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Pulsed Sonochemistry

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Very few papers are devoted to the study of the chemical effects of pulsed ultrasound in the low-frequency range. The present work consists of a systematic experimental study of the effects of pulsed ultrasound in the 20 kHz range using an immersed titanium horn. The light scattered by the bubble cloud, the acoustic pressure, and the sonochemical activity were measured. The sonochemical activity was studied by measuring the light emitted by a fast chemiluminescent reaction (oxidation of luminol). The chemiluminescence behavior observed at 20 kHz was compared with the behavior observed at 1.7 MHz. The chemiluminescence takes time to install when sonication starts and, at 20 kHz, the luminescence intensity decreases monoexponentially when sonication stops. Interestingly, at 1.7 MHz, the luminescence intensity decreases biexponentially with an important fast component. The interpretation of these various behaviors requires that the acoustical characteristics of the ultrasound generator and of the vessel, and also the properties of the bubble field, be considered.

Introduction

Pulsed ultrasound in the high-frequency range (>1 MHz) is extensively used in medical diagnosis. Many papers devoted to the study of the sonochemical effects of pulsed ultrasound in this frequency range have been published during these past years.[1−11] For example, the rates of sonochemical reactions, like the formation of nitrite and nitrate[4,6] or iodide oxidation,[9] have been studied for various pulse lengths (T_{on}) and also for various $T_{\mathrm{on}}/T_{\mathrm{off}}$ ratios at constant acoustical energy. It was observed that for long pulse lengths, the yield was substantially equal to that obtained with continuous irradiation, regardless of the value of the $T_{\mathrm{on}}/T_{\mathrm{off}}$ ratio. However, with decreasing pulse length and for low $T_{\mathrm{on}}/T_{\mathrm{off}}$ ratios, a rapid decrease of the chemical yield was observed. On a qualitative basis, these results were explained by taking into account, on the one hand, the time required to "activate" the system at the start of the pulses (i.e., the time to reach the maximum chemical activity of the bubble cloud) and, on the other, the time required to "deactivate" the system after the end of each pulse (i.e., the time to reach the level of zero observable chemical activity). Depending on the $T_{\mathrm{on}}/T_{\mathrm{off}}$ value, the maximum activity of the bubble cloud is (i) obtained during each pulse, (ii) obtained after a few pulses, or (iii) never obtained (this situation occurs when T_{on} is shorter than the activation period and T_{off} longer than the deactivation period).[3−7,9]

By solving the Rayleigh−Plesset−Noltingk−Neppiras−Prosperetti (RPNNP) equation numerically, Leighton[12] predicted that at the start of insonation the violence of the collapse can be enhanced because the minimum volume reached by the bubbles is smaller than that expected during the steady-state motions. The temperature reached by the adiabatically compressed gas inside the cavities would therefore be higher. The study of the sonoluminescence of water under a 10 kHz pulsed irradiation seems to verify these predictions.[13] The intense flashes of sonoluminescence observed at the beginning of each pulse suggest that the conditions attained in the bubbles at the start of the irradiation are more drastic than those during steady-state irradiation.

On the whole, very few papers are devoted to the study of the chemical effects of pulsed ultrasound in the low-frequency range. The present work contains a systematic experimental study of the effects of pulsed ultrasound in the 20 kHz range using an immersed titanium horn. The light scattered by the bubble cloud, the acoustic pressure, and the sonochemical activity were measured as a function of time. The sonochemical activity was studied by measuring the light emitted by the fast chemiluminescent oxidation of luminol. This reaction was also studied under the influence of a 1.7 MHz pulsed wave in order to compare pulsed sonochemistry at high and low frequencies. The comparison of the two frequency domains is of particular interest in the general context of the origin of the frequency effect in sonochemistry.

Experimental Section

Physical Measurements. The bifrequency generator used for this work was a home-built Chemsonic instrument. An automatic frequency tracking system (used in the 20 kHz range) or an auto-oscillating loop (used in the 1.7 MHz range) lead to a good control of the stability of the electric power sent to the transducers. In both frequency ranges the typical value for the electric power used was 25 W. The electrical pulses produced by the Chemsonic generator consisted of a train of sinusoidal waves with a square envelope.

The experimental apparatus used in this study is given in Figure 1. The 20 kHz emitter was a 370 mm long titanium stepped horn with an emitter surface of 1 cm^2. The tip of the horn was placed at 75 mm from the bottom of the reaction cell. The 1.7 MHz emitter was a 4.5 cm^2 transducer placed at the bottom of the reaction cell in direct contact with the solution. The glass cell was equipped with three optic faces of 24 mm

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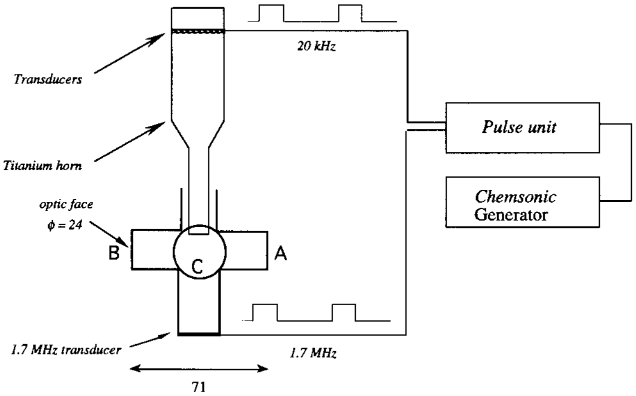

Figure 1. Experimental apparatus. All the measurements are in millimeters. A, B, and C correspond to the three optic faces of the reactor.

diameter and was filled with 105 cm^3 of solution. No temperature stabilization was necessary because of the large volume of the cell and the short duration of the experiments. All the experiments were performed at 20 ± 2 °C.

The light scattering measurements were performed using an experimental setup composed of a stabilized xenon lamp (300 W Osram Xm-300-5-H5), a monochromator (Applied Photophysics, f:1,4) and a five-stage photomultiplier (Applied Photophysics). The incident light ($\lambda = 450$ nm) was transmitted to the reactor through face A (Figure 1). The light scattered by the bubble cloud was detected by the photomultiplier through face C which is at 90° with respect to the incident light.

A Bruel-Kjaër hydrophone (model 8103) was used in the 20 kHz range to analyze the acoustic field. The response of the hydrophone is linear in the 0−100 kHz domain and its response time is 60 μs, a value much shorter than the characteristic times of the processes studied in this work. The fast Fourier transform (FFT) of the signal recorded in the time domain was obtained using a spectrum analyzer (PC Storage Oscilloscope 32 MS/s, Velleman).

The chemiluminescent signal produced by the oxidation of luminol, characterized by $\lambda_{max} = 425$ nm, was measured using a five-stage photomultiplier (Applied Photophysics). For the light scattering and the chemiluminescence measurements, a light-proof box was used to eliminate stray light sources. The response time of the five-stage photomultiplier was evaluated at 300 μs, a value much shorter than the characteristic times of the processes studied in this work.

The pulse unit of the Chemsonic instrument was used to trigger the spectrum analyzer and the photomultiplier.

Chemical Experiments. The chemiluminescent reaction studied was the oxidation of luminol (5-amino-1,2,3,4-tetrahydrophthalazine-1,4-dione) in a basic water solution at atmospheric pressure. 28 mg of luminol (Fluka) was dissolved in 1 dm^3 of distilled water adjusted to a pH of 10 with KOH. Solutions were prepared 12 h before use to ensure that all the luminol was dissolved.

In order to compare the chemiluminescent results at 20 kHz and at 1.7 MHz, a previously described relative method was used.[14] The power output at both frequencies was adjusted in order to obtain the same rate for the Weissler reaction[15] carried out under air. A reactor similar to the one used for the physical measurements but without the lateral extensions was used. It was filled with 50 cm^3 of a 0.1 M solution of KI in distilled water containing 10% of distilled water saturated in CCl_4. The iodide oxidation by $Cl^\bullet$ radicals or Cl_2 (products of the sonocleavage of CCl_4)[16,17] was followed by absorption spectroscopy (absorption band of I_3^- ($I_2 + I^-$) at 352 nm).

TABLE 1: Characteristic Times ($\tau^s$and τ^l) and Relative Intensities ($I^s$and I^l) of the Biexponential Decrease ($I(t) = I^s e^{-t/\tau^s} + I^l e^{-t/\tau^l}$) of the Intensity of the Light Scattered by the Bubble Cloud ($I = I_{scat}$), the Acoustic Pressure ($I = P_A$), and the Chemiluminescence Signal Recorded at 1.7 MHz ($I = I_{CL,1.7\ MHz}$). Characteristic Time (τ^l) of the Monoexponential Decrease ($I(t) = I^l e^{-t/\tau^l}$) of the Chemiluminescence Signal Recorded at 20 KHz ($I = I_{CL,20\ KHz}$)

I	τ^s (ms)	I^s (%)	τ^l (ms)	I^l (%)
I_{scat}	30 ± 1	75	290 ± 5	25
P_A (in water)[a]	1.5 ± 0.5	50	14 ±1	50
P_A (in water−glycerol)[a]	1.5 ± 0.5	50	14 ±1	50
P_A (in air)[b]	0.5 ± 0.5	66	26 ±2	33
$I_{CL,20\ kHz}$			17 ± 2	100
$I_{CL,1.7\ MHz}$	2 ± 0.5	62	28 ± 1	38

[a] Signal measured by hydrophone. [b] Signal measured through the direct piezoelectric effect of the horn transducers.

Results and Discussion

Study of the Bubble Population under Pulsed Irradiation. In order to obtain information about the time evolution of the bubble cloud created by a pulsed 20 kHz acoustic field, the bubble field was illuminated and the light scattered by the bubbles in the solution was measured. In the absence of any existing theoretical model which describes the intensity of the light scattered by a large but unknown number of oscillating and collapsing bubbles of various size immersed in water, the assumption was made that the intensity of scattered light is proportional to the average number of bubbles in the incident light beam.

When a 250 ms pulse train ($T_{on}/T_{off} = 1/5$) propagates through the solution, the scattered light builds up gradually during approximately 50 ms at the start of each pulse before reaching a constant value. At the end of the electrical exciting pulse, the intensity decreases progressively during several tens of milliseconds. The decay of the intensity can be adjusted to a biexponential function (eq 1). The values of the characteristic times (τ^s_{scat} and τ^l_{scat}) and of the preexponential factors (I^s_{scat} and I^l_{scat}) were found to be independent of the pulse length (T_{on}), the T_{on}/T_{off} ratio of the pulse train and the ultrasonic intensity. They are given in Table 1.

$$I_{scat}(t) = I^s_{scat} e^{-t/\tau^s_{scat}} + I^l_{scat} e^{-t/\tau^l_{scat}} \qquad (1)$$

It is possible to explain this particular evolution (Figure 2, curve a), when the history of the bubbles under pulsed irradiation is considered. Ordinary samples of liquid contain stabilized gas nuclei.[18−20] When a 20 kHz pulse wave is emitted in this liquid, these nuclei grow either by rectified diffusion[21] or through coalescence in response to the secondary Bjerkness forces which arise between pulsating bodies.[22,23] On reaching a limiting radius, the pulsating bubbles become unstable and break down into smaller ones. By this process, the number of bubbles in the solution will rise progressively. This is evidenced by the increase in the intensity of the light scattered at the start of the exciting pulse. Some of the smaller bubbles will dissolve away due to the external pressure generated by surface tension[18] while others may be expected to renucleate the liquid and the cycle will repeat. Under these conditions, the number of bubbles, and therefore the light scattered, will be constant. This steady

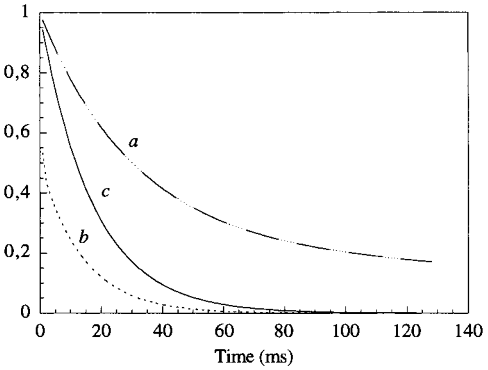

Figure 2. Evolution of (a) the bubble population, (b) the amplitude of the acoustic pressure, and (c) the luminol chemiluminescence intensity during the nonirradiation periods of the 20 kHz pulse train. The origin of the time axis corresponds to the end of the exciting electrical pulse. The lines correspond to the best fits of the experimental data.

state, characterized by the same size distribution of bubbles as that generated by a continuous wave field,[24] is reached after about 50 ms. When the ultrasound source is interrupted, a random range of bubble sizes exists in the liquid. The smallest bubbles will dissolve.

Epstein and Plesset[25] estimated the expected lifetime of air bubbles in water when their translational motion is neglected: for water which is 50% under-saturated, an air-filled bubble of 0.1 mm diameter will dissolve in 240 ms. 50% under-saturated water corresponds to the relative air concentration in water irradiated at a frequency of 16 kHz.[26] In our work, the frequency is slightly higher, and the stationary gas concentration is probably very similar, but we are working with a large number of interacting bubbles and the majority of them are of a smaller size. It is therefore difficult to compare the estimated characteristic time for dissolution estimated by Epstein and Plesset[25] and the experimental characteristic times for light scattering as measured in our work. The only qualitative comment which can be made is the following: the dissolution on the one hand and the coalescence on the other hand are probably the two processes which are responsible for the biexponential decrease of the bubble concentration in the liquid. Buoyancy seems to play a negligible role. This line of reasoning is consistent with the prediction of Flynn and Church[27] concerning the bubble population evolution under high-frequency pulsed irradiation.

Study of the Acoustic Field under Pulsed Irradiation. To determine if the interruption of the pressure wave emission influences the acoustic field, the frequency spectra of the acoustic field under continuous and pulsed irradiation in water were compared. In both cases subharmonics and harmonics were detected with approximately the same relative intensities. Even if the transient nature of the cavitation process and the instability in time of the bubble field makes the quantification of the peak intensities difficult, this result seems to indicate that the acoustic field is not altered by the periodic interruption of the emission of the wave in the solution.

The time evolution of the acoustic pressure in water subject to a pulsed wave was also recorded. The electrical exciting pulse supplied by the Chemsonic generator to the titanium horn transducers does not have the same waveform as the corresponding acoustic pulse detected by the hydrophone probe in water. A buildup in pressure, which is probably due to the buildup of the acoustic wave in the whole system (i.e., the titanium horn and the liquid medium), is observed during 600 μs at the start of the pulse detected by the hydrophone, and a residual pressure wave, characterized by a steeply decreasing amplitude, is detected after the end of the exciting pulse. We have qualified this residual pressure as the "acoustic relaxation" of the system. The acoustic relaxation is best fitted to a biexponential function (eq 2) and is plotted in Figure 2 (curve b):

$$P_A(t) = P_A^s e^{-t/\tau_A^s} + P_A^l e^{-t/\tau_A^l} \qquad (2)$$

The values of the characteristic times (τ_A^s and τ_A^l) and of the preexponential factors (P_A^s and P_A^l) were found to be independent of the pulse length (T_{on}), the T_{on}/T_{off} ratio of the pulse train, and the ultrasonic intensity. They are given in Table 1.

The residual pressure wave is present due to the inertia of the system, and its attenuation will be due to loss of energy to the medium. This loss is given by eq 3 in the case of a plane progressive wave traveling through a homogeneous medium characterized by an amplitude attenuation constant (α). P_A^0 is the amplitude of the pressure wave at the source while P_A is the amplitude of the pressure wave at a distance x from the source.

$$P_A/P_A^0 = e^{-\alpha x} \qquad (3)$$

This equation cannot, however, be used in the case of a cavitating liquid which is necessarily inhomogeneous and is characterized by a highly nonlinear response. Furthermore, in the case of the relaxation phenomenon studied here, the bubble field created during the irradiation period disappears during the nonirradiation period. The relaxation phenomenon which characterizes the acoustic field is also related to the relaxation of the emitter system itself. It is certainly also related to the loss of acoustical energy by transmission through the liquid−air interface and liquid-vessel walls interfaces.

In order to obtain an estimation of the contribution of the relaxation of the emitter system to the global relaxation, as it is measured with the hydrophone, we studied the time evolution of the direct piezoelectric effect of the horn ceramics when the horn is immersed in air. The alternative pressure wave acting on the horn transducer during the off period of the pulse gives rise to an alternative electrical current which can be used to characterize the acoustic signal. The reflection of the pressure wave at the horn−air interface is certainly higher than at the horn−liquid interface due to the difference in the acoustic impedance between the horn and air on the one hand and between the horn and water on the other hand. Nevertheless, as shown in Table 1, the relaxation behavior of the emitter in air is not very different from what is observed for the emitter immersed in a liquid. It is also best fitted by a biexponential function. Moreover, as also shown in Table 1, the relaxation as measured through the hydrophone directly immersed into the liquid does not depend on the nature of the liquid.

Considering the complexity of the acoustic system under study and the small differences between the values recorded in Table 1, we can conclude that the relaxation of the acoustic field is essentially due to the relaxation of the transducers, the titanium horn and the countermass.

The biexponential behavior of the time evolution of the signals cannot be interpreted. We used a best-fit program with which an experimental curve can be adjusted by various analytical functions. A monoexponential does not fit the data in an acceptable manner while a biexponential does. For obvious reasons, we did not try other functions with a higher

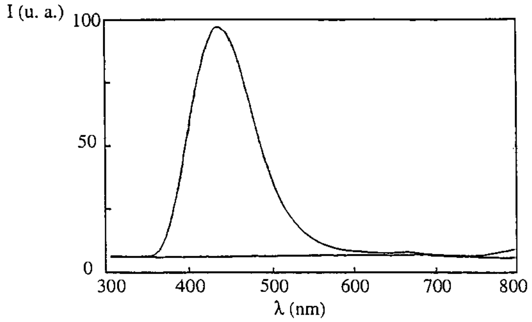

Figure 3. Chemiluminescence spectrum of luminol recorded under pulsed irradiation. The ordinates are noted in arbitrary units (pH = 10, $T = 20$ °C).

number of adjustable parameters but do not claim that the biexponential feature represents a true physical phenomenon.

Study of the Luminol Chemiluminescent Oxidation under Pulsed Irradiation. As described in the previous sections, the time evolutions of the acoustic pressure and of the bubble population after the end of the exciting pulse are both biexponential. The decrease of the pressure amplitude in water ($\tau^{s}_{A} = 1.5 \pm 0.5$ ms and $\tau^{l}_{A} = 14 \pm 1$ ms) is generally more rapid than the decrease of the bubble population ($\tau^{s}_{scat} = 30 \pm 1$ ms and $\tau^{l}_{scat} = 290 \pm 5$ ms). Consequently, after the end of the exciting pulse, a pressure wave and bubbles are simultaneously present in solution. As long as the acoustic pressure is greater than the transient cavitation threshold, these bubbles are active and generate reactive species in solution.[28,29] When the acoustic pressure amplitude is inferior to this threshold, the bubbles are no longer active.

In order to obtain more information about the period during which the bubbles are sonochemically active and produce free radicals, the chemiluminescence oxidation of luminol was studied. The short-lived hydroxyl radicals generated by the sonolysis of water inside transient bubbles[30,31] are probably the oxidizing agent of luminol.[32] The detailed mechanism of the multistep oxidation of luminol into the fluorescent aminophthalate anion is only partially known. More precisely, the number of the $OH^{\bullet}$ radicals involved in the process remains a subject of debate.[33−36] Nevertheless, the detection of the chemiluminescence signal constitutes an efficient way to follow the production of the $OH^{\bullet}$ radicals.

The chemiluminescence spectrum of luminol in aqueous solution recorded under a 20 kHz pulsed irradiation is shown in Figure 3. This spectrum is identical to the spectrum obtained with continuous irradiation and to the spectrum obtained by classical oxidation procedures,[37] indicating that only one species, i.e., the 3-aminoterephthalate anion, is responsible for the light emitted.

Figure 4 shows a chemiluminescence pulse emitted by a luminol solution exposed to a 20 kHz pulse train of 100 ms and a T_{on}/T_{off} ratio of 1. At the start of the electrical exciting pulse sequence, a buildup of the chemiluminescence is observed before a constant value is reached. No abnormal light emission, like that observed for sonoluminescence,[13] is observed at the beginning of the chemiluminescence of luminol. This confirms that sonoluminescence and sono-induced chemiluminescence are different processes. After the end of pulses, the intensity decreases progressively. Henglein et al.[3,4,6] reported a similar pattern in the high-frequency range. Crum et al.[2] interpreted this data and equated the progressive increase in the chemiluminescence intensity to the formation of more and more transient bubbles. The bubble population evolution observed in this study at 20 kHz fits in with this interpretation.

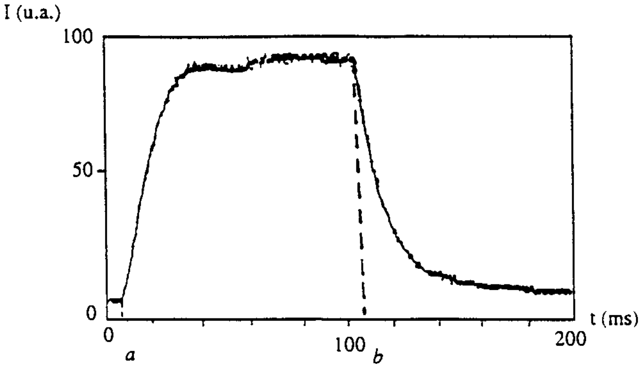

Figure 4. Chemiluminescence pulse produced by a 10^{-4} M luminol solution (pH = 10, $T = 20$ °C) exposed to a 20 kHz pulsed irradiation of 100 ms length and with a T_{on}/T_{off} ratio of 1. The ordinates are noted in arbitrary units. *a* and *b* correspond, respectively, to the start and to the end of the exciting electrical pulse.

The residual chemiluminescence signal observed in this study after each pulse clearly demonstrates that sonochemical reactions are occurring during the off period of the pulse train. The decay was analyzed according to a first-order process and a characteristic time, ($\tau^{o}_{CL,20\ kHz}$), of 17 ± 2 ms was obtained (Figure 2, curve c). This characteristic time was found to be independent of the pulse length (T_{on}), the T_{on}/T_{off} ratio of the pulse train and the ultrasonic intensity. This characteristic time is within experimental error identical to the largest of the two characteristic times associated with the time evolution of the acoustic pressure in solution (see Table 1). It is tempting to conclude that since chemistry, and therefore chemiluminescence, occur only while active bubbles are present in the liquid medium, that the population of sonochemically active bubbles decreases with the acoustic pressure. It should be noted that the shortest characteristic time associated with the time evolution of light scattering, and therefore the time evolution of the bubble field, are also similar to the chemiluminescence characteristic time (see Table 1). It is, however, difficult to relate the time evolution of the active bubbles to the time evolution of the bubble field. A definitive conclusion concerning the factors which govern the postpulse chemiluminescence evolution cannot be reached, but in any case, these factors are physical factors related to acoustic cavitation and/or damping of the emitter system and the vessel.

To further investigate our conclusion, we decided to perform the chemiluminescence study in the high-frequency range (1.7 MHz). In this case, the emitter is a piezoelectric ceramic directly sealed to the bottom of the glass cell and is in direct contact with the solution. Such a system is characterized by a lower vibrational inertia than the heavy ceramics-horn-countermass emitter used in the 20 kHz range. We can therefore predict that the postpulse chemiluminescence evolution should be shorter at 1.7 MHz than at 20 kHz. The data in Table 1 shows clearly that this is indeed the case. At 1.7 MHz the postpulse luminescence evolution can be fitted by a biexponential function with an important fast component.

Figures 5 and 6 show the time evolution of the chemiluminescence response to a pulse train in the 20 kHz and 1.7 MHz range, respectively. The difference between the signals in the 20 kHz (Figure 5) and the 1.7 MHz range (Figure 6) is clearly visible when the off period of the pulse train is short (10 ms). In the low-frequency range, a residual chemiluminescence is still observed before the emission of the next pulse (Figure 5, a and b) while in the high-frequency range, the chemiluminescence is reduced to zero (Figure 6, a and b). When the off period of the pulse is longer, the same behavior is observed at

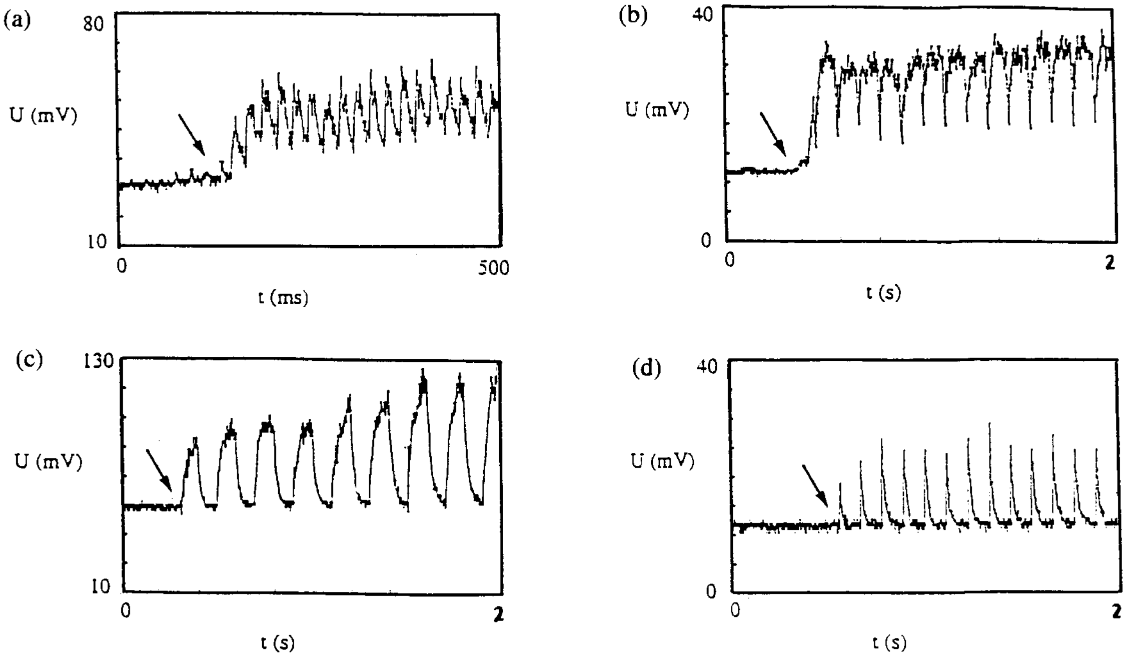

Figure 5. Shape of chemiluminescence pulses in a luminol aqueous solution upon application, in the 20 kHz range, of (a) a 10 ms ultrasonic pulse train with a T_{on}/T_{off} ratio of 1/1, (b) a 100 ms ultrasonic pulse train with a T_{on}/T_{off} ratio of 10/1, (c) a 100 ms ultrasonic pulse train with a T_{on}/T_{off} ratio of 1/1, and (d) a 10 ms ultrasonic pulse train with a T_{on}/T_{off} ratio of 1/10. The arrow indicates the start of the electrical excitation of the horn transducers.

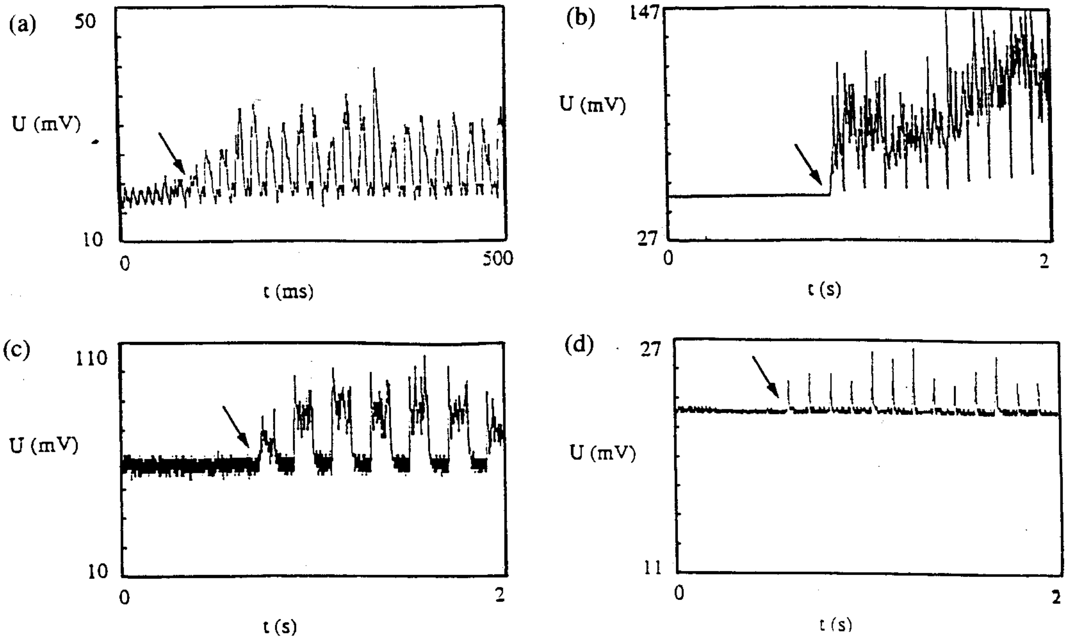

Figure 6. Shape of chemiluminescence pulses in a luminol aqueous solution upon application, in the 1.7 MHz range, of (a) a 10 ms ultrasonic pulse train with a T_{on}/T_{off} ratio of 1/1, (b) a 100 ms ultrasonic pulse train with a T_{on}/T_{off} ratio of 10/1, (c) a 100 ms ultrasonic pulse train with a T_{on}/T_{off} ratio of 1/1, and (d) a 10 ms ultrasonic pulse train with a T_{on}/T_{off} ratio of 1/10. The arrow indicates the start of the electrical excitation of the horn transducers.

both frequencies. For a 100 ms pulse, the chemiluminescence intensity reaches a plateau value and after the pulse the intensity decreases progressively to zero before the next pulse (Figures 5c and 6c). For a 10 ms pulse, each pulse produces some chemiluminescence which does not reach a plateau and decreases to zero before the next pulse occurs (Figures 5d and 6d). It must be noted that unfortunately the intensity of the different figures cannot be compared since, due to technical constraints, the detector sensitivity varied from one recording to the next.

The comparison of our chemiluminescence measurements at 20 kHz and at 1.7 MHz, and also their comparison with the measurements performed at 800 kHz by Henglein,[4] seem to evidence a frequency effect in pulsed sonochemistry. However, for a reason which is frequently underestimated by sonochemists, the interpretation of this effect is not straightforward. Indeed, frequency, intensity, bubble field topology, retro-action of the reflected pressure waves on the ceramics or horn, and vibrational modes of the vessel are all interdependent parameters. This interdependence cannot easily be studied experimentally in a nonlinear system like a cavitating liquid in a vessel containing an ultrasound emitter. So as to limit, but probably not eliminate, the risk of an artifact which could be due to an intensity difference at the two frequencies, the intensities at 1.7 MHz and 20 kHz were adjusted in our study in order to obtain the same rate for the Weissler reaction at both frequencies.[14] Since the decay of the chemiluminescent signal and the acoustic relaxation seem to be correlated, it is reasonable to attribute the observed frequency effect to the wave production system even if the exact acoustic relaxation mechanism is not known. The rate of decrease of the bubble population could also be different at both frequencies. The small bubbles generated at 1.7 MHz could dissolve more rapidly than the bubbles generated at 20 kHz. It was unfortunately not possible to perform light scattering measurements at high frequencies since the bubble field topology is different at the two frequencies and the cell was optimized for the measurement of the light scattered by the bubble field located just below the horn used at 20 kHz. The hydrophone measurements were also not performed at high frequency since the equipment used in the high-frequency domain was not available in our laboratory.

Conclusions

In this paper we have presented an experimental study of 20 kHz pulsed irradiation. The measurement of the bubble population, the acoustic pressure, and the chemiluminescence of the bubble field showed that the sonochemical production of highly reactive species is limited at the start of the electronic pulse by the bubble production rate and after the end of the exciting electrical pulse, by the maximum amplitude of the acoustic pressure. These results may be indicative of a difference between sonochemistry under continuous irradiation and sonochemistry under pulsed irradiation.

The comparison between the chemiluminescence pulse pattern under 20 kHz and 1.7 MHz pulsed irradiation seems to indicate that a frequency effect exists in pulsed sonochemistry. In order to interpret this effect it is necessary to achieve a better understanding of the interdependence of the different parameters governing the cavitation in a sonochemical reactor. The only hope of reaching a better knowledge of this complex system depends on our ability to perform computer experiments. Indeed, computer experiments offer the advantage, at least in principle, to simulate the behavior of a complex system and to study, in a systematic way, the influence of the various parameters and their interdependence. Work is in progress in Brussels to reach this goal.

Sonochemistry is the result of an interaction between chemistry and nonlinear acoustics. Acoustic cavitation is at the heart of sonochemistry but the physical study of a cavitating liquid is far from trivial. This study, performed on what could seem at first to be a very simple system, shows how complex the observed phenomena are. More physicochemical studies will be necessary in order to achieve a good understanding of all the parameters that govern sonochemistry. This is a prerequisite before being able to use sonochemistry in a predictive way for complex systems.

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References and Notes

(1) Ciaravino, V.; Flynn, H. G.; Miller, M. W. *Ultrasound Med. Biol.* **1981**, *7*, 159.
(2) Crum, L. A.; Fowlkes, J. B. *Nature* **1986**, *319*, 52.
(3) Henglein, A.; Gutiérrez, M. *Int. J. Radiat. Biol.* **1986**, *50*, 527.
(4) Henglein, A.; Ulrich, R.; Lilie, J. *J. Am. Chem. Soc.* **1989**, *111*, 1974.
(5) Henglein, A.; Gutiérrez, M. *J. Phys. Chem.* **1990**, *94*, 5169.
(6) Henglein, A.; Herburger, D.; Gutiérrez, M. *J. Phys. Chem.* **1992**, *96*, 1126.
(7) Henglein, A.; Gutiérrez, M. *J. Phys. Chem.* **1993**, *97*, 158.
(8) Henglein, A. *Ultrasonics Sonochem.* **1995**, *2*, 115.
(9) Gutiérrez, M.; Henglein, A. *J. Phys. Chem.* **1990**, *94*, 3625.
(10) Roy, R. A.; Madanshetty, S. I.; Apfel, R. E. *J. Acoust. Soc. Am.* **1990**, *87*, 2451.
(11) Roy, R. A.; Church, C. C.; Calabrese, A. In *Cavitation produced by short pulses of ultrasound*; Elsevier Science Publishers Ltd.: London, 1990; p 476.
(12) Leighton, T. G. *Ultrasonics* **1989**, *27*, 50.
(13) Leighton, T. G.; Walton, A. J.; Field, J. E. *Ultrasonics* **1989**, *27*, 370.
(14) Dekerckheer, C.; Dalhem, O.; Reisse, J. *Ultrasonics Sonochem.* **1997**, *4*, 205.
(15) Weissler, A.; Cooper, H. W.; Snyder, S. *J. Am. Chem. Soc.* **1950**, *72*, 1769.
(16) Weissler, A.; Pecht, I.; Anbar, M. *Science* **1965**, *150*, 1288.
(17) Rosenthal, I.; Mossoboa, M. M.; Riesz, P. *J. Magn. Reson.* **1981**, *45*, 359.
(18) Crum, L. A. *Appl. Sci. Res. (Sect. A)* **1982**, *38*, 101.
(19) Sirotyuk, M. G. *Sov. Phys. Acoust.* **1970**, *16*, 237.
(20) Harvey, E. N.; Barnes, D. K.; McElroy, W. D.; Whiteloy, A. H.; Peace, D. C.; Cooper, K. W. *J. Cell. Comput. Physiol.* **1944**, *24*, 1.
(21) Crum, L. A. *Ultrasonics* **1984**, *22*, 215.
(22) Blake, F. G. *J. Am. Chem. Soc.* **1949**, *21*, 551.
(23) Crum, L. A. *J. Acoust. Soc. Am.* **1975**, *57*, 1363.
(24) Sehgal, C. M.; Wang, S. Y. *J. Am. Chem. Soc.* **1981**, *103*, 6606.
(25) Epstein, P. S.; Plesset, M. S. *J. Chem. Phys.* **1950**, *18*, 1505.
(26) Kapustina, O. A. *Sov. Phys. Acoust.* **1970**, *15*, 328.
(27) Flynn, H. G.; Church, C. C. *J. Acoust. Soc. Am.* **1984**, *76*, 505.
(28) Suslick, K. S. *Ultrasound: Its Chemical, Physical and Biological Effects*; V. C. H. Publishers, Inc.: New York, 1988.
(29) Mason, T. G.; Lorimer, J. P. *Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry*; Ellis Horwood Ltd.: Chichester, UK, 1988.
(30) Makino, K.; Mossoba, M. M.; Riesz, P. *J. Am. Chem. Soc.* **1982**, *104*, 3537.
(31) Makino, K.; Mossoba, M. M.; Riesz, P. *J. Phys. Chem.* **1983**, *87*, 1369.
(32) Gundermann, K. D.; McCapra, F. *Chemiluminescence in Organic Chemistry*; Springer-Verlag: Berlin, 1987; p 217.
(33) Würzberg, E.; Haas, Y. *Chem. Phys. Lett.* **1978**, *55*, 250.
(34) Baxendale, J. H. *J. Chem. Soc., Chem. Commun.* **1971**, 1489.
(35) White, E. H.; Bursey, M. M. *J. Am. Chem. Soc.* **1964**, *86*, 941.
(36) White, E. H.; Roswell, D. F. *Acc. Chem. Res.* **1970**, *3*, 54.