Sonoluminescence from Nonaqueous Liquids: Emission from Small Molecules

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Abstract: Sonoluminescence spectra from nonaqueous liquids under a variety of gases are presented. Ultrasonic irradiation of alkanes under Ar leads to emission from C2, C3H, and CH. When nitrogen is present, emission is seen from CN. When oxygen is present, emission from CO2, CH, and OH is observed. Ultrasonic irradiation of tetrachloroethylene or CCl4 leads to emission from Cl2. The intensity of sonoluminescence decreases as the liquid vapor pressure increases. The properties of the dissolved gas also influence the sonoluminescence observed. Sonoluminescence is caused by chemical reactions of high energy species formed during cavitation collapse. It is a form of chemiluminescence. The principal source of sonoluminescence is not blackbody radiation or electrical discharge.

Ultrasonic irradiation of liquids can produce light. This phenomenon, known as sonoluminescence (SL), was first observed from water in 1934 by Frenzel and Schultes1 and from organic liquids in 1937 by Chambers.2 Although sonoluminescence from aqueous solutions has been studied in some detail,3,4 little work on sonoluminescence from nonaqueous liquids has been reported. We present here sonoluminescence spectra from several nonaqueous liquids in the presence of various gases. We conclude that sonoluminescence from organic liquids is caused by emission from small free radicals and molecules, such as C2, CN, CO2, and Cl2. A preliminary report5 of this work has been published.

There has been some dispute over the mechanism of sonoluminescence.3 All of the theories of SL invoke acoustic cavitation6 (the formation, growth, and implosive collapse of bubbles in solution), as the source of the phenomenon. Noltink and Neppiras proposed SL was from blackbody emission7 of the heated cavity. Electrical discharge8 inside the bubble has been proposed several times as the source of SL, most recently by Margulis.8d Vaughan and Leeman have recently proposed a shock-wave model9 where SL is caused by a shock-wave from the collapsing bubble wall. In the hot-spot chemiluminescence model,10,11 which is the best

developed theory, emission is from species that are formed by the high temperature of the cavitation event. The data presented here are consistent only with the hot-spot model. Differences between the behavior predicted by the other theories and the observed data are significant and will be discussed later.

Acoustic cavitation converts the low-density acoustic energy of a sound field into high-density thermal energy by intensely heating gas- and vapor-filled bubbles in a liquid. Bubbles are formed during a rarefaction phase of the sound wave at nucleation sites in the liquid, typically gas-filled crevices in particulate contaminants. Once formed, bubbles can grow by a variety of mechanisms.\(^5\) If the sound field is intense enough, rapid expansion of a resonant bubble can occur due to inertial effects, until bubble motion is no longer strongly coupled to the acoustic field. At this point, the acoustic pressure of the sound field rapidly compresses the bubble, heating the contents. This localized hot spot causes most homogeneous sonochemistry.\(^12\)

The actual temperatures and pressures present during the cavitation event remain to be fully characterized. Lord Rayleigh calculated temperatures\(^13\) in excess of 10,000 K and pressures greater than 1000 atm. Current hydrodynamic models give temperatures in the range 1000 to 10,000 K.\(^14\) The temperature of the cavitation event in aqueous media has been determined in several sonoluminescence studies,\(^15\) but aspects of these studies have been questioned.\(^4\) The effective temperature reached during cavitation in alkane solvents at a vapor pressure of several 1000 atm. Current hydrodynamic models give temperatures in the range 1000 to 10,000 K.\(^14\) The temperature reached upon addition of a resonant bubble.

The sonoluminescence spectrum of water consists of a peak at 310 nm and a broad continuum throughout the visible region. The sonoluminescence spectrum of dodecane under \(\text{Ar} \) at 4 °C, vapor pressure = 0.012 Torr. Spectrum is the concatenation of four spectra, each of the average of 10 100-s spectra. Howlett observed neutron-induced cavitation from degassed tetrachloroethylene. The effect of dissolved gases on the SL intensity from water, alcohols, and alkanes has been reported by several workers.\(^21\)\(^22\) Chadk and Fogler studied SL from CCl\(_4\) in water, and CCl\(_4\)/water mixtures\(^23\) with a filter spectrometer and a photomultiplier tube. They observed a broad continuum across the entire range of their filters. They assigned this feature to emission from CCl\(_4\)* based on the similarity to the absorption spectrum. This assignment has been questioned by Verrall and Sehgal,\(^3\) who pointed out that absorption and emission spectra of the same species are seldom superimposable.

**Experimental Section**

A block diagram of the equipment used in this study is shown in Figure 1. High-intensity ultrasound was generated by a titanium immersion horn (Heat Systems Ultrasonics Model W375) operating at 20 kHz and -60 W/cm\(^2\). The stainless-steel cell with gas ports, cooling jacket, and quartz window has been described elsewhere.\(^24\) The sonochemical rates generally decrease as the gas is changed from \(\text{Ar} \) (\(\gamma = 1.67\)) to \(\text{N}_2 \) (\(\gamma = 1.44\)) to \(\text{CO}_2 \) (\(\gamma = 1.31\)) to freons (\(\gamma = 1\)). In addition, the thermal conductivity of the dissolved gas is important. Higher thermal conductivities produce lower temperatures during cavitation collapse, because heat is efficiently removed from the collapsing bubble.

The nonlinearities of the high-speed detectors limit the range of pressures for which they can perform experiments. The most homogeneous sonochemistry.\(^12\)

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(13) Lord Rayleigh, Phil. Mag. 1917, 34, 94.


nm, which we assign to the A^2Δ - X^2Π transition of CH. Emission from CH is more prominent from systems that contain oxygen and will be discussed below.

Figure 2 shows a continuum extending from 340 nm to beyond 700 nm underlying the peaks that are assigned to C2 and CH. In order to probe the origin of this continuum, sonoluminescence spectra of dodecane under He, Ne, a He/Ar mixture, and Ar were studied. The total SL intensity decreased as the thermal conductivity of the gas increased, until, under pure He, SL was too weak to be detected. The shape of the continuum, and the relative intensity of the C2 peaks to the continuum, remained unchanged in spite of the different cavitation temperatures caused by the different thermal conductivities of the gases. This indicates that the continuum is from a process that is highly correlated with C2 emission, and that it is clearly not from blackbody emission. The SL spectra from dodecane and 2,2,4,4,6,8,8-heptamethylnonane, under Ar and at the same vapor pressure, were also compared. Both have continuum emission and C2 emission, but the highly branched alkane favors the continuum.

Although the origin of the sonoluminescence continuum cannot be definitively assigned at this time, we propose that it is emission from C2H+. The published emission spectrum of C2H+ is similar to the SL continuum, although the SL spectrum extends farther into the UV; the higher temperature during cavitation may account for this difference. The high degree of correlation between the C2* emission and the continuum as the cavitation temperature is changed is consistent with this assignment, since similar chemical processes lead to C2* and C2H+ (see eq 2-5 below). Furthermore, the difference in the SL spectra between branched and linear alkanes is consistent with this assignment, since the concentration of hydrogen-bearing fragments is higher with the branched alkane.

There are, however, other possible explanations for this SL continuum. One is radiative mediation of the radical reactions that form C2*, where the excess translational energy of colliding species is converted to light. Another possibility is liquid-phase emission of C2*. A third possibility is unresolved overlap of emission from multiple species.

We propose that C2* and C2H+ are formed during cavitation by condensation reactions of two C2 fragments, such as eq 2-5.

\[
\begin{align*}
\text{CH} + \text{C} & \rightarrow \text{C2}^* + \text{H} \\
\text{CH} + \text{CH} & \rightarrow \text{C2}^* + \text{H2} \\
\text{C} + \text{CH} & \rightarrow \text{C2}^* + \text{H2} \\
\text{CH} + \text{CH} & \rightarrow \text{C2H}_2^* + \text{H} \\
\end{align*}
\]

Equation 2 has been proposed to be the C2* forming reaction in both methane flames and microwave discharges. The scrambling of isotopically labeled carbon atoms during the combustion of acetylene led Ferguson to propose that eq 1 was important, since CH* emission is also seen in flames. All three equations, and others involving species with more hydrogens, were recognized as being possible mechanisms for the formation of C2* during the IR multiphoton photolysis of partially labeled ethylene. Grebe and Homann studied the chemiluminescence of the C2H2/O/H system in a low-pressure discharge flow reactor and concluded from kinetic arguments that eq 2 and 3 were unimportant and that eq 4 was responsible for the formation of C2*. They also recorded a continuum emission in the visible that they attributed to C2H* and that they proposed that it was formed by eq 5. Continuous emission assigned to C2H* has also been observed during UV and IR irradiation of acetylene. Re-
actions similar to eq 5 involving more hydrogens are also candidates for the production of $C_3H^\cdot$. SL from 2,2,4,4,6,8-heptamethylnonane favors the continuum; this is consistent with eq 5, since a branched alkane will produce more hydrogenated carbon fragments than a linear one.

The relative contributions of reactions 2-4 during the ultrasonic irradiation of dodecane are unknown, as they are in many systems where multiple reaction pathways can occur. Radical mechanisms have been proposed for many sonochemical reactions, including the sonolysis of alkanes. For example, the major sonodegradation products of decane are $H_2$, $CH_4$, $C_2H_2$, and $C_2H_4$, and the relative ratio of these and other products is consistent with a Rice radical chain mechanism. The radicals $C$, $CH$, and $CH_2$ fit easily into such a mechanism, and $C_2$ can be converted into acetylene by a variety of propagation and termination steps.

The vapor pressure dependence of sonoluminescence from linear alkanes (dodecane, decane, octane) is shown in Figure 4. This plot shows the behavior that we have come to expect for gas-phase chemical reactions (in this case proportional to the SL intensity) decreases with increasing vapor pressure, because the peak temperature reached during cavitation decreases with increasing vapor pressure. If Arrhenius behavior is followed, then from hydrodynamic models, one can predict roughly the relationship

$$I_{SL} \propto B \cdot e^{-CP}$$

where $I_{SL}$ is the intensity of sonoluminescence, $P$ is the total system vapor pressure, $B$ contains the activation entropy of the reaction and the true $\gamma$ of the bubble contents. Given the complex set of reactions responsible for the formation of $C_3^\cdot$, further analysis of these proportionality constants is not possible. The fit of the data to this expected relationship, however, is quite good, as shown in Figure 4.

**Nitrogen-Containing Systems.** The sonoluminescence spectra from liquids with a nitrogen-containing solute or gas all have a common feature: a major peak at 388 nm, as shown in Figure 5. This peak is assigned to the $B^2\Pi^+_C - X^2\Sigma^+_g^o$ ($\Delta v = 0$) transition of CN. The peaks at 421.6 nm and 359.0 nm correspond to $\Delta v = -1$ and +1 of this transition. This emission is also seen from other high-energy processes when nitrogen is present. The source of the nitrogen can be either dissolved gas or a volatile solute; SL from dodecane in the presence of $N_2$, $NH_3$, and 1,2-diaminoethane all give similar spectra. The Swan bands from $C_3$ are visible but reduced in intensity in these spectra. A continuum beneath all the peaks is still apparent. Plausible reactions for the formation of $CN^\ast$ include eq 7 and 8.

$$C + N + (M) \rightarrow CN^\ast + (M) \quad (7)$$
$$C + N_2 \rightarrow CN^\ast + N \quad (8)$$

of $CN^\ast$ has been observed in a discharge containing nitrogen and carbon atoms, and eq 7 (with third body mediation) was proposed as the mechanism. Bulewicz mentioned eq 8 in reference to low-pressure $C_2N_2O_2$ flames, although it was noted that in those systems the reaction is not exothermic enough to form $CN^\ast$. The higher temperatures of cavitation collapse may provide enough energy for eq 8 to be important. Reactions similar to eq 7 and 8 but with hydrogenated species may also play a role in $CN^\ast$ formation. These reactions are consistent with the radical scheme mentioned above for the formation of $C_3^\ast$. 

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Sonoluminescence from Nonaqueous Liquids

Figure 7. Sonoluminescence from systems containing oxygen. Each spectrum is the concatenation of four spectra, each the average of 10 100-s spectra. Peaks from CO2, OH, CH, and C2 are indicated: (a) SL from dodecane under O2 at 4 °C, vapor pressure = 0.012 Torr; (b) SL from dodecane under 10% O2/90% Ar at 4 °C, vapor pressure = 0.012 Torr. Spectrum multiplied by two (2.0) for clarity of presentation. (c) SL from 1-octanol under Ar at 12 °C, vapor pressure = 0.015 Torr. (d) SL from nitroethane under Ar at -9 °C, vapor pressure = 2.4 Torr.

The variation of the sonoluminescence intensity of the 388-nm CN peak as a function of N2 concentration is shown in Figure 6. We attribute the shape of this curve to two competing processes. The initial increase in intensity with increasing nitrogen is due to simple kinetics: increasing the concentration of N2 increases the rate of the reactions that produce CN*. At higher nitrogen concentrations, however, the decreasing γ of the bubble contents decreases the maximum temperature reached during cavitation collapse, which decreases the rate of reaction.

Oxygen-Containing Systems. The sonoluminescence spectra of several oxygen-containing systems are shown in Figure 7. We assign the continuum that starts around 360 nm and peaks around 420 nm to emission from CO2, the so-called CO flame spectrum. Visible emission assigned to CO2 is not common. Reaction of oxygen atoms with CO van der Waals molecules in a crossed molecular beam experiment leads to CO2* emission.

Fluorescence and thermoluminescence of CO2 have been reported at cryogenic temperatures, and CO2 emission has also been seen from CO–O2 explosions and in a CO2 flowing afterglow. All of these systems have CO or CO2 as a reactant, a significant difference from this work. Radical reactions for the formation of CO2* during ultrasonic irradiation of dodecane under O2 are

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2* \]  
(9)

\[ \text{C} + \text{O} + \text{O} \rightarrow \text{CO}_2* \]  
(10)

\[ \text{C}_2* + \text{O}_2 \rightarrow \text{CO}_2* + \text{C} \]  
(11)

The effect of the O2 concentration in the gas stream on the sonoluminescence spectra of dodecane is shown in Figure 8. As O2 is introduced the intensity of the entire spectrum (both the peaks from C2 and the continuum) decreases. A small increase in the entire spectrum is further increased, and the O2 continuum grows in until, under pure O2, it is as intense as the original spectrum. The initial decrease in the entire spectrum upon the addition of small amounts of O2 leads us to believe that the O2 is directly quenching the excited-state C2. A comparison of the sonoluminescence intensity versus concentration of N2 or CO and O2 shows that the C2* peaks fall off faster with O2 than with N2 or CO. At higher concentrations of O2, eq 9–11 (which must have a smaller rate constant than the quenching reaction) begin to dominate and CO2* becomes the dominant emitting species. As a further check on our assignments, the gaseous products of a 6-h sonication of dodecane under pure O2 were analyzed by gas chromatography, and CO2 was observed as the primary product.

In the sonoluminescence spectrum of dodecane under 10% O2 and 90% Ar (Figure 7, curve b), two new peaks are present at 391 nm and 431 nm, which we assign to emission from CH. Emission from CH is a dominant feature of flame spectra and eq 12 and 13 are typically proposed to account for the emission.

\[ \text{C}_2 + \text{OH} \rightarrow \text{CH}^* + \text{CO} \]  
(12)

\[ \text{CH}_2 + \text{O} \rightarrow \text{CH}^* + \text{OH} \]  
(13)

A weak emission from OH can be seen as a small peak in Figure 7 from 305 to 315 nm. Emission from OH is also a dominant feature of flame spectra and has been detected in the SL from water. Equation 14 has been often proposed for the formation of OH* in flames.

\[ \text{CH} + \text{O}_2 \rightarrow \text{OH}^* + \text{CO} \]  
(14)

In our previous report we assigned SL from nitroethane to emission from NO. This is not supported by spectrum d in Figure 7, which is corrected for wavelength response. Based on the similarity of the nitroethane spectrum to those from dodecane under O2 and from octanol, we now believe this to be CO2 emission. The sharp edge in the emission spectrum at 390 nm is from the UV cutoff of nitroethane.

Chlorine-Containing Systems. Sonoluminescence spectra from halocarbons under Ar is shown in Figure 9. We assign the broad

conductivity does not change the shape of the spectrum.

Our sonoluminescence spectra are similar to the chemiluminescence spectra of Browne and Ogryzlo obtained from C{l}_4 afterglow experiments. Formation of radicals from the sonolysis of halocarbons is well documented, and C{l}_2 is a major product of the sonolysis of CCl_4. A simple reaction is presented in eq 15 for the formation of C{l}_2^*.

\[ 2\text{Cl} \rightarrow \text{Cl}_2^* \] (15)

Chendke and Fogler reported a sonoluminescence spectrum similar to ours from a water/CCl_4 system, which they assigned to emission from CCl_4^*, due to its similarity to the absorption spectrum. There are no other reports of emission from CCl_4^*, and Verrall and Sehgal have questioned the validity of this assignment, pointing out that absorption and emission spectra of the same species are seldom superimposable.

**Other Theories of SL.** The data presented here are most consistent with the hot-spot chemiluminescence model of sonoluminescence. The emission reported here is clearly not blackbody emission, since the addition of an inert gas with higher thermal conductivity does not change the temperature significantly. The continuum seen in the SL from alkanes is not blackbody emission either, since the addition of an inert gas with higher thermal conductivity does not change the shape of the spectrum.

The sonoluminescence spectra reported here are not consistent with electrical discharge theories either. While emission from C_2 and CN is observed from electrical discharges, under these conditions emission from excited state N_2 and N_2^* is also expected. This is not observed. Additionally, electrical discharge through C{l}_2 results in emission from excited-state C{l}_2^*. Again, SL spectra fail to show any such emission. The emission spectra of N_2, N_2^*, and Cl_2^* are all easily identifiable banded spectra. For these reasons, the electrical discharge theory is inconsistent with SL from nonaqueous liquids.

The shock-wave theory proposed by Vaughan and Leeman is essentially a thermal theory, since shock waves promote chemical reactions by heating the gas through which they travel. This theory ascribes the differences seen in SL intensity as changes in the thermal conductivity of the gas and the speed of sound through the gas. For Ar and N_2 these two properties have the same values to within 10%, but under Ar there is considerable SL intensity, while under N_2 none could be detected with our system. These experimental results are clearly inconsistent with the shock-wave theory.

In summary, all of the observations presented here are consistent with the hot-spot chemiluminescence model of sonoluminescence. All of the emitting species that are conclusively identified by their band spectra (C_2, CN, CH, OH) are formed in other high-temperature processes, as are the species with broader spectra that we have proposed (C_2H, CO_2, Cl_2). The change in the SL intensity from alkanes as a function of vapor pressure can be modeled by application of Arrhenius theory to bubble collapse. The sonoluminescence intensity as a function of diatomic gas concentration is also consistent with the hot-spot model.

**Conclusions.**

The sonoluminescence spectra presented here provide conclusive evidence that high-energy species are produced during the ultrasonic irradiation of liquids. We have interpreted these results in terms of the hot-spot model of the chemical effects of ultrasound, which is based on acoustic cavitation. Well-precedented reactions have been proposed for the sonochemical production of the excited-state species responsible for the observed sonoluminescence.

Several general conclusions can be made from these studies. First, sonoluminescence is caused by chemical reactions of high-energy species formed during cavitation collapse. It is a form of chemiluminescence. The principal source of sonoluminescence is not blackbody radiation. Emission from charged species is not observed, which indicates that electrical discharge is not an important excitation mechanism. Second, the local, transient temperature reached during the cavitation event determines the rate of the chemical reactions that occur and the intensity of the luminescence observed. The factors that affect the temperature of cavitation collapse include the nature of the gas (γ and thermal conductivity) and the vapor pressure of the liquid. Third, the chemistry responsible for sonoluminescence depends on the contents of the collapsing bubble, including both the dissolved gas and the vapor of the liquid.

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(41) Some differences between Figure 9 and our previously published SL spectrum of tetrachloroethylene can be noted. Our earlier spectrum was not corrected for wavelength response, and the photomultiplier tube used (RCA 1P28) had a poor response in the red region of the spectrum. The short wavelength cutoff of the spectra also differ due to the considerable darkening of the tetrachloroethylene over the >2 min needed to collect the spectrum with the PMT. The spectrum presented in Figure 9 was collected with the diode array detector during the first 5 min of ultrasonic irradiation, during which time darkening was minimal.


