and connected to a gas buret to ensure a constant pressure (1 atm).

The 487 kHz ultrasonic wave was emitted from a ceramic titanate–lead zirconate disk transducer, diameter 2.5 cm (Quartz et Silice P 7/62), fixed on a stainless steel plate having a thickness of half a wavelength (5.84 mm). The system is driven by a homemade high-frequency power supply.

The 20 kHz irradiations were carried out with commercial equipment from Branson (Sonifier 450) equipped with a titanium probe (diameter 2.5 cm).

The ultrasonic power dissipated into the reactors was estimated by the calorimetric method in order to ensure comparative ultrasonic conditions at the two frequencies.[39,40] The same ultrasonic power, 30 W, was delivered at each run. Following the manufacturer chart, the electric power output was 70 W at 20 kHz, and 60 W were supplied to the 487 kHz piezoelectric emitter.

Results and Discussion

Phenol Degradation. Exposure of 200 mL of phenol solution (5×10^{-4} M) to ultrasound at 20 or 487 kHz shows a higher rate of loss for the higher frequency. In the two cases, hydroquinone (HQ), catechol (CC), and benzoquinone (BQ) are detected as primary intermediates of the degradation process (Figure 2). These results corroborate a few observations,[28,41] among them, the work of Chen et al., who earlier in 1966, working at 25, 55, and 800 kHz, found an ultrasound frequency effect on the rate of phenol degradation.[42]

Products other than HQ, CC, and BQ were not detected in the present work, but when the reactor was closed, analysis of the atmosphere showed CO_2 as the only final gaseous product (Scheme 1). At 20 kHz, 2% of the carbon theoretical amount was recovered in the gaseous phase after 300 min of treatment; 15% was found for the same irradiation time at 487 kHz.

Initial rates of degradation have been determined when the proportion of degraded phenol does not surpass 40% ($k_{20kHz} = 1.12 \times 10^{-6}$ M min^{-1}, $k_{487kHz} = 4.6 \times 10^{-6}$ M min^{-1}). After this point it is more difficult to define a kinetic law. This could be attributed to the competition between phenol and products of the reaction. The reaction was carried out with solutions of different initial concentrations ranging from 0.05 to 10 mM (0.05, 0.1, 0.23, 0.5, 1, 2.3, 5, and 10 mM). In each case, the initial rate of phenol degradation was determined. As shown in Figure 3, the rate is found to be dependent on the initial concentration, reaching a value limit of 1.84×10^{-6} M min^{-1} at 20 kHz and 11.6×10^{-6} M min^{-1} at 487 kHz.

Connections with $^{\bullet}$OH Production. The physical phenomena leading to sonochemical effects in water are complex and not yet fully elucidated. Nevertheless, whatever the theoretical model describing the origins of the molecular activation (thermal and/or electrical), the place where the molecules are brought to an excited state and dissociate is the interior of the bubble of cavitation, which is filled with gas and vapor.[13,14,16,43–49] In the case of water saturated with air, the first step appears to be the cleavage of water and the dioxygen molecule.[13,18,50–53]

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

$$O_2 \rightarrow 2O \quad (2)$$

Inside the bubble or in the liquid shell surrounding the cavity, these radicals can combine in various ways or react with gases and vapor present, leading to the detection in the medium of HNO_3, HNO_2, and H_2O_2.[54–61]

$$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O \quad (3)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow O + H_2O \quad (4)$$

$$O + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \quad (5)$$

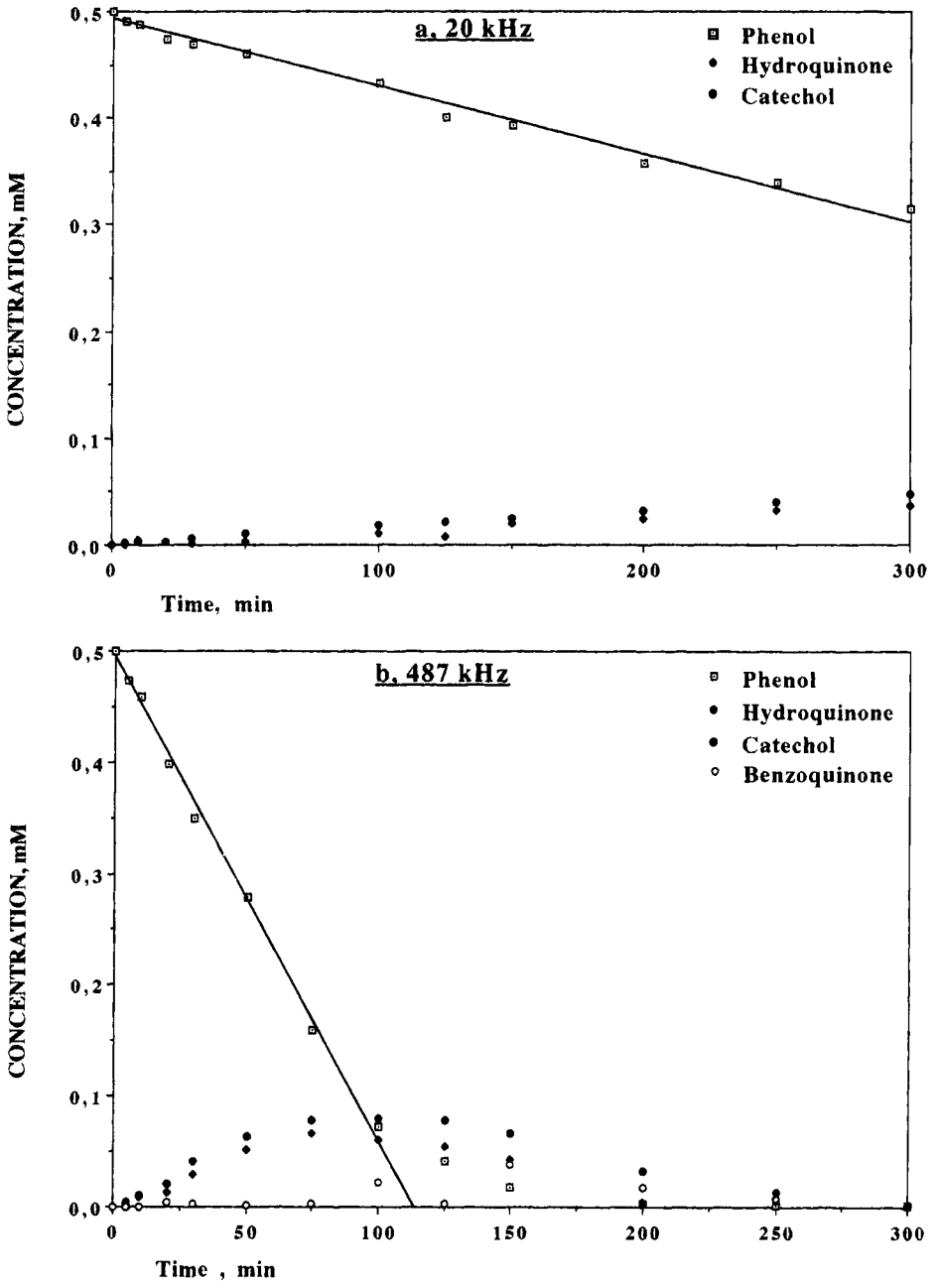


Figure 2. Concentration of phenol, hydroquinone, catechol, and benzoquinone as a function of insonation time: (a) 20 kHz; (b) 487 kHz.

$$H^{\bullet} + O_2 \rightarrow HOO^{\bullet} \quad (6)$$

$$H^{\bullet} + O_2 \rightarrow {}^{\bullet}OH + O \quad (7)$$

$${}^{\bullet}OH + N_2 \rightarrow N_2O \longrightarrow NO_2^-, NO_3^- \quad (8)$$

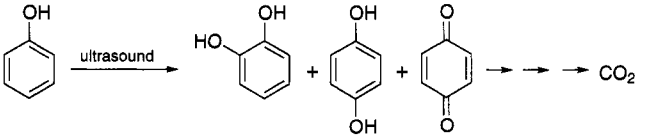
$$O + N_2 \rightarrow N_2O, NO, N \longrightarrow NO_2^-, NO_3^- \quad (9)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (10)$$

$${}^{\bullet}OOH + {}^{\bullet}OOH \rightarrow H_2O_2 + O_2 \quad (11)$$

Following the work of P. Riesz and colleagues, with the use of DMPO as spin trapping reagent, identification of the radicals escaping out of the bubble of cavitation has been performed in electron spin resonance (ESR) experiments.[18,20] In our case, for water saturated with air, in the absence of substrate, for the two frequencies, only the signal which corresponds to •OH trapping has been found (DMPO—OH), without any indication of the presence of H• or HOO• radicals. It has to be noted that for the specific hydroperoxyl radical case, DMPO—OOH has never been encountered in sonochemical conditions, even in water saturated with oxygen. Yet, in different papers this short-lived species was detected by its ability to bring about specific reactions.[60,62-63]

SCHEME 1: Products Detected during Degradation of Phenol in Aerated Aqueous Solution



The main fraction of the H_2O_2 formed during water sonolysis seems to come from the •OH and •OOH radicals, which combine in the bubble or in the layer surrounding the bubble of cavitation in the absence of substrate[19,64-65] (reactions 10, 11). The amount of H_2O_2 produced at each of the two frequencies was

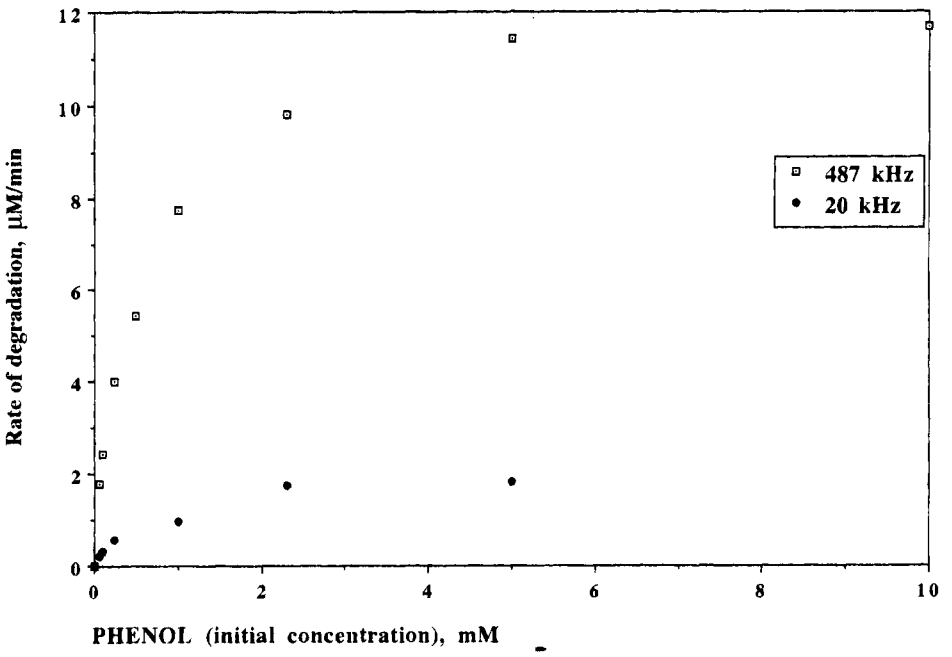


Figure 3. Initial rate of phenol degradation versus phenol initial concentration.

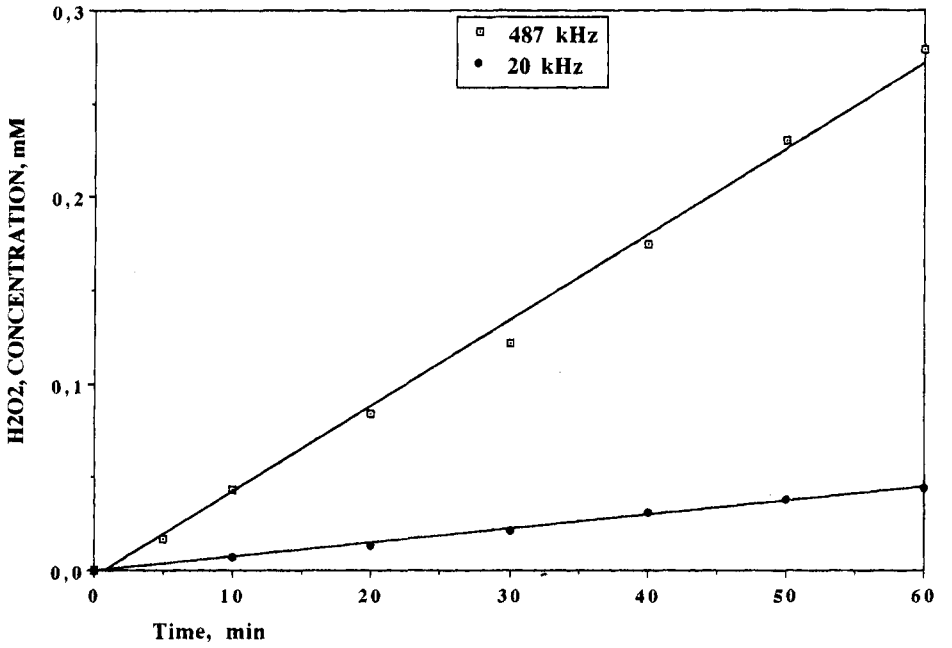


Figure 4. Concentration of H_2O_2 produced as a function of insonation time in aerated water.

determined (Figure 4). The concentration of hydrogen peroxide increases linearly vs time and the rate of formation was found higher at 487 kHz (4.9×10^{-6} M min^{-1}) than at 20 kHz (0.75×10^{-6} M min^{-1}). With these results in hand H_2O_2 production was examined in the presence of various concentrations of phenol at 487 kHz. Figure 5 shows that there is a close relationship between phenol degradation and H_2O_2 production. The hydrogen peroxide yield decreases when the phenol concentration increases. There is always H_2O_2 formation, this may be due to the fact that part of the hydrogen peroxide originates through reaction 11 and cannot be inhibited by phenol.

If it is assumed that the first step of the phenol degradation results from •OH radical reaction in a site close to the surface of the bubble, there is in this volume a competition between reaction 10 ($k = 5.5 \times 10^9$ L mol^{-1} s^{-1}), reaction 12 ($k = 6.6 \times 10^9$ L mol^{-1} s^{-1}), and reaction 13 ($k = 6.6 \times 10^9$ L mol^{-1} s^{-1}), which lowers hydrogen peroxide formation in the absence of substrate.

$$C_6H_5{-}OH + {}^{\bullet}OH \rightarrow C_6H_5(OH)_2 \qquad (12)$$

$$^{\bullet}OH + {}^{\bullet}OOH \rightarrow H_2O + O_2 \qquad (13)$$

We believe that if pyrolysis of phenol can occur in the interfacial area, it has only a minor contribution, because acetylene and methane, which are products of sonochemical destruction of volatile aromatic compounds, were not detected in this case.[5,6,66] In addition, phenol degradation is completely inhibited by *n*-butanol (5 mM).

The sonochemical phenol degradation which proceeds more rapidly at high than at low frequency can be related to a better release of •OH in the solution in the former case. The basis of this discrepancy is not yet well understood, but one can consider

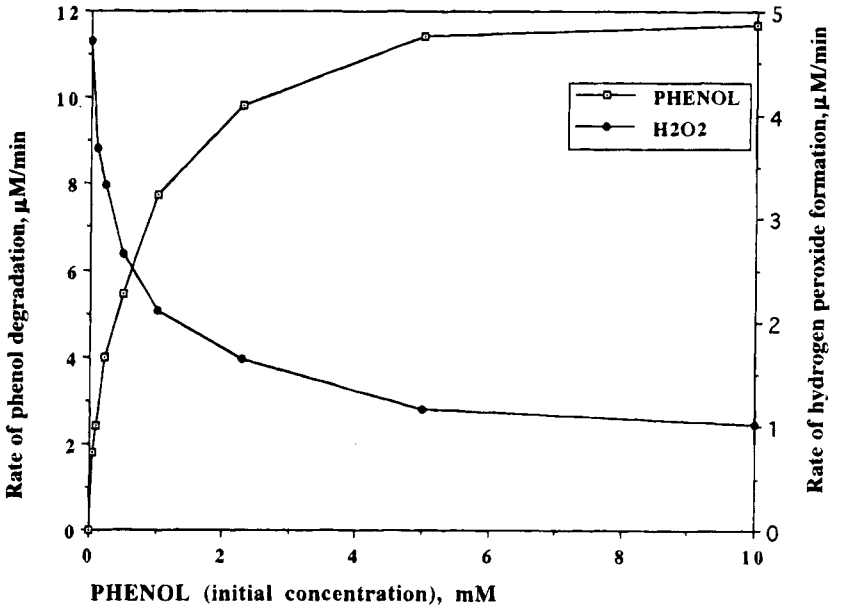
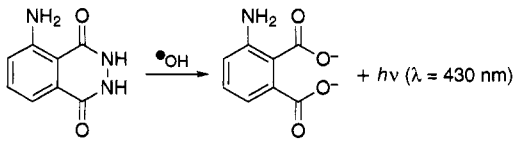


Figure 5. Initial rate of phenol degradation and rate of hydrogen peroxide formation as a function of different initial concentrations of phenol at 487 kHz.

SCHEME 2



some differences between the behavior of a 20 kHz and a 487 kHz bubble:[67] The more important cavitational effects occur when the frequency of the ultrasonic wave is equal to the resonance frequency of the bubble.[68] The resonance radius of a bubble excited at 20 kHz is 170 μm and 6.6 μm at 487 kHz. Besides, the duration of the collapse (less than one-fifth of a period of vibration) is shorter at 487 kHz (4.1×10^{-7} s) than at 20 kHz (100×10^{-7} s).[4,14,15,68] In such conditions, at high frequency, •OH radicals could be ejected more efficiently in the solution before they have time to combine in the bubble of cavitation.[36,43]

•OH Localization in an Ultrasonic Field. There are several reports in the literature which demonstrate that the sonochemical yields are related to the configuration of the reactor. For instance, iodide oxidation and carbon tetrachloride degradation were reported to proceed faster when a standing wave system is created in the column of liquid above the emitting surface.[69-71] Boucher has also emphasized the differences between high- and low-frequency ultrasonic field. The high-frequency wave generates a directive acoustic beam which induces convection currents and fountain effects at the surface of the liquid, the acoustic field being spread at low frequency.[67] In order to get more information on the alteration of the chemical yields induced by a change of the frequency, it was then of importance to determine where the site of the sonochemical reaction in the 20 and 487 kHz reactors was located. Since the •OH radical is the reagent involved in the sonochemical phenol degradation, the place where it is produced was studied with the help of sonochemically induced luminescence of luminol. In basic medium, luminol reacts with hydroxyl radicals, giving aminophthalate anions and a blue fluorescence[72-75] (Scheme 2).

Figure 6 shows the two very different patterns observed with this method for the two frequencies and confirms the earlier observations of Negishi.[76] In the two cases, the surface of the solution is heavily disturbed, which prevents the standing waves in the medium. At 20 kHz the luminescence is located on the surface of the titanium horn. At 487 kHz, most of the fluorescence originates from a wider volume close to the surface of the liquid, without any light at the suface of the emitter. It can be noted that modifications on the height of the liquid do not change the location of the luminescence zone nor the yield of phenol degradation.

One of the consequences is that handling the solution which has been treated with ultrasound is more convenient at 487 kHz than at 20 kHz. In the former case, as cavitation is located at the gas–liquid interface, there is no formation of particles coming from the erosion of the emitting surface.

The difference between the two reacting zones may be explained by considering the fact that cavitation is closely dependent on the frequency of the ultrasonic wave and on the amount of dissolved gas. To bring water into cavitation requires more energy at 487 kHz than at 20 kHz, and the threshold of cavitation is lower for water saturated with air than for degassed water.[67,68,71]

In our experimental conditions, the determination of the dissolved dioxygen concentration, after 20 min of irradiation, has shown that the ultrasonic degassing effect is more pronounced at high (5.2 mg/L) than at low frequency (6.8 mg/L). Consequently, at 20 kHz the cavitation occurs mainly at the surface of the emitter, where the amplitude of the pressure is maximum. The bubble cloud absorbs most of the energy and hinders the propagation of the wave. At 487 kHz the degassing effect could be important at the surface of the emitter, which increases the threshold of cavitation. Then the cavitation can take place only at the high disturbed gas–liquid interface, where the concentration of dissolved gases is higher than in the lower part of the reactor.

Localization and size of the zones of cavitation show different patterns which indicate changes in the concentration of efficient bubbles. Hence, the collapse time of the cavitation bubble is not the only occurrence which can have important consequential effects in the yield of a sonochemical reaction.

Concluding Remarks. The experimental data of this work demonstrated that the ultrasonic frequency has an important effect on the yield of the sonochemical degradation of phenol. Because of the complexity of the phenomenon, it appears difficult to provide a complete interpretation of the experimental

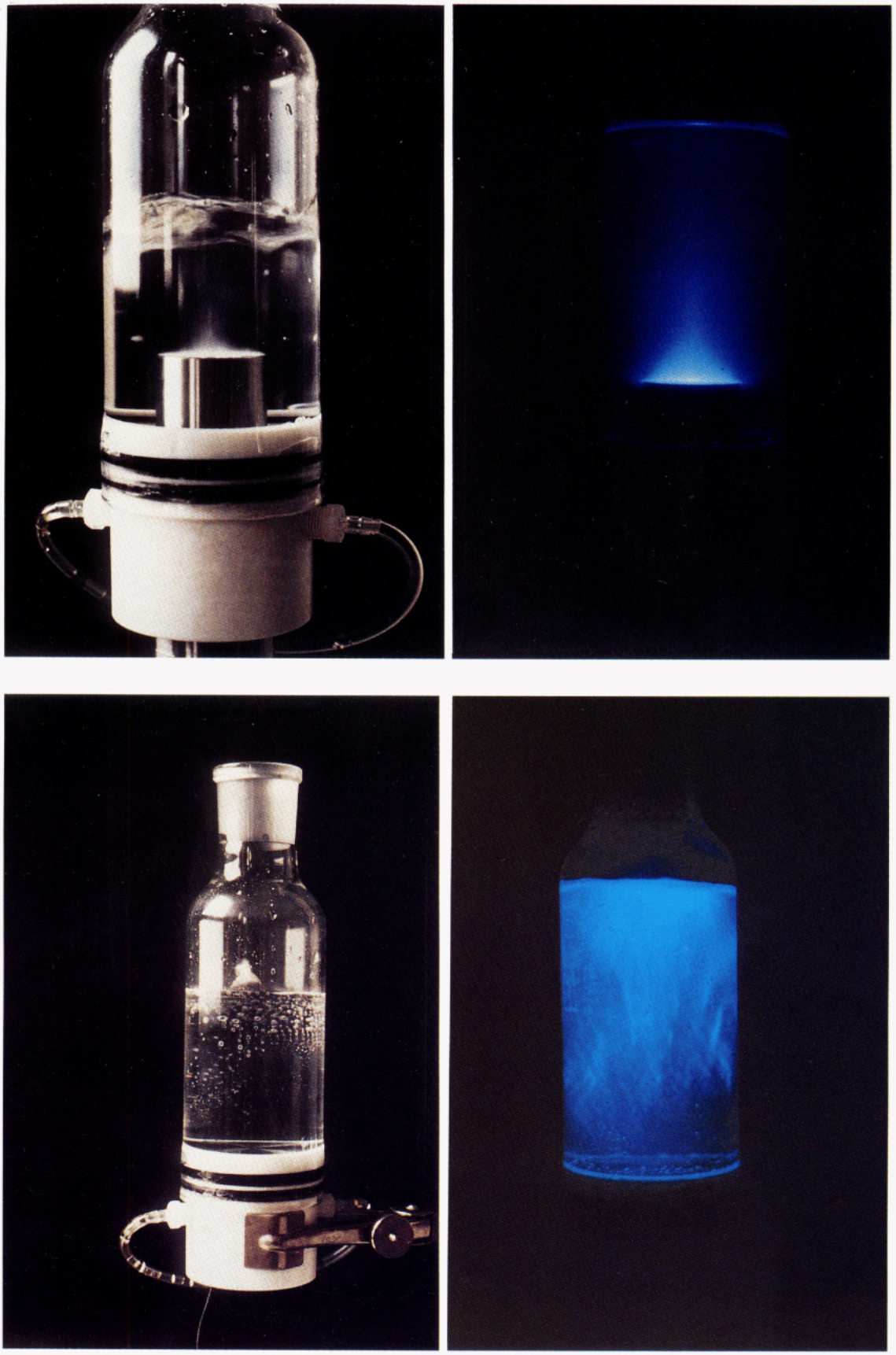


Figure 6. Sonochemical equipment and sonochemical-induced luminol luminescences at 20 kHz (a, top) and 487 kHz (b, bottom).

data. For economic considerations and from a fundamental point of view, studies of frequency effects seem to be of interest. We are currently building equipment at other frequencies to look at the behavior of compounds with different physical and chemical properties.

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