

as a purely additive composite of single terminal oscillators, it is striking to see its good description of experimental  $\tau_{\Delta}$  values. Taking the empirical values  $k_{XY}$  of the heavy-atom-containing oscillators C-Cl, C-Br, and C-I for aromatic and aliphatic solvent molecules and for the rest of oscillators  $k_{XY}$  values resulting from the corresponding  $E_{XY}$  and from the fitted curve of Figure 2, it is possible to calculate  $\tau_{\Delta}$  values using eq 1 and 8. The linear least-squares fit of a logarithmic plot of calculated vs experimental  $^1\text{O}_2$  lifetimes shown in Figure 4 results in slope 1.00, intercept 0.00, and a correlation coefficient of 0.99. The only value deviating considerably (by a factor of 3) is  $\tau_{\Delta}$  measured in  $\text{D}_2\text{O}$ . Thus the excellent quantitative description of the experimental  $^1\text{O}_2$  lifetimes by the collisional  $\text{E} \rightarrow \text{V}$  energy-transfer model is demonstrated.

The fitted curve of Figure 2 and the above-mentioned empirical values of  $k_{XY}$  can of course be used to calculate approximate  $^1\text{O}_2$  lifetimes for solvents not included in Figure 4. For that purpose it is only necessary to take from the fit  $\ln k_{XY}$  values using literature data on  $E_{XY}$  for the desired oscillators X-Y (e.g.,  $E_{\text{C}=\text{O}} = 1750 \text{ cm}^{-1}$ ). Since  $\tau_{\Delta}$  values have been measured in highly purified solvents using low irradiation powers, the estimated lifetimes are only realistic in weakly deactivating solvents under corresponding conditions.

### Conclusions

The radiationless deactivation of  $^1\text{O}_2$  by solvent molecules occurs under partial penetration of the electron clouds as a collisional

$\text{E} \rightarrow \text{V}$  energy transfer from  $^1\text{O}_2$  to single oscillators X-Y (=terminal atom pairs) of the solvent molecule. Its rate constant  $k_{XY}$  correlates exponentially with the energy of the maximum vibrational quantum, which X-Y can accept. Consequently, a mass dependence results and solvents with light-atom oscillators like C-H deactivate  $^1\text{O}_2$  much stronger than solvents with oscillators C-F. Since  $^1\text{O}_2$  deactivation includes an intercombination transition, a strong internal heavy-atom effect takes place if a heavy atom is part of the deactivating oscillator. However, as heavy-atom substitution in X-Y results in a decrease of vibrational frequency of X-Y, the actual spin-orbit interaction dependent effect on  $k_{XY}$  is weakened and operates only in the range of small rate constants  $k_{XY}$ . That is the reason why a clear heavy-atom effect on  $\tau_{\Delta}$  is observed only in weakly deactivating solvents but not in hydrogen-containing solvents. The magnitude of the internal heavy-atom effect is described quantitatively by the theoretical model on spin-orbit interaction developed by McClure. The external heavy effect exerted from heavy-atom-substituted solvents on radiationless deactivation of  $^1\text{O}_2$  is very weak.

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## 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  $\text{C}_2$ ,  $\text{C}_2\text{H}$ , and CH. When nitrogen is present, emission is seen from CN. When oxygen is present, emission from  $\text{CO}_2$ , CH, and OH is observed. Ultrasonic irradiation of tetrachloroethylene or  $\text{CCl}_4$  leads to emission from  $\text{Cl}_2$ . 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 Schultes<sup>1</sup> and from organic liquids in 1937 by Chambers.<sup>2</sup> Although sonoluminescence from aqueous solutions has been studied in some detail,<sup>3,4</sup> 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  $\text{C}_2$ , CN,  $\text{CO}_2$ , and  $\text{Cl}_2$ . A preliminary report<sup>5</sup> of this work has been published.

There has been some dispute over the mechanism of sonoluminescence.<sup>3</sup> All of the theories of SL invoke acoustic cavitation<sup>6</sup> (the formation, growth, and implosive collapse of bubbles in solution), as the source of the phenomenon. Noltink and Neppiras proposed SL was from blackbody emission<sup>7</sup> of the heated cavity. Electrical discharge<sup>8</sup> inside the bubble has been proposed several times as the source of SL, most recently by Margulis.<sup>8d</sup> Vaughan

and Leeman have recently proposed a shock-wave model,<sup>9</sup> where SL is caused by a shock-wave from the collapsing bubble wall. In the hot-spot chemiluminescence model,<sup>10,11</sup> which is the best

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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<sup>6</sup> 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.<sup>6</sup> 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.<sup>12</sup>

The actual temperatures and pressures present during the cavitation event remain to be fully characterized. Lord Rayleigh calculated temperatures<sup>13</sup> 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.<sup>14</sup> The temperature of the cavitation event in aqueous media has been determined in several sonoluminescence studies,<sup>15</sup> but aspects of these studies have been questioned.<sup>4</sup> The effective temperature reached during cavitation in alkane solvents at a vapor pressure of 5 Torr under argon has been recently determined<sup>11</sup> by chemical rate thermometry; this study reports an effective temperature of  $\sim 5000$  K in the gas phase and  $\sim 2000$  K in an initially liquid shell around the bubble.

The effects of the bubble contents on the temperature generated in the localized hot spot are well understood. Two properties of gases, the ratio of the heat capacities ( $\gamma = C_p/C_v$ ) and the thermal conductivity, are important. The temperature reached upon compression of a gas depends on  $\gamma$ , which is inversely related to the number of internal degrees of freedom of the gas. During compression the heat produced partitions across all the degrees of freedom of the gas, and the lower the  $\gamma$  is, the lower the final temperature reached. For this reason, sonochemical rates generally decrease as the gas is changed from Ar ( $\gamma = 1.67$ ) to N<sub>2</sub> ( $\gamma = 1.44$ ) to CO<sub>2</sub> ( $\gamma = 1.31$ ) to freons ( $\gamma \approx 1$ ). 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 sonoluminescence spectrum of water consists of a peak at 310 nm and a broad continuum throughout the visible region. The emission at 310 nm is from OH\*, but the continuum is difficult to interpret.<sup>16</sup> Parts of this continuum are quenched upon addition of nitric acid,<sup>17</sup> which demonstrates that the continuum is from chemical species and was not blackbody emission. SL from aqueous solutions of metal salts is characterized by atomic emission:<sup>15a,18</sup> SL from salt solutions of Li, Na, K, Ca, Sr, Ba, and Cu has been reported.

Sonoluminescence from nonaqueous liquids was reported by Chambers<sup>2</sup> in 1937 and Jarman in 1959.<sup>19</sup> In 1967, West and

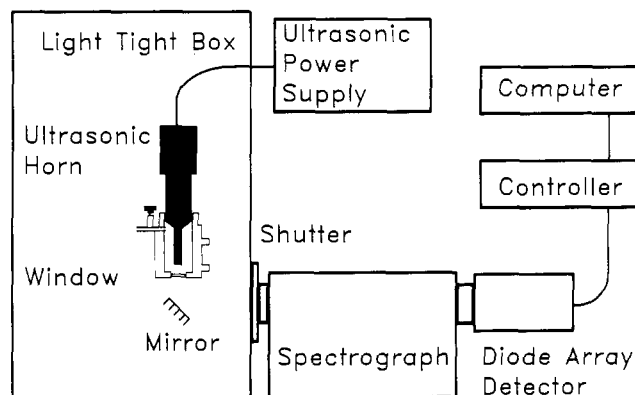


Figure 1. Schematic of experimental apparatus.

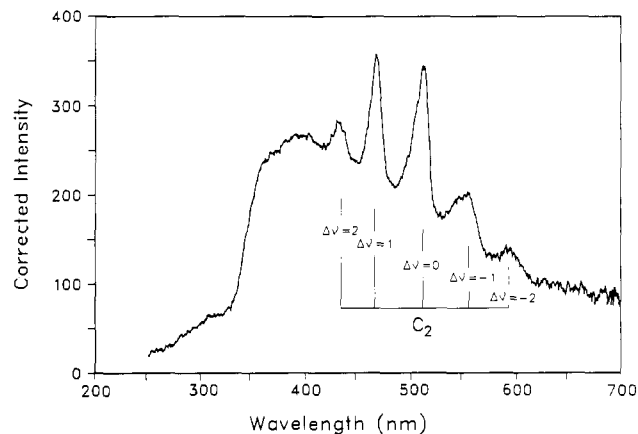


Figure 2. Sonoluminescence spectrum of dodecane under Ar at 4 °C, vapor pressure = 0.012 Torr. Spectrum is the concatenation of four spectra, each of the average of 10 100-s spectra.

Howlett<sup>20</sup> 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.<sup>21,22</sup> Chendke and Fogler studied SL from CCl<sub>4</sub>, water, and CCl<sub>4</sub>/water mixtures<sup>23</sup> 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<sub>4</sub><sup>+</sup> based on the similarity to the absorption spectrum. This assignment has been questioned by Verrall and Sehgal,<sup>3</sup> 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  $\approx 60$  W/cm<sup>2</sup>. The stainless-steel cell with gas ports, cooling jacket, and quartz window has been described elsewhere.<sup>24</sup> The sonoluminescence was dispersed with a Thermo Jarrell-Ash MonoSpec-18 0.25 meter spectrograph. Low-resolution spectra were collected with a 300-grooves/mm grating blazed at 300 nm with a 150- $\mu$ m entrance slit; medium-resolution spectra were collected with a 1200-grooves/mm grating blazed at 500 nm with a 50- $\mu$ m entrance slit. The detector was a Princeton Instruments IRY 512N intensified diode array controlled by a ST120 optical multichannel analyzer. Mercury, neon, and krypton

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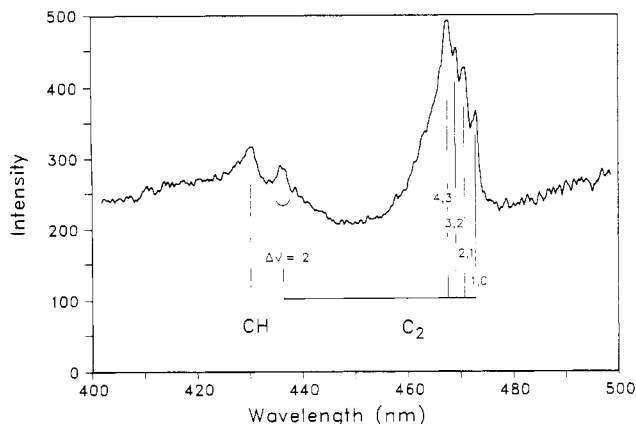
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**Figure 3.** Sonoluminescence spectrum of Dow 200 silicone oil (dimethylpolysiloxane, 20 cs viscosity), under Ar at 4 °C. Vapor pressure is  $\sim 0.01$  Torr. Spectrum is the concatenation of two spectra, each collected for 100 s. The first four transitions of the  $\Delta\nu = 1$  manifold of the Swan bands are indicated, as well as the  $\Delta\nu = 2$  peak. Emission from CH is also marked.

low-pressure lamps were used for wavelength calibration. Relative response functions for the low-resolution spectra were determined by two different methods. The correction function from 400 nm to 700 nm was determined with a 360-W tungsten lamp which had been calibrated against a 1000-W tungsten secondary standard lamp from the Eppley Laboratory. The correction function from 320 nm to 400 nm was determined from the fluorescence of triphenylbenzene.<sup>25</sup>

Argon was purified by passage through an activated copper-on-alumina catalyst tower (BTS from BASF) immediately before use. Other gases were  $>99.6\%$  pure and used as supplied from Linde Corp. Gases were mixed with needle valves, and flow rates were measured by rotometers that are accurate to  $\pm 10\%$ . Liquids were sparged before ultrasonic irradiation for 30 min and during spectra acquisition. Liquids and solids were either  $>99\%$  pure and used as received or were purified by standard techniques.<sup>26</sup> Vapor pressures were calculated from the Antoine equation

$$\log(V_p) = A - B/(t + C) \quad (1)$$

where  $V_p$  is the vapor pressure,  $t$  is the temperature in °C, and  $A$ ,  $B$ , and  $C$  are empirical constants for each liquid.<sup>27</sup> The temperature of the reaction cell was measured with a copper-constantan thermocouple.

## Results and Discussion

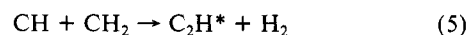
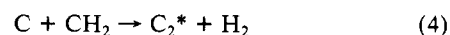
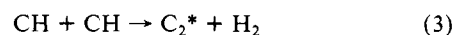
**Hydrocarbons under Ar.** The sonoluminescence spectrum from dodecane during a continuous Ar purge is shown in Figure 2. Spectra from alkanes, arenes, and Dow Corning 200 silicone oil (20-centistoke viscosity) have similar features. The peaks with band heads at 563.6, 516.5, 473.7, and 438.2 nm are assigned<sup>28</sup> to  $\Delta\nu = -1, 0, +1$ , and  $+2$  of the  $d^3\Pi_g - a^3\Pi_u$  Swan transition of  $C_2$ , respectively. This very common emission is seen from flames,<sup>29a</sup> in plasmas,<sup>29b</sup> and even after the implosion of Xe-filled glass spheres in paraffin oil.<sup>30</sup> The vibrational structure of the 473.7-nm peak can be seen in the medium-resolution SL spectrum of silicone oil, shown in Figure 3. The peaks, going from high to low wavelength, correspond to the  $(\nu' - \nu'')$  transitions (1-0), (2-1), (3-2), and (4-3). This indicates that the emission is from the gas phase, since resolution of the vibrational bands is not expected from liquid-phase emission. In addition, Figure 3 shows the  $C_2$  Swan  $\Delta\nu = +2$  peak at 438.3 nm and a weak peak at 431.2

nm, which we assign to the  $A^2\Delta - X^2\Pi$  transition<sup>28</sup> 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  $C_2$  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  $C_2$  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  $C_2$  emission, and that it is clearly *not* from blackbody emission. The SL spectra from dodecane and 2,2,4,4,6,6,8,8-heptamethylnonane, under Ar and at the same vapor pressure, were also compared. Both have continuum emission and  $C_2$  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  $C_2H^*$ . The published emission spectrum<sup>31</sup> of  $C_2H^*$  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  $C_2^*$  emission and the continuum as the cavitation temperature is changed is consistent with this assignment, since similar chemical processes lead to  $C_2^*$  and  $C_2H^*$  (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  $C_2^*$ , where the excess translational energy of colliding species is converted to light.<sup>32</sup> Another possibility is liquid-phase emission of  $C_2^*$ . A third possibility is unresolved overlap of emission from multiple species.

We propose that  $C_2^*$  and  $C_2H^*$  are formed during cavitation by condensation reactions of two  $C_1$  fragments, such as eq 2-5.



Equation 2 has been proposed to be the  $C_2^*$  forming reaction in both methane flames<sup>33a</sup> and microwave discharges.<sup>33b</sup> The scrambling of isotopically labeled carbon atoms during the combustion of acetylene<sup>33c</sup> led Ferguson to propose that eq 3 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  $C_2^*$  during the IR multiphoton photolysis of partially labeled ethylene.<sup>33d</sup> Grebe and Homann<sup>31</sup> studied the chemiluminescence of the  $C_2H_2/O/H$  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  $C_2^*$ . They also recorded a continuum emission in the visible that they attributed to  $C_2H^*$ , and they proposed that it was formed by eq 5. Continuous emission assigned to  $C_2H^*$  has also been observed during UV<sup>34a</sup> and IR<sup>34b</sup> irradiation of acetylene. Re-

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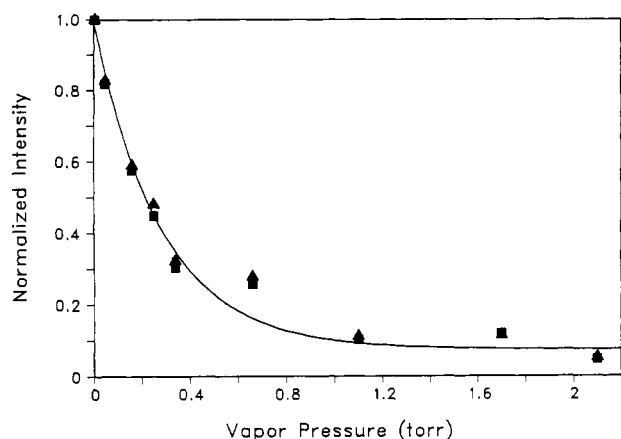
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**Figure 4.** The vapor pressure dependence of SL from alkanes under Ar, normalized to emission from dodecane at 0.006 Torr: ( $\Delta$ ) peak at 465 nm, ( $\blacksquare$ ) peak at 510 nm, (—) fit curve (see text). Data are from dodecane, decane, and octane.

actions similar to eq 5 involving more hydrogens are also candidates for the production of  $C_2H^*$ . SL from 2,2,4,4,6,8,8-heptamethylnonane favors the continuum; this is consistent with eq 5, since a branched alkane will produce more hydrogenated carbon fragments than a linear one.

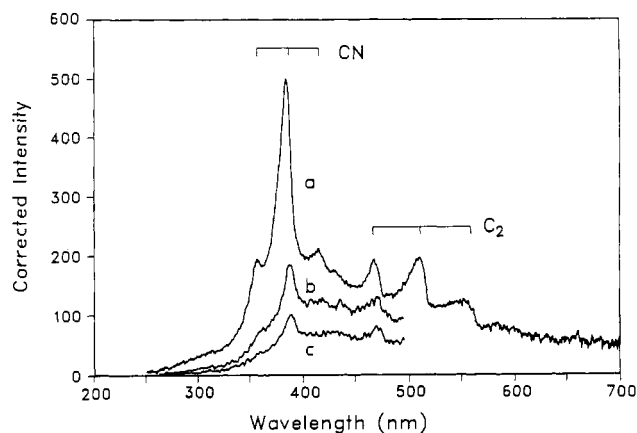
The relative contributions of reactions 2–4 during the ultrasonic irradiation of dodecane are unknown, as they are in many systems where multiple reaction pathways can occur. Radical mechanisms have been proposed for many sonochemical reactions,<sup>35</sup> including the sonolysis of alkanes. For example, the major sonodegradation products of decane<sup>35a</sup> 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 sonochemical reactions:<sup>35a,36</sup> the rate of homogeneous sonochemical 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<sup>21a</sup> the relationship

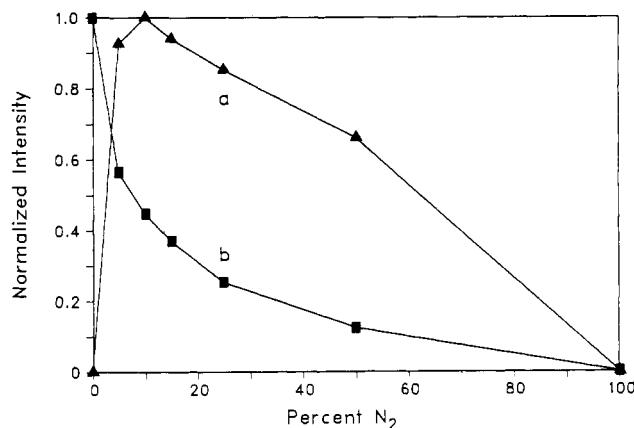
$$I_{SL} \approx Be^{-CP} \quad (6)$$

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 volume undergoing cavitation, and  $C$  contains the activation enthalpy of the reaction and the true  $\gamma$  of the bubble contents. Given the complex set of reactions responsible for the formation of  $C_2^*$ , further analysis of these proportionality constants is not possible. The fit to 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  $B^2\Sigma^+ - X^2\Sigma^+$  ( $\Delta\nu = 0$ ) transition of CN. The peaks at 421.6 nm and 359.0 nm correspond to  $\Delta\nu = -1$  and  $+1$  of this transition.<sup>28</sup> This emission is also seen from

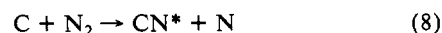
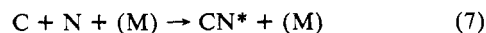


**Figure 5.** Sonoluminescence from systems containing nitrogen. Each spectrum is the average of 10 100-s spectra. Peaks from CN and  $C_2$  are indicated: (a) SL from dodecane under 15%  $N_2$ /85% Ar at 4 °C, vapor pressure = 0.012 Torr. Spectrum is the concatenation of four spectra: (b) SL from 0.025 M 1,2-diaminoethane in dodecane under Ar at 4 °C; (c) SL from dodecane 20 min after saturation with  $NH_3$  followed by Ar purge.



**Figure 6.** SL intensity under  $N_2$ /Ar mixtures: (a) CN peak at 388 nm, (b)  $C_2$  peak at 510 nm.

other high-energy processes when nitrogen is present.<sup>29,37,38</sup> 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  $C_2$  are visible but reduced in intensity in these spectra. A continuum beneath all the peaks is still apparent. Plausible reactions for the formation of  $CN^*$  include eq 7 and 8. The formation



of  $CN^*$  has been observed<sup>39a</sup> in a discharge containing nitrogen and carbon atoms, and eq 7 (with third body mediation) was proposed as the mechanism. Bulewicz<sup>39b</sup> mentioned eq 8 in reference to low-pressure  $C_2N_2-O_2$  flames, although it was noted that in those systems the reaction is not exothermic enough to form  $CN^*$ . 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  $CN^*$  formation. These reactions are consistent with the radical scheme mentioned above for the formation of  $C_2^*$ .

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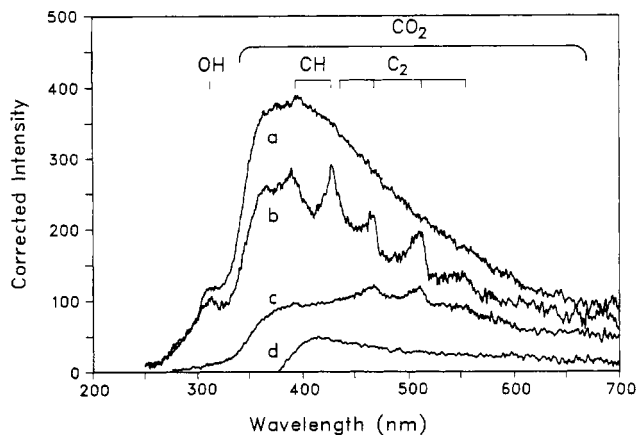
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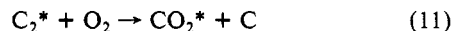
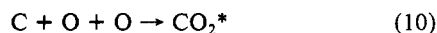
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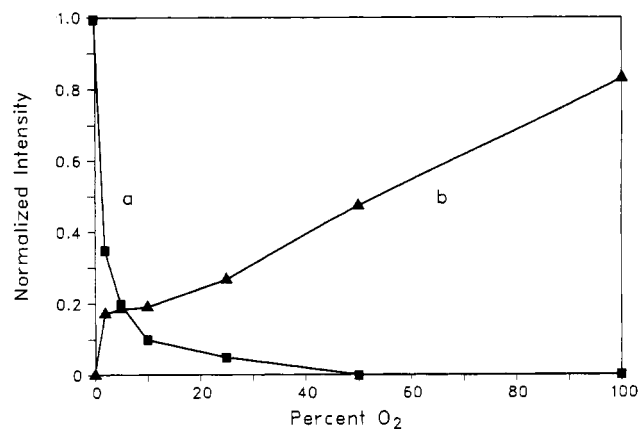
**Figure 7.** Sonoluminescence from systems containing oxygen. Each spectrum is the concatenation of four spectra, each the average of 10 100-s spectra. Peaks from  $\text{CO}_2$ , OH, CH, and  $\text{C}_2$  are indicated: (a) SL from dodecane under  $\text{O}_2$  at 4 °C, vapor pressure = 0.012 Torr; (b) SL from dodecane under 10%  $\text{O}_2$ /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  $\text{N}_2$  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  $\text{N}_2$  increases the rate of the reactions that produce  $\text{CN}^*$ . At higher nitrogen concentrations, however, the decreasing  $\gamma$  of the bubble contents decreases the maximum temperature reached during cavitation collapse, which decreases the rate of reaction.

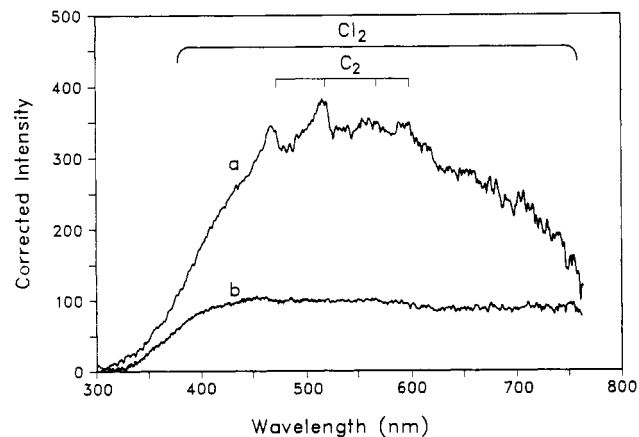
**Oxygen-Containing Systems.** The sonoluminescence spectra of several oxygen-containing systems are shown in Figure 7. We assign the continuum that starts around 360 nm and peaks around 420 nm to emission from  $\text{CO}_2$ , the so-called CO flame spectrum.<sup>28</sup> Visible emission assigned to  $\text{CO}_2$  is not common. Reaction of oxygen atoms with CO van der Waals molecules in a crossed molecular beam experiment leads to  $\text{CO}_2^*$  emission.<sup>40a</sup> Fluorescence<sup>40b</sup> and thermoluminescence<sup>40c</sup> of  $\text{CO}_2$  have been reported at cryogenic temperatures, and  $\text{CO}_2$  emission has also been seen from CO- $\text{O}_2$  explosions<sup>40d</sup> and in a  $\text{CO}_2$  flowing afterglow.<sup>40e</sup> All of these systems have CO or  $\text{CO}_2$  as a reactant, a significant difference from this work. Radical reactions for the formation of  $\text{CO}_2^*$  during ultrasonic irradiation of dodecane under  $\text{O}_2$  are



The effect of the  $\text{O}_2$  concentration in the gas stream on the sonoluminescence spectra of dodecane is shown in Figure 8. As  $\text{O}_2$  is introduced the intensity of the entire spectrum (both the peaks from  $\text{C}_2$  and the continuum) decreases. As the  $\text{O}_2$  concentration is further increased, the  $\text{CO}_2$  continuum grows in until, under pure  $\text{O}_2$ , it is as intense as the original spectrum under argon. The initial decrease in the entire spectrum upon the addition of small amounts of  $\text{O}_2$  leads us to believe that the  $\text{O}_2$  is directly quenching the excited-state  $\text{C}_2$ . A comparison of the sonoluminescence intensity versus concentration of  $\text{N}_2$  or CO and  $\text{O}_2$  shows that the  $\text{C}_2^*$  peaks fall off faster with  $\text{O}_2$  than with  $\text{N}_2$  or CO. At higher concentrations of  $\text{O}_2$ , eq 9–11 (which must have a smaller rate constant than the quenching reaction) begin to



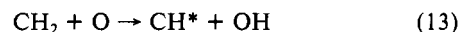
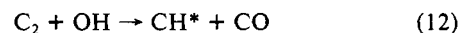
**Figure 8.** SL intensity under  $\text{O}_2$ /Ar mixtures: (a)  $\text{C}_2$  peak at 510 nm, (b)  $\text{CO}_2$  peak at 400 nm.



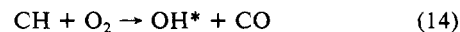
**Figure 9.** Sonoluminescence spectra of halocarbons: (a) SL from tetra-chloroethylene under Ar at 0 °C, vapor pressure = 4.1 Torr. Spectrum is the concatenation of three spectra, each the average of three 100-s spectra. (b) SL from  $\text{CCl}_4$  under Ar at -7 °C, vapor pressure = 23 Torr. Spectrum is the concatenation of three spectra, each the average of 20 100-s spectra.

dominate and  $\text{CO}_2^*$  becomes the dominant emitting species. As a further check on our assignments, the gaseous products of a 6-h sonication of dodecane under pure  $\text{O}_2$  were analyzed by gas chromatography, and  $\text{CO}_2$  was observed as the primary product.

In the sonoluminescence spectrum of dodecane under 10%  $\text{O}_2$  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.<sup>28</sup> Emission from CH is a dominant feature of flame spectra,<sup>29a</sup> and eq 12 and 13 are typically proposed to account for the emission.



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<sup>29a</sup> and has been detected in the SL from water.<sup>16</sup> Equation 14 has been often proposed<sup>29a</sup> for the formation of  $\text{OH}^*$  in flames.



In our previous report<sup>5</sup> 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  $\text{O}_2$  and from octanol, we now believe this to be  $\text{CO}_2$  emission. The sharp edge in the emission spectrum at 390 nm is from the UV cutoff of nitroethane.<sup>5</sup>

**Chlorine-Containing Systems.** Sonoluminescence spectra from halocarbons<sup>41</sup> under Ar is shown in Figure 9. We assign the broad

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continuum without resolvable features to the  $A^3\Pi_0-X^1\Sigma^+$  transition of  $Cl_2$ . Weak peaks from  $C_2^*$  are also apparent in the spectrum of tetrachloroethylene. Our sonoluminescence spectra are similar to the chemiluminescence spectra of Browne and Ogryzlo obtained from  $Cl_2$  afterglow experiments.<sup>42</sup> Formation of radicals from the sonolysis of halocarbons is well documented,<sup>43</sup> and  $Cl_2$  is a major product of the sonolysis of  $CCl_4$ .<sup>44</sup> A simple reaction is presented in eq 15 for the formation of  $Cl_2^*$ .



Chendke and Fogler reported a sonoluminescence spectrum<sup>23</sup> 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,<sup>3</sup> 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 radiation, since it shows vibrationally resolved bands that are assigned to emission from excited-state diatomic molecules. The SL spectra change dramatically upon the addition of small amounts of reactive gas, e.g.,  $O_2$ ,  $N_2$ , and  $NH_3$ , which would not be expected to 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.<sup>37</sup> This is not observed. Additionally, electrical discharge through  $Cl_2$  results in emission from excited-state  $Cl_2^+$ .<sup>28</sup> 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.<sup>28</sup> For these reasons, the electrical discharge theory is inconsistent with SL from nonaqueous liquids.

The shock-wave theory proposed by Vaughan and Leeman<sup>9</sup> is essentially a thermal theory, since shock waves promote chemical reactions by heating the gas through which they travel.<sup>45</sup> This

theory ascribes the differences seen in SL intensity to 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 ( $\gamma$  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<sup>9</sup> 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 >20 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.

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