

The effect of fluorocarbon gases on sonoluminescence: a failure of the electrical hypothesis

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Received 29 January 1993; revised 2 August 1993

Ultrasonic irradiation of solutions containing volatile organometallic complexes results in intense emission from excited-state metal atoms. We have determined the effect of dissolved gases (Xe, Kr, Ar, Ne, He, CF₄, C₂F₆, CO, N₂) on the intensity of the sonoluminescence resulting from ultrasonic irradiation of silicone oil solutions of Cr(CO)₆. This provides a well-defined, spectrally resolved probe of sonoluminescence with emission resulting from a single species, the chromium atom excited states. As predicted by the hot-spot, thermal mechanisms of sonoluminescence, the intensity of excited-state Cr emission decreases with increasing thermal conductivity of the noble gases. The intensity of sonoluminescence increases with increasing γ (i.e. C_p/C_v), which is also in accord with a thermal mechanism. Sonoluminescence is substantially diminished by the addition of even small amounts ($\approx 1\%$) of CF₄ or C₂F₆, even though they are capable of supporting electrical discharge. This is in agreement with a thermal mechanism, but is in direct conflict with electrical theories of sonoluminescence.

Keywords: sonochemistry; sonoluminescence; hot spots; fluorocarbons; organometallics; metal atoms

There remains disagreement concerning the mechanism of sonochemical reactions: does the cavitation event induce principally localized heating^{1–4} or is there an electrical microdischarge component?^{5–7} In a recent study, Reisse and coworkers^{8,9} reported alkene isomerization from the sonolysis of halocarbons even in the presence of perfluorocarbon gases, CF₄ and C₂F₆. They noted that these gases are useful in gas-phase plasma chemistry; if there is an electrical discharge mechanism for sonochemical reactions, then these gases should serve as inert and efficient gases in homogeneous sonochemistry^{8,9}. On the other hand, polyatomic gases such as CF₄, C₂F₆, CO and N₂ would be expected to suppress heating by shockwave or adiabatic collapse during cavitation because of their low ratio of C_p/C_v . We

decided to utilize these gases as a test of the mechanism of sonoluminescence and sonochemistry. To this end, we have examined the spectrally resolved sonoluminescence of Cr(CO)₆ solutions under CF₄, C₂F₆, CO, N₂, and the noble gases. As expected for thermal mechanisms, the intensity of sonoluminescence decreases with increasing thermal conductivity of the noble gases. We also find that CO, N₂, and the perfluorocarbons dramatically suppress sonoluminescence. This experimental evidence supports a thermal mechanism for sonochemistry and sonoluminescence, but not an electrical discharge mechanism.

Sonoluminescence, the light emitted during ultrasonic irradiation of liquids, derives from acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid^{4,10,11}. In thermal mechanisms, the rapid collapse of these bubbles causes heating of the gas and vapour contained in the bubbles, either through direct compression or through the formation of shock waves in the bubble interior during collapse. Upon collapse, light is emitted in flashes of less than 50 ps in duration¹² with the emission occurring from excited-state species that are formed by the cavitation event^{4,10,11,13}. The effective temperature of chemical species present during acoustic cavitation has been experimentally determined by chemical rate thermometry¹⁴, and by spectrally resolved sonoluminescence^{15,16} of excited state C₂, to be roughly 5000 K.

Among the experimental parameters known to affect the conditions created during cavitation, the nature of dissolved gases in the irradiated solution is especially important^{17,18}. In order to monitor these effects, the intensity of sonoluminescence can serve as a useful probe. It is critical to note that the nature and relative concentrations of the emitting species can change as conditions of cavitation change. For this reason, the effect of dissolved gases on spectrally resolved sonoluminescence from well-defined emitting species is especially key information. Spectrally resolved studies, however, have only rarely been accomplished¹³.

We have recently discovered that the ultrasonic irradiation of solutions containing volatile organometallic complexes results in intense emission from excited state metal atoms¹⁹. Silicone oil solutions containing 0.0025 M Cr(CO)₆ were maintained at 70 °C and sparged with argon for 10 minutes prior to and during ultrasonic irradiation. High intensity ultrasound was generated using a titanium immersion horn (Heat Systems Model W375) operating at 20 kHz and $\approx 85 \text{ W cm}^{-2}$. Spectra were collected using a Princeton Instruments IRY 512N diode array detector with a Thermo Jarrell-Ash Monospec-18 0.25 m spectrograph. Under the conditions used in this study, no emission above background levels was observed from neat silicone oil.

The effect of dissolved gas on sonoluminescence from Cr(CO)₆ in silicone oil is shown in *Figure 1*. As predicted by a thermal mechanism, the intensity of the Cr* emission under the noble gases varies inversely with thermal conductivity of the gas. Gases that have high thermal conductivities, such as helium and neon, produce lower cavitation temperatures since they dissipate heat from the collapsing bubble at a faster rate^{1–4}. The lower

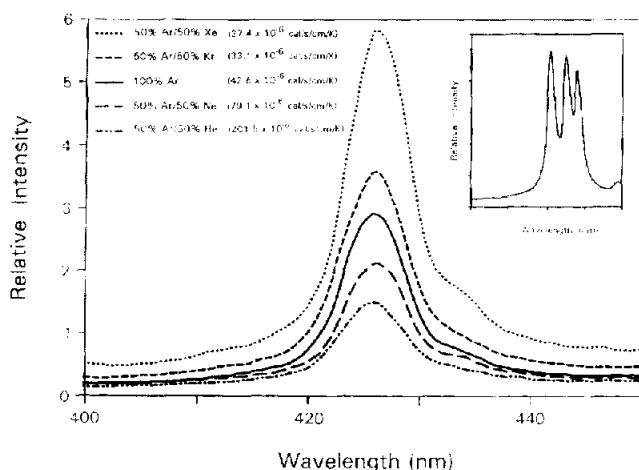


Figure 1 Sonoluminescence spectra from the ultrasonic irradiation of 0.0025 M $\text{Cr}(\text{CO})_6$ in silicone oil at a cell temperature of 70 °C under various mixtures of noble gases. Calculated thermal conductivities for the mixtures are given in parentheses. The inset figure is a high resolution sonoluminescence spectrum from $\text{Cr}(\text{CO})_6$. Individual atomic emission lines are at 425.4 nm, 427.5 nm and 429.0 nm, and arise from $(4\text{p}^1\text{z}^1\text{P}_0^0 \rightarrow 4\text{s}^1\text{a}^1\text{S}_3)$, $(4\text{p}^1\text{z}^1\text{P}_3^0 \rightarrow 4\text{s}^1\text{a}^1\text{S}_3)$, and $(4\text{p}^1\text{z}^1\text{P}_2^0 \rightarrow 4\text{s}^1\text{a}^1\text{S}_3)$ transitions, respectively

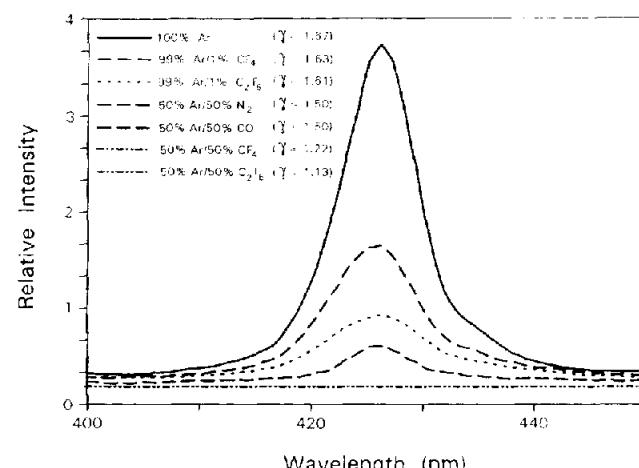


Figure 2 Sonoluminescence spectra from the ultrasonic irradiation of 0.0025 M $\text{Cr}(\text{CO})_6$ under a mixture of argon, N_2 , CO , and perfluorocarbon gases. Solutions sparged with gas mixtures containing 50% Ar/50% CO and 50% Ar/50% N_2 gave the same intensity of sonoluminescence and are shown as a single line. Solutions sparged with gas mixtures containing 50% Ar/50% CF_4 and 50% Ar/50% C_2F_6 emitted no sonoluminescence and are also shown as a single line. Calculated γ values for the mixtures are given in parentheses; to calculate γ , mole fraction averages were made for C_p and for C_v and then the ratio determined

temperatures result in slower sonochemical rates and therefore produce lower sonoluminescence intensity.

The results obtained here correlate well with the earlier sonoluminescence results of Young and of Verrall and coworkers^{17,18}. These previous studies, however, involved broadband sonoluminescence from water in which there are several different emitting species (e.g. multiple excited states of H_2O and OH^\bullet , among others) whose relative concentrations are likely to vary with cavitation conditions. Sonoluminescence from $\text{Cr}(\text{CO})_6$ is from a single emitting species, the excited states of the chromium atom, and is therefore a more accurate probe of sonoluminescence.

As shown in Figure 2, the addition of small quantities of polyatomic gases such as N_2 , CO , CF_4 , or C_2F_6 dramatically diminishes the intensity of Cr^\bullet emission.

Even 1% mixtures of the perfluorocarbon gases substantially suppress sonoluminescence. This is consistent with thermal mechanisms for sonoluminescence. The polyatomic gases have low γ (i.e. C_p/C_v) values compared with the noble gases. The value of γ is inversely related to the number of internal degrees of freedom that a molecule has. When a gas is compressed, the heat produced is partitioned across all the degrees of freedom of the gas. Therefore, the lower the value of γ , the lower the effective cavitational temperature and the less the intensity of sonoluminescence^{4,20}.

Our results are in direct conflict with electrical discharge theories of sonochemical reactions, since CF_4 is known to be an efficient gas for plasma chemistry and will support an electrical discharge⁸. In a recent sonochemical study of the radical-induced isomerization of diethyl maleate into diethyl fumarate, the reaction was found to proceed as rapidly under CF_4 as it did under Ar or N_2 ^{8,9}. Parallels were therefore drawn between plasma chemistry and sonochemistry and support was given to an electrical discharge mechanism of sonochemistry. It was proposed that both CF_4 and C_2F_6 could serve as efficient gases for homogeneous sonochemistry^{8,9}. This type of radical-induced isomerization, however, is a poor choice of reaction to be used in the study of the sonochemical effect of gases: any secondary reactions of these gases can affect the initiation, propagation, or termination steps of the radical chain reaction, which will also substantially affect the overall sonochemical rate of isomerization. Such interferences are especially likely in halogen-induced alkene isomerization. Spectrally resolved sonoluminescence from a single emitting species, such as an excited state metal atom, avoids this problem and gives an accurate probe of the effect of dissolved gases.

As predicted by the thermal mechanism of sonochemistry and sonoluminescence, the intensity of sonoluminescence from $\text{Cr}(\text{CO})_6$ was found to vary inversely with the thermal conductivity of the noble gases. In addition, sonoluminescence was dramatically diminished by the addition of polyatomic gases, such as CO , N_2 , CF_4 , or C_2F_6 . Since CF_4 is known to be an efficient gas for plasma chemistry and will support an electrical discharge, our results are in direct conflict with electrical hypotheses⁸⁻⁹.

Acknowledgements

This work was supported by the US National Science Foundation.

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