Luminescence and Chemical Action by Pulsed Ultrasound

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Abstract: Luminol and iodide solutions were irradiated with pulse trains of 800 kHz ultrasound, the corresponding luminescence trains analyzed and the iodide yields determined. The first pulses applied produce less luminescence which is explained in terms of an "activation" of the solution for cavitation. With increasing interval between pulses, a pulse of given length becomes less efficient. At sufficiently long intervals, the luminescence and iodide oxidation become zero, although the pulses still consist of many hundreds of cycles. These effects are explained by a "deactivation" during the intervals. The results are also discussed in terms of two types of nuclei: natural nuclei of long life, X_n, which very efficiently promote chemically active cavitation, and nuclei produced by ultrasound, X_u, which are short lived. Luminescence and chemical action have the same dependence on pulse length and on/off ratio. In continuous irradiation, the luminescence and chemical yield increase with increasing sound intensity up to about 2.5 W/cm^2 but rapidly decrease at higher intensities. These effects are discussed in terms of the relative contributions of "stable" and "transient" cavitation. The results are also discussed with respect to the use of ultrasonic pulses in medicine.

History and Aim of Present Work. Since the first observation of chemical reactions initiated by ultrasound in solution[1] and the detection of sonoluminescence,[2] many papers have appeared in both fields.[3] Both effects are due to the high temperatures of several 1000 K that exist in the adiabatic compression phase of oscillating or collapsing gas bubbles. Chemically active cavitation is generally produced by ultrasound only in the presence of a mono- or diatomic gas as the large ratios or the specific heats in these gases are favorable for obtaining high temperatures upon compression. The migration and oscillation of cavitation bubbles[4] as well as their formation from nuclei and their growth[5] have been studied in many theoretical papers.

A method to obtain information about cavitation and chemical action consists of using ultrasound in the form of pulse trains of different pulse lengths and on/off ratios. The first studies of this kind were made more than 30 years ago using ultrasound of 500 kHz[6,7] and audible sound of 10 kHz.[8] A surprising phenomenon, not quite understood at the time, was observed that, under certain conditions, pulses of ultrasound are not chemically active although they may consist of hundreds or even thousands of cycles. Three years ago, experiments with pulsed ultrasound were resumed, and the results were explained by a simple theory which is described in the second part of this Introduction. In this theory the chemical effects are related to certain aspects of bubble dynamics.[9]

Our understanding of the chemical effects of pulsed ultrasound is important with regard to the use of ultrasound in medicine, such as in diagnosis and therapy, for example, kidney stone disintegration. In these applications, in which very short microsecond pulses are applied and the interval time between the pulses is in the millisecond (diagnosis) or second range (disintegration), the time averaged acoustic energy supplied is low. However, the instantaneous intensity in the pulses is extremely high, 150 W/cm^2 (diagnosis) or even 10 000 W/cm^2 (disintegration). Chemical reactions initiated in ordinary ultrasonic generators already occur at intensities of a few W/cm^2. In fact, as demonstrated recently, pulses from a lithotripter (an apparatus for kidney stone disintegration) are able to produce iodine from iodide, as is known from ordinary ultrasound.[10] Furthermore, free radicals were detected by an ESR spin trapping method when water was irradiated with ultrasonic pulses under simulated diagnosis conditions.[11]

In the present work, the oxidation of iodide by pulses of 800 kHz ultrasound was reinvestigated. To compare the chemical yield to that observed in a continuous irradiation experiment, one has to apply a longer irradiation time

$$t = t_0(1 + 1/R) \qquad (1)$$

to expose the solution to the same amount of acoustic energy. t_0 is the time used in the continuous irradiation, $R = T/T_0$ is the on/off ratio, where T is the duration of a pulse and T_0 the duration of the interval between the pulses. The chemical yield was measured after irradiation with a rather large number of pulses, i.e., the measured yield reflects an integration over the action of many pulses. No information was obtained about the efficiency of the various single pulses of the train. According to the simple theory mentioned above, the pulses at the beginning of the train may have an efficiency different to the later ones. In order to obtain additional information, luminescence experiments were performed. An ultrasonic pulse train produced a luminescence pulse train which was recorded and analyzed. Two kinds of luminescences were studied: (1) The sonoluminescence produced in water under air, which is due to the formation of hot molecules and excited radicals in the cavitation bubbles, and (2) the chemoluminescence of luminol (5-amino-1,2,3,4-tetrahydropthalazin-1,4-dion), which is generated when oxidizing radicals react with this solute. The experiments with luminol are the ones most easily performed, as the intensity is higher by a factor of about 100 than in the sonoluminescence experiments.

Current Theory. An attempt was made to describe the chemical yield at various pulse lengths and on/off ratios in terms of two times, τ_1 and τ_2, characteristic for the cavitating system.[9] τ_1 is the "activation time", i.e., the time required to produce and grow chemically active gas bubbles. It is assumed that a pulse is not immediately chemically active but first requires time τ_1 to

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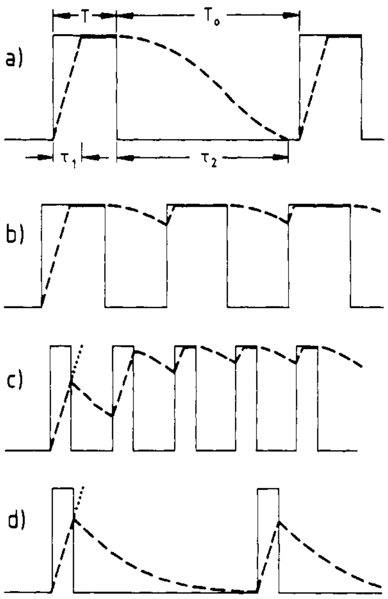

Figure 1. Various pulse trains (full line) and activation of the system (dashed): T, pulse duration; T_0, interval duration; τ_1, time of activation; τ_2: time of deactivation.

"activate" the system, before promoting chemical reactions during time $T - \tau_1$. Clearly, chemical reactions cannot occur when $T < \tau_1$. τ_2 is the "deactivation time" of the system. After a pulse, the solution contains bubbles and nuclei upon which ultrasound can efficiently act to produce chemical reactions, but they decay more or less rapidly during the interval. If time T_0 is longer than τ_2, the following pulse has to reactivate anew. If the subsequent pulse arrives earlier, some activation is still present and enables the pulse to be more efficient.

Various conceivable cases are shown in Figure 1a–d, where the pulse train is shown by a full line and the activation during the pulse and deactivation during the interval by dotted line (the exact shape of this curve is unknown). The case $\tau_1 < T$ and $\tau_2 < T_0$ is shown in Figure 1a, i.e., each pulse has to activate the solution. In Figure 1b pulses of the same length as in Figure 1a are shown, but the interval is shorter, i.e., $\tau_2 > T_0$. Under these conditions, the subsequent pulse finds some activity, the result being a greater efficiency to produce chemical reactions. Figure 1d shows the case, where $\tau_1 > T$ and $\tau_2 < T_0$. This is the most unfavorable situation, in which each pulse builds up some activation which, however, is not sufficient to produce chemical reactions, and even this activation is lost between the pulses. In Figure 1c, $\tau_1 > T$, but $\tau_2 > T_0$, the first few pulses building up more and more activity until sufficient activity is present to allow chemical reactions to occur under the influence of the later pulses.

This theory is based on two assumptions which are probably not quite fulfilled: (1) It is assumed for the sake of simplicity that chemical reactions do not occur unless a certain level of activation is reached. In a real system one may expect the chemical efficiency to increase gradually as the activation increases. It was hoped to obtain information on this point by the luminescence experiments. (2) It is assumed that τ_1 and τ_2 are independent of each other as well as of pulse length. In spite of these obvious shortcomings, the simple theory is used in the present work as a starting point to discuss the results.

Experimental Section

Figure 2 shows the irradiation setup. The 800 kHz ultrasound was emitted from a ceramic transducer (Valvo, type PXE 41; 50 mm diameter) through a λ/2 aluminum flange into the glass vessel which contained 25 mL of solution. The planar bottom of the vessel had a thickness of half a wavelength. The heat produced was removed by cooling water. The high frequency was delivered by an oscillator (Wavetex, Model 164) and an amplifier (EIN, Model 2100L). The oscillator produced either continuous or pulsed high frequency. Most experiments were performed with a hf-power of 70 W producing an intensity of 2 W/cm² in the solution. The intensity was calorimetrically measured under noncooling conditions. The luminescence signals were recorded by a photomultiplier (Hamamatsu, type R 1387-01).

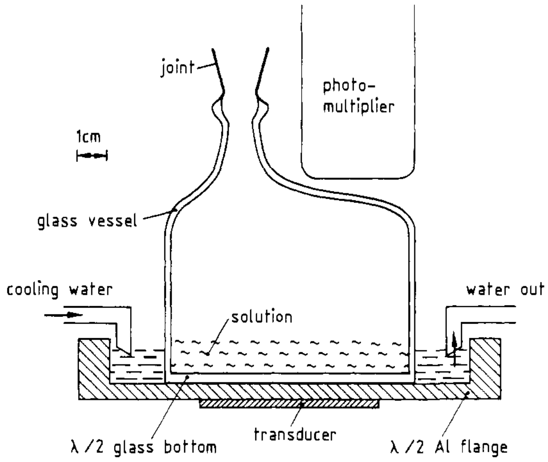

Figure 2. Schematic drawing of the irradiation setup.

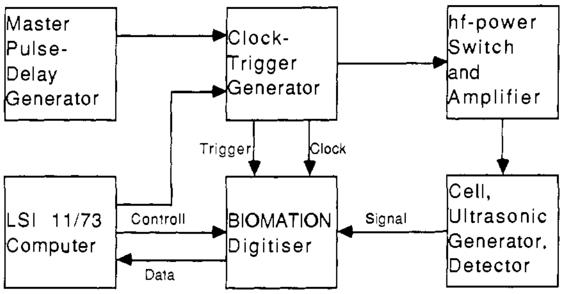

Figure 3. Scheme of the electronics for recording luminescence pulses.

Data was acquisitioned with a DEC LSI 11/73 microcomputer in a multiuser environment and a BIOMATION 8100 transient digitizer. A problem existed that in cases where the interval between the ultrasonic pulses was much longer than the pulses themselves, most of the data collection would take place when no useful information was present. The transient recorder was programmed for external timing, and a circuit set up to supply clock pulses to the digitizer only during the time of the ultrasonic pulses and shortly thereafter. In this manner no data were collected during the intervals and full resolution of the recorder was available.

Figure 3 illustrates the principle. A master pulse-delay generator delivers control pulses of variable length (10^{-4} to 1 s) with a variable pulse/interval ratio. This pulse train is fed into a clock-trigger generator. The clock impulses are gated with pulses from the master and define the external time base of the digitizer. A pulse-stretching circuit extends the gate period by a variable time (mostly 10^{-3} s) to allow the observation of processes directly after the ultrasonic pulses and to supply markers for the end of each pulse. On command of the computer the transient recorder is armed, measuring the photomultiplier signal without ultrasound (base line measurement). At the beginning of an interval period the transient recorder is triggered, and transfer of the pulse train to the hf-amplifier is started, applying ultrasound to the solution. By using this method, it is guaranteed that the measurement starts at the first pulse applied, that the starting point is well defined, and that all pulses including the first one have the same length. After 2000 data points are collected, the application of the pulses is stopped, and the data are transferred to the computer for storage and evaluation. Depending on the ratio of the clock time to the pulse length, between one and several hundred pulses are recorded. An evaluation program in the computer normalizes the data and displays them graphically on the terminal. A cursor allows a choice of data for detailed evaluation.

Results

Continuous Irradiation: Yield and Sound Intensity. Figure 4 shows how the iodine yield of a 0.2 M iodide solution and the luminescence of water depended on the hf-power applied. In both cases, the irradiation occurred under air. Above a threshold of about 10 W the yields increased with increasing power, reached a maximum at about 100 W, and decreased at higher powers. The reproducibility of the data was 5–10% in the increasing part and only 30–50% in the decreasing part of the curve. Note that

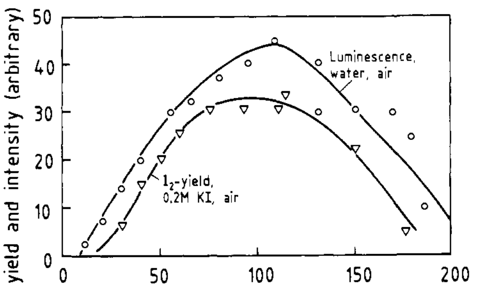

Figure 4. Iodine yield and luminescence intensity as functions of the hf-power.

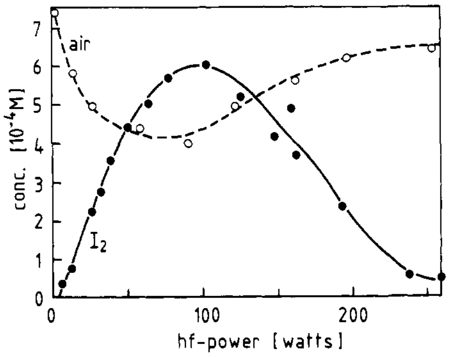

Figure 5. Iodine yield and gas content after 1-min irradiation as functions of the hf-power.

chemical yield and luminescence intensity parallel each other.

In the maximum of the curves in Figure 4, a "fountain" was produced, and the atmosphere in the vessel contained a lot of fog, i.e., very small water particles. At first sight, one could be inclined to attribute the decrease in yield at high sound intensities to the well-known degassing effect of ultrasound. An experiment was performed in which the solution was irradiated for 1 min; 5–10 mL of the solution were taken off with a syringe, i.e., under conditions where regassing was avoided, and the gas content was analyzed in a Van Slyke apparatus. Figure 5 shows the result. The concentration of gas in the liquid first decreases with increasing hf-power but increases again at higher powers. It thus displays a behavior opposite to that of the chemical yield and the luminescence intensity. Clearly, the amount of gas present in the irradiated liquid cannot be related to the yields. The shape of the gas curve in Figure 5 is explained by more and more degassing with increasing hf-power until the liquid is so much agitated at higher sound intensities that the uptake of gas from the atmosphere almost compensates the gas loss.

These experiments show a drastic change in quality of cavitation at high sound intensities. In another series of experiments, a rubber sheet of 1 mm thickness floated on the solution. It prevented the formation of the "fountain". At low hf-powers the iodine yield was almost the same as in the absence of the sheet. At higher powers, the yield remained constant and did not decrease as in Figure 4. It seems that the quality of cavitation at low intensities, which is favorable for chemical action, was at least partly maintained at higher intensities when the sheet was present.

It has previously been reported that the liquid does not luminesce homogeneously but in certain spots which are separated by $\lambda/2$.[12] The spots were identified as the antinodes of standing waves. This observation was also made in the present work.

Chemiluminescence of Luminol. The luminescence intensity of 2.3×10^{-3} M luminol solution of pH = 12.7 under continuous sonication changes with time, as is shown by Figure 6. The luminescence was not fully developed immediately after the application of the ultrasound but increased to a maximum value within about 0.5 s. This increase occurred in two steps, as can be recognized from the inset of the figure. At longer sonication times the luminescence intensity decreased. Repetition of these experiments with pure water sonicated under air showed that sonoluminescence also required a buildup time but did not decrease afterwards. The initial increase is attributed to the buildup of activation, i.e., the formation of more and/or more efficient nuclei for cavitation. The decrease at longer times in the case of luminol does not seem to be characteristic of changes in the cavitation

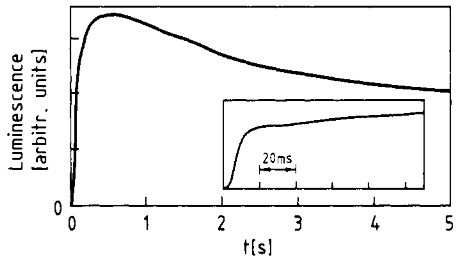

Figure 6. Luminescence intensity of a 2.3×10^{-3} M luminol solution as a function of irradiation time. Sonication under air. Power: 70 W.

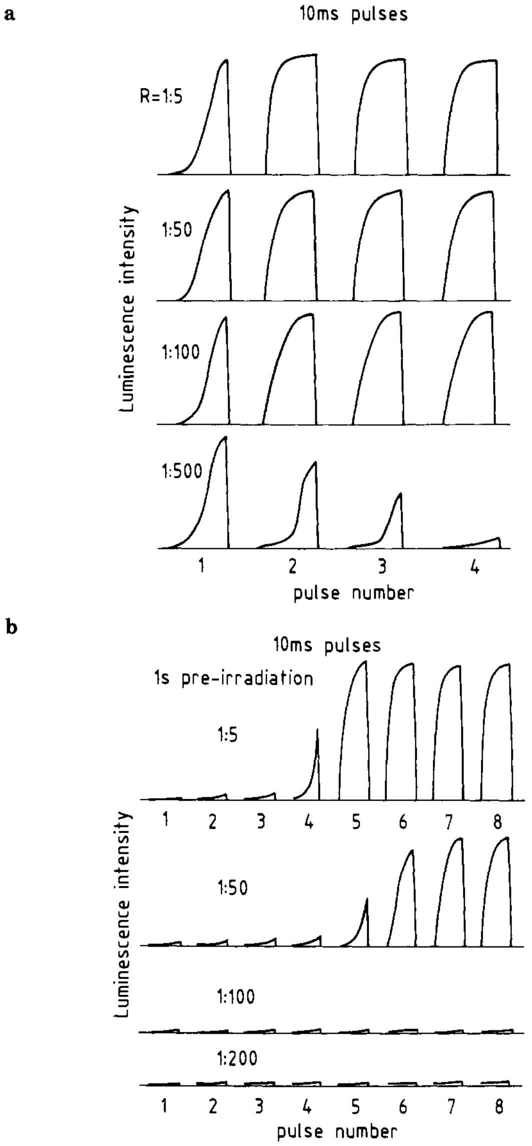

Figure 7. (a) The first four luminescence pulses in a luminol solution produced by a 10-ms pulse train. Different on/off ratios *R*. Power: 70 W. (b) The first eight luminescence pulses of a luminol solution exposed to a 10-ms pulse train. Different on/off ratios *R*. The solution had been preirradiated during 1 s. Power: 70 W.

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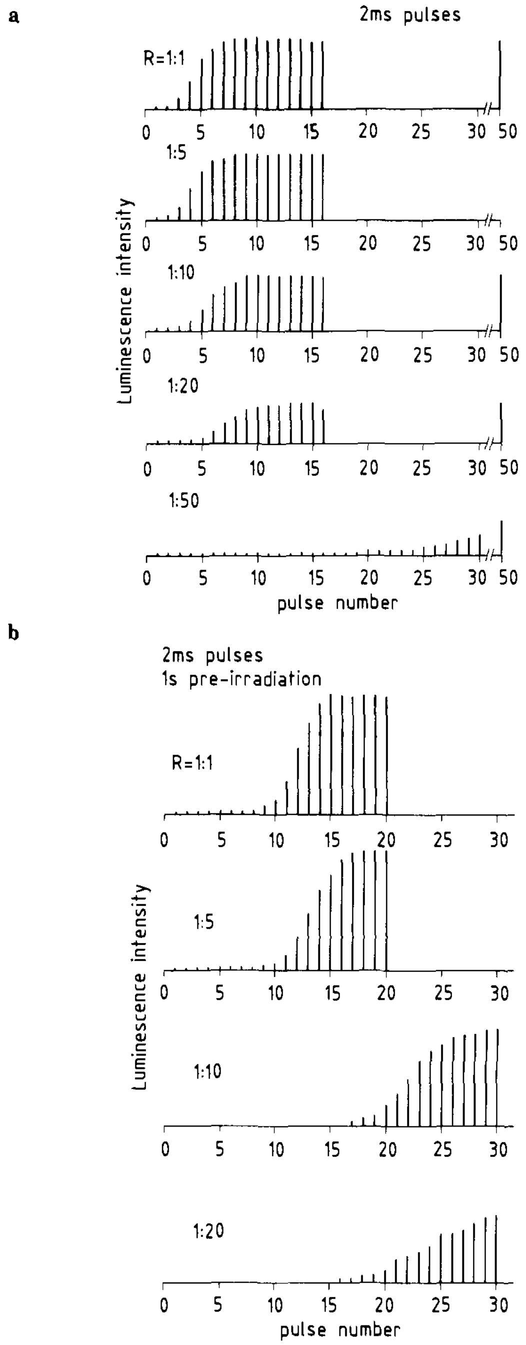

Figure 8. (a) The first 16 or 30 luminescence pulses and the 50th pulse of a luminol solution exposed to a 2-ms pulse train. Different on/off ratios *R*. (b) Luminescence pulses of a luminol solution exposed to a 2-ms pulse train after 1-s preirradiation. Different on/off ratios *R*.

quality but is explained by a change in the chemistry of the solution. It seems probable that a product is formed in the oxidation of luminol that quenches the excited state responsible for light emission. One should, therefore, use luminol as a probe for chemically active cavitation only under very low conversion conditions.

A train of 10 ms ultrasonic pulses was used in the experiments of Figure 7 (parts a and b). The figures show the shape of the luminescence pulses produced. The interval between successive pulses is not correctly given in these figures. From the *R* values one recognizes that the interval was 5–500 times longer than the 10-ms pulses. The difference in the experiments of the two figures consists in the pretreatment of the solution. In Figure 7a, no preirradiation was applied. The figure shows the first four pulses of the train. In Figure 7b, the solution was preirradiated for 1 s, and the 10-ms pulse train was applied after 2 s. The first eight pulses were recorded here.

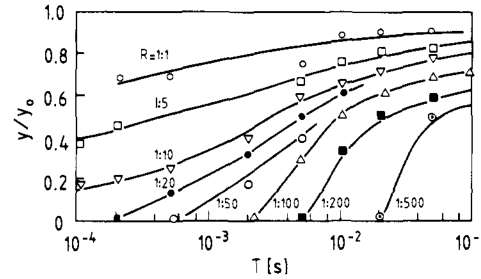

Figure 9. Relative yield of luminescence of luminol as a function of the pulse length for various on/off ratios.

The ultrasonic pulses were rectangular. The first luminescence pulse in Figure 7a was not rectangular as the luminescence was built gradually during this pulse along a S-shaped curve. The succeeding pulses had a faster rise time. However, this rise time became longer going from R = 1:5 to 1:50 and finally 1:100, i.e., the luminescence efficiency per pulse decreased with decreasing ratio of R. Finally, at R = 1:500 a new phenomenon occurred: The pulses following the first one rapidly became weaker, the final luminescence intensity being almost zero. In all the cases discussed the higher number pulses had the same shape as the fourth one.

Turning attention to Figure 7b, comparison with Figure 7a shows that the 1-s preirradiation had a drastic effect: At R = 1:5, it took four pulses to build up luminescence until the same intensity as in Figure 7a was reached. At R = 1:50, the buildup required even more pulses, and the final height was lower than at R = 1:5. At R = 1:100 and 1:200, the luminescence was almost zero even at much longer irradiations than shown in the figure.

Figure 8 (parts a and b) shows similar results obtained with trains of 2-ms pulses. The shape of the pulses is not shown here but only the final height of each luminescence pulse. At this short pulse length, a certain number of pulses is required to build up luminescence even in the case where the solution had not been preirradiated. With decreasing R, this buildup required more and more pulses, and the final height of the luminescence pulses became lower and lower. In the case of the preirradiated solution still more pulses were required for producing luminescence. In this case, a pulse train with R = 1:50 was already completely inefficient. The luminescence pulses were not rectangular but had a certain rise time, which increased with decreasing ratio R.

Figure 9 shows how the relative yield y/y_0 of luminescence depended on the pulse length T for various on/off ratios R. y_0 is the total amount of luminescence emitted during a 10-s irradiation as measured by the square area under the curve of Figure 6. y is the integrated luminescence under pulse conditions using the irradiation time of eq 1. It is recognized that a pulse of given length is more effective the shorter the time interval is between the pulses. In the case of long intervals a pulse length can be found below which the luminescence intensity is zero. This critical pulse length becomes shorter with decreasing interval length. The shortest pulses applied had a duration of 5×10^{-5} s. To investigate even shorter pulses did not seem meaningful, as the chemical reaction of luminol leading to luminescence is not infinitely fast.

Iodide Oxidation and Sonoluminescence. A 0.5 M KI solution was used in these experiments. The irradiation time for continuous exposure was 10 s. In the case of pulsed irradiation the time was calculated from eq 1. The concentration of iodine formed was determined spectrophotometrically by using a 2-cm cell ($\epsilon_{350\mathrm{nm}} = 2.6 \times 10^4$ M^{-1} cm^{-1}). The sonoluminescence of this solution was recorded during the whole irradiation period. In Figure 10, plots of y/y_0 vs pulse length are shown for various on/off ratios. In the case of I^- oxidation, y_0 was the iodine yield by continuous irradiation and y the yield by pulsed irradiation. In the case of sonoluminescence, y_0 and y were obtained as described above for luminol solutions.

It can be seen that iodine formation and sonoluminescence parallel each other. As already described in the case of chemoluminescence (Figure 9), the relative yields decrease with decreasing pulse length, this effect being more pronounced for smaller on/off ratios. A comparison between the corresponding curves

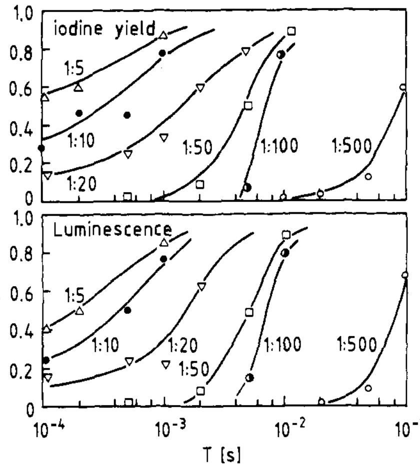

Figure 10. Relative yield of iodide oxidation (upper) and of sonoluminescence (lower) as a function of pulse length for various on/off ratios.

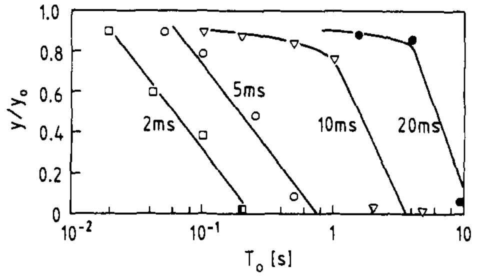

Figure 11. Iodide oxidation: Relative yield as a function of interval length for pulses of different lengths.

in Figure 9 and Figure 10 shows that the curves in Figure 10 decrease more steeply with decreasing T. A clear explanation of this fact cannot be given. It might be that the more complex chemistry involved in the luminol system somehow causes a slightly different dependence of the yield on pulse length.

Figure 11 shows a plot of the relative iodine yield vs interval length for pulses of different lengths. In the case of short pulses (2 and 5 ms), the yield decreases linearly in a semilogarithmic plot. As revealed by the simultaneous sonoluminescence, the decrease is mainly due to the decreasing signal height of the pulses. In the case of long pulses (10 and 20 ms) a smooth decrease occurs at short interval times, followed by a very abrupt decrease at longer times. The latter had poor reproducibility. During the smooth decrease the pulses reached about the same height, but the rise time was longer. The abrupt decrease took place when the phenomenon shown at the bottom of Figure 7a appeared, i.e., when very small pulses of luminescence were suddenly produced at $R = 1:500$.

Discussion

Yield vs Intensity: Stable and Transient Cavitation. A maximum in the yield vs intensity curve (Figures 4 and 5) has already been reported by other authors, such as Haissinsky[13] and Sehgal.[14] According to Haissinsky, a standing wave field is established as the sound wave is reflected at the surface of the solution. At high intensities, the "fountain" diminishes the reflection, and the standing wave field is distorted. Our experiment with the floating thin rubber sheet, which improved the yield as it prevented the fountain formation at high intensities, seems to corroborate Haissinsky's explanation. In a field of standing waves the strongest oscillations of bubbles occur in the antinodes of pressure, and in these spots one can see the luminescence with the naked eye. At higher intensities these spots are less defined. Again, this seems to be in agreement with the conclusion that chemical effects and luminescence at sound intensities of a few watts/cm^2 are produced with substantial yields only in a standing wave field.

In the current theory[4] of cavitation, a distinction is made between stable and transient cavitation, although this distinction is often not clear-cut. One speaks of stable cavitation when a bubble contains mainly a permanent gas such as air and when the bubble lives for a period very much longer than a cycle of the ultrasound. During the growth of the bubble, as long as its resonance frequency is higher than that of the ultrasound, it is driven into the antinodes of pressure where it produces chemical reactions. Transient cavitation is a phenomenon of shorter duration, consisting of the rapid formation of a cavity, often containing mainly the vapor of the liquid, and a vigorous collapse after a few cycles. At intensities of a few watts/cm^2, probably both kinds of cavitation occur. The overwhelming part of the theoretical work during the past three decades has been devoted to transient cavitation and this might be the reason why this type of cavitation is often regarded as being the most efficient in producing chemical reactions. This is possibly true for experiments where the formation of standing waves is avoided and high sound intensities are applied. However, it could be that under low intensity conditions, where standing waves are necessary to obtain substantial yields, most chemical reactions are produced via stable cavitation. Besides the effect of the deterioration of the standing wave field, the coalescence of oscillating gas bubble may lead to a decreased bubble number, i.e., a decreased yield.[14] The change in the quality of cavitation on both sides of the maxima in Figures 4 and 5 may thus be due to both a change in the number of bubbles and a change in the relative contributions made by stable and transient cavitation, the latter occurring mainly at higher intensities and being chemically less efficient than stable cavitation.

Activation and Deactivation of Cavitation. The luminescence observations in Figures 6–8 confirm a postulate of the simple theory described above that chemical action and luminescence should not be present immediately after switching on the ultrasound but require some time to develop. In the case of continuous irradiation (Figure 6) this development is seen as an increase in luminescence intensity during about 0.5 s. It is understood in terms of the formation of more and more gas bubbles on which the ultrasound can act. However, the process is complex as it occurs in two steps: during the first 10 ms of sonication a rather rapid increase in luminescence takes place which is followed by a very much slower one (inset of Figure 6).

In the experiments of Figures 7a and 8a, luminescence was already recorded in the first ultrasonic pulse. However, it was not fully developed at the beginning of the pulse but built up during the pulse. In the case of the 10-ms pulse train (Figure 7a), the intensity reached at the end of the first pulse was already close to the point where the first step of the increase (inset of Figure 6) ended. The following pulses produced about the same intensity, but the rise time was shorter. This is explained by a certain activity of the solution which survived the interval time and enabled the next pulse to build up luminescence more rapidly. By comparing the rise times at the various on/off ratios (i.e. 1:5, 1:50, and 1:100) in Figure 7a, one recognizes that it became a little longer with increasing interval time, i.e., more and more activation was lost during the interval. It can be said that the deactivation time τ_2 must be longer than 1 s under these conditions.

In the case of the 2-ms pulse train, the luminescence produced during the first pulse was very low (Figure 8a). However, it built up during the subsequent pulses until a final signal height was reached. The number of pulses required to build up the final signal became greater with decreasing on/off ratio, i.e., with increasing interval time, and the final signal became smaller. The effect indicates that activation gained during a pulse is lost to an appreciable extent during the interval. One would estimate from the results in Figure 8a that the deactivation time, τ_2, is shorter than 50 ms. Comparing this with the time of at least 1 s for the 10-ms train, it must be concluded that τ_2 is not a constant, as it is assumed in the simple theory but strongly depends on the pulse length of the train. The bubbles or nuclei generated by a 2-ms pulse obviously are much shorter lived than the ones resulting from

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a 10-ms pulse. This could perhaps be understood if the bubbles generated by a 2-ms pulse are much smaller than those resulting from a 10-ms pulse. They dissolve more rapidly because of their greater internal pressure $2\sigma/r$ (σ, surface energy; r, radius).

The new phenomenon is discussed now which was observed in the experiments of Figure 7a when the on/off ratio was 1:500. Under these circumstances the pulses after the initial one became rapidly less efficient. The effect can be understood if one postulates that the fresh solution contained "natural" nuclei, X_n, which are particularly efficient to promote chemically active cavitation. These nuclei are destroyed to a large extent by the first pulse. The pulse itself produces nuclei, X_u, which are, however, short-lived. Their lifetime is long enough, i.e. >1 s, as pointed out above, so that trains with an interval time <1 s are still efficient. On the other hand, their lifetime is shorter than 5 s, thus the train with an interval time of 5 s is not able to produce substantial luminescence.

The existence of two types of nuclei enables one to understand also the effects of preirradiation (Figures 7b and 8b). After removal of X_n nuclei by preirradiation, a much larger number of pulses is required to build up luminescence than without preirradiation. In addition, the interval length where the pulses cease to be efficient is much shorter.

In the present work, changes in the chemical efficiency of single pulses of an ultrasonic pulse train are reported for the first time. They have to be explained by the formation and life time of bubbles acting as nuclei for chemically active cavitation. The simple theory offered can only give a qualitative explanation of the effects. The pulse experiments were carried out only at a hf-power of 70 W, i.e., on the left side of the maximum in Figure 4, where stable cavitation is believed to be dominant. The influence of the sound intensity on luminescence and chemical action by pulsed ultrasound will be reported later. Of special interest will be the very short pulses of extremely high intensity used in medicine. The first observations indicate that the activation time is very short for these pulses, but a rather long time of deactivation exists under these conditions.[10]

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Chemistry of Semiconductor Clusters: A Survey of the Reactions of Si_{25}^+ Using Low-Energy Ion Beam Techniques

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Abstract: The chemical reactions of Si_{25}^+ clusters with D_2, CH_4, O_2, C_2H_4, CO, and N_2 have been studied using low-energy ion beam techniques. The results complement our previous studies of Al_{25}^+ and allow a comparison between the reactions of metal clusters and semiconductor clusters. With D_2, CH_4, C_2H_4, and N_2, metastable adducts (arising from chemisorption on the Si_{25}^+ cluster) were directly observed, but with O_2 and CO only chemical reactions (resulting in cluster fragmentation) occur. Activation barriers for dissociative chemisorption were determined from the experimental results. The activation barriers for chemisorption of D_2, CH_4, O_2, and C_2H_4 on Si_{25}^+ are similar to those for chemisorption on Al_{25}^+. However, activation barriers for chemisorption of CO and N_2 on Si_{25}^+ are significantly larger than for chemisorption on Al_{25}^+. While there are similarities between the activation barriers for chemisorption on Si_{25}^+ and Al_{25}^+, the products of the chemical reactions are different. Si_{25}^+ shows a tendency to undergo fission in its chemical reactions, similar to the processes observed in a number of recent studies of the dissociation of the bare clusters.

We have recently reported several studies of the chemical reactions of aluminum cluster ions.[1-5] In addition to studies of the reactions with O_2 and D_2 as a function of cluster size,[1-3] we have also investigated the reactions of Al_{25}^+ with a number of simple molecules.[4,5] Al_{25}^+ was selected for detailed study because we expected its chemistry to be typical of the larger clusters where the reactivity generally changes quite slowly with cluster size. Here we describe a similar survey of the reactions of Si_{25}^+. Little is known about the structure and bonding of either Al_{25}^+ or Si_{25}^+. Detailed ab initio calculation are not available for either cluster. By analogy with the bulk materials we expect the bonding in Al_{25}^+ to be metallic with delocalized valence electrons, and the bonding in Si_{25}^+ to be covalent with localized valence electrons and directional bonding. The bonding in these two clusters is thus expected to be quite different.

In our previous work on the reactions of Al_{25}^+ we found a correlation between the activation barriers for dissociative chemisorption and the cluster HOMO → molecule LUMO promotion energies. This correlation (analogous to the one previously discussed by the Exxon group[6,7]) suggests that charge transfer (electron donation) stabilizes the transition state and lowers the activation barrier for dissociative chemisorption. We noted that other factors could also be important in determining the size of the activation barrier. The motivation for the work described in this paper was to compare the chemistry of metal and semiconductor clusters and to further probe the factors important in determining the size of the activation barriers for dissociative chemisorption on atomic clusters.

The reactions of small silicon cluster ions containing up to eight atoms have previously been studied by Mandich, Reents, and Bondybey[8-11] and Creasy, O'Keefe, and McDonald[12] using Fourier

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