

Sonochemical Synthesis of C₆₀H₂

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C₆₀H₂ has been synthesized by ultrasonically irradiating solutions of C₆₀ in decahydronaphthalene. This synthesis can be understood as a secondary reaction arising from the production of atomic hydrogen during sonolysis of the solvent. Continued sonication results in the eventual disappearance of both C₆₀ and C₆₀H₂ from the solution as monitored by UV–vis spectrophotometry. This disappearance, along with the complete absence of more highly hydrogenated derivatives, suggests that the C₆₀ experiences a high-energy environment during ultrasonic irradiation.

Introduction

Although the present understanding of the chemical effects of ultrasound is far from complete, it is generally agreed that sonochemistry results from acoustic cavitation—i.e., the ultrasonically-driven formation, growth, and violent collapse of bubbles in a liquid. When a cavitation bubble collapses, a tiny “hot spot” is formed. It has been shown¹ that the temperature and pressure inside the collapsing bubbles can exceed 5000 K and 500 atm and that the associated cooling rate can exceed 10⁹ K/s. There is also evidence that the liquid itself can experience temperatures as high as 2000 K.² This liquid is thought to be either in the form of a thin “shell” surrounding the cavitation bubbles^{2,3} or as liquid injected into the interior of the bubble and heated to high temperatures or even to incandescence.^{4–6} The sonochemical environment is a unique, high-energy environment. Because the associated chemical reactions take place far from equilibrium, many intriguing and unexpected results have been obtained thus far.⁷

Fullerenes, as the fourth allotropic form of carbon, have justifiably received an enormous amount of attention in recent years. Unlike graphite, diamond, and amorphous carbon, however, fullerenes are soluble in many organic liquids.⁸ This characteristic, coupled with the fact that they can undergo a wide variety of reactions, makes fullerenes excellent candidates for fundamental sonochemical investigations. Surprisingly, such investigations have not previously appeared in the literature.

The chemistry of fullerenes has proven to be much richer than initially imagined, primarily due to the localization of electrons resulting from the avoidance of double bonds in the pentagonal rings. Fullerenes have been found to be strongly electron-accepting and to undergo reactions characteristic of alkenes.⁹ They are so reactive, in fact, that fullerenes have been described as a “sponge” for radicals.¹⁰

A liquid undergoing acoustic cavitation is a potent source of radicals, and the high temperatures and pressures produced during cavitation are sufficient to break chemical bonds and send charged species streaming into the bulk of the liquid.⁷ Given the affinity of C₆₀ for radicals, it should be possible to synthesize many derivatives simply by dissolving C₆₀ in the

appropriate solvent and irradiating the solution with high-intensity ultrasound. Moreover, although the vapor pressure of C₆₀ at room temperature is so small that no C₆₀ will be inside the cavitation bubbles, it is likely that the C₆₀ will still experience a high-energy environment, either within the liquid injected into the bubbles or from a reaction with a highly excited radical. Accordingly, under the highly non-equilibrium conditions that occur during ultrasonic irradiation, it may be possible to synthesize derivatives of C₆₀ that are not easily accessible using other reaction routes.

This paper reports the synthesis of C₆₀H₂ by ultrasonically irradiating solutions of C₆₀ in decahydronaphthalene. Decahydronaphthalene was chosen as a solvent because its sonochemistry is fairly well-understood, fullerenes are quite soluble in it, and its low vapor pressure generates highly energetic cavitation bubbles. Mass spectrometry and liquid chromatography were used to identify the major reaction product resulting from the sonication of C₆₀.

Hydrogenated fullerenes, particularly C₆₀H₂ and C₆₀H₄, have been the subject of several previous studies^{11–21} and, therefore, represent a good starting point for these investigations. Furthermore, hydrogenated fullerenes are interesting in their own right due to the high acidity of the C₆₀–H bond; this acidity may lead to important applications.⁹ Hydrogenated fullerenes are also promising candidates for hydrogen storage;¹⁷ accordingly, any synthetic technique that can be easily scaled up, such as ultrasonic processing, may be of considerable practical interest.

Experimental Section

The ultrasonic irradiations were performed using a 1/2-in.-diameter 20-kHz titanium horn driven with a lead zirconate titanate transducer (Misonix, Inc., formerly Heat-Systems Ultrasonics, Model XL2010). A sapphire-tipped horn was also used on one sample to ensure that any cavitation-induced erosion from the Ti tip was not affecting the results. The total acoustic power delivered to the sample was determined calorimetrically to be 30 ± 5 W. The calorimetric measurements were performed by measuring the temperature increase vs time of a decahydronaphthalene standard not containing C₆₀. A 15-mL glass reaction vessel with a design similar to that originally described by Suslick *et al.*²⁴ was used to contain the solutions during irradiation. All irradiations were performed under a high-purity Ar atmosphere. The reaction vessel was cooled using a

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0 °C bath; during irradiation the steady-state temperature inside the vessel remained constant at 25 ± 5 °C.

The decahydronaphthalene (Aldrich, 99+%, anhydrous, unspecified mixture of *cis* and *trans*) was used as received. The C_{60} was purchased from SES Research, Inc. (Houston, TX) with a stated purity of 99.99%. Solutions were made by placing the C_{60} and solvent in a tightly sealed amber bottle and stirring for 24 h. The solutions were then filtered with a 0.2- μ m filter and sparged with Ar for 20 min before irradiation.

Mass spectra were obtained on a Finnigan FTMS-2000 Fourier transform mass spectrometer equipped with a 3-T superconducting magnet. The third harmonic of a pulsed Spectra-Physics DCR-11 Nd:YAG laser (355 nm, $\sim 10^7$ W/cm²) was used to simultaneously desorb and ionize the samples. Positive ions from a single laser pulse can be trapped and detected in the ion cell, although several laser shots were averaged for the mass spectra reported here.

High-performance liquid chromatography (HPLC) was performed using a Hewlett-Packard HP 1090M liquid chromatograph equipped with a ternary solvent delivery system, an auto injector, a built-in photodiode array detector, and a computerized data acquisition system. The chromatograph was fitted with a column (250 \times 4.6 mm i.d.) packed with a 5- μ m Buckyclutterer I²⁵ stationary phase (Regis Chemical Co., Morton Grove, IL). The mobile phase was toluene:hexane, initially 50:50, which was then programmed linearly to 100% toluene over 8 min and held for 35 min. The mobile-phase flow rate was 1.0 mL/min, and UV-vis detection was employed at 330 nm. Fractions were collected using a Gilson 203 fraction collector.

Results and Discussion

Typically, saturated solutions of C_{60} in decahydronaphthalene (~ 3 mg/mL) were placed in the reaction vessel and irradiated for 2–4 h. During the irradiation, the color of the solutions changed from violet to a turbid brown. The solutions were removed from the reaction vessel and stored under Ar in glass vials. These vials were kept under refrigeration until the HPLC separations were performed. The samples were centrifuged and filtered prior to injection.

After concentrated solutions were irradiated, a brown precipitate was observed to settle on the bottom of the vials over the course of hours and days. This precipitate was definitely associated with the presence of C_{60} , as it was not observed in samples of irradiated solvent that did not contain C_{60} . It was also not observed after irradiation of dilute (≤ 0.1 mg/mL) solutions. We find that the precipitate is sparingly soluble in a great many solvents²⁶ (including solvents such as tetrahydrofuran which do not dissolve C_{60}). Precipitates have been observed in other studies of hydrogenated fullerenes,⁹ and although these precipitates have not been well-characterized, they are of interest because they tend to be soluble in polar solvents such as dimethyl sulfoxide.^{9,18} One study¹⁸ associated the presence of a brown precipitate with fullerol formation. Although fullerol formation cannot be completely ruled out, it is unlikely in the present experiments since precautions were taken against oxygen contamination during the ultrasonic irradiations, and only occasional traces of fullerols (or $C_{60}O$) were observed in the mass spectrum of the precipitate.

In the initial characterization of the reaction products, a heat lamp was used to evaporate away the decahydronaphthalene immediately after ultrasonic irradiation. After washing with pentane and filtering, a reddish-brown powder remained that appeared to be homogeneous under an optical microscope. A typical positive ion laser desorption mass spectrum obtained for this powder appears in the upper panel of Figure 1. The

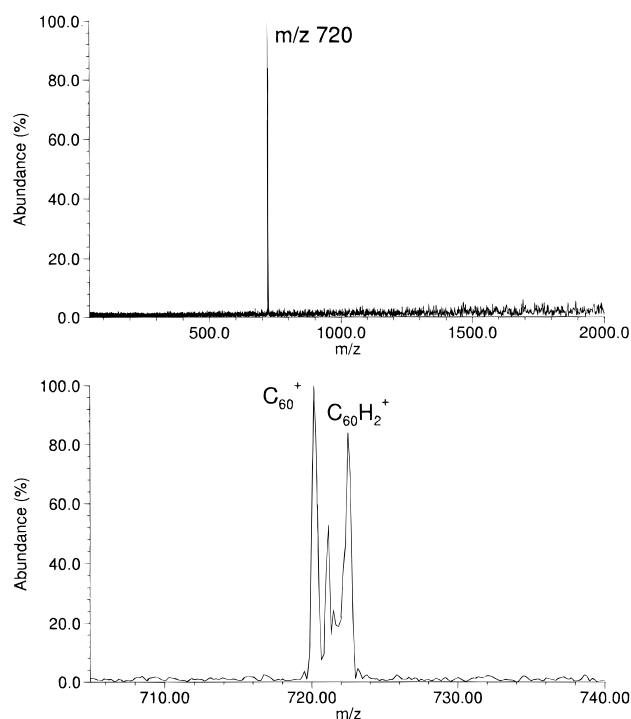


Figure 1. Upper panel: positive ion laser desorption mass spectrum obtained on the reddish-brown powder produced by ultrasonically irradiating a saturated solution of C_{60} in decahydronaphthalene for 4 h. Lower panel: expanded view of the spectrum shown above. The high abundance of the peak at m/z 722 was the first indication that $C_{60}H_2$ was being formed.

spectrum is quite clean, with one main peak at m/z 720. An expanded view of the spectrum appears in the lower panel of Figure 1. The excess intensity of the peak at m/z 722 over that expected from the ^{13}C isotopes of C_{60} was the first indication that $C_{60}H_2$ was being formed. Figure 2 illustrates how the mass spectrum changes as the laser is repeatedly fired at the same spot on the sample. In the upper panel, the signal-averaged mass spectrum of the first five laser shots on a new spot of the sample is shown; the lower panel shows the signal-averaged mass spectrum of the next four laser shots on the same spot. Note that m/z 722 is virtually gone and m/z 720 is now the most abundant peak. Each shot of the laser apparently converts some of the remaining $C_{60}H_2$ to C_{60} . Further evidence that $C_{60}H_2$ was formed is provided by the UV-vis spectrum, in hexane, of the synthesized powder. The spectrum is virtually identical with previously published^{11,12} spectra of $C_{60}H_2$.

Mass spectrometric detection of $C_{60}H_2$ is difficult due to the interferences of the ^{13}C -isotopic peaks of C_{60} . The following table illustrates the natural abundances of the ions observed in the positive ion mass spectra of pure C_{60} :

ion	nominal m/z	accurate m/z	rel abundance (%)
$^{12}C_{60}^+$	720	719.9995	100.0
$^{13}C_1^{12}C_{59}^+$	721	721.0028	66.7
$^{13}C_2^{12}C_{58}^+$	722	722.0062	21.9
$^{13}C_3^{12}C_{57}^+$	723	723.0095	4.7
$^{13}C_4^{12}C_{56}^+$	724	724.0129	0.7

The high abundance of m/z 722 from $^{13}C_2^{12}C_{58}^+$ of pure C_{60} makes it difficult to detect $C_{60}H_2^+$, which also occurs at m/z 722. To alleviate this problem, C_{60} was sonicated in deuterated decahydronaphthalene (Sigma, *cis*-decahydronaphthalene- d_{18} , 98+% D) in hopes of generating $C_{60}D_2$, which would be observed at m/z 724 (note that the abundance of m/z 724 from $^{13}C_4^{12}C_{56}^+$ is quite low from pure C_{60}). Evaporation of the

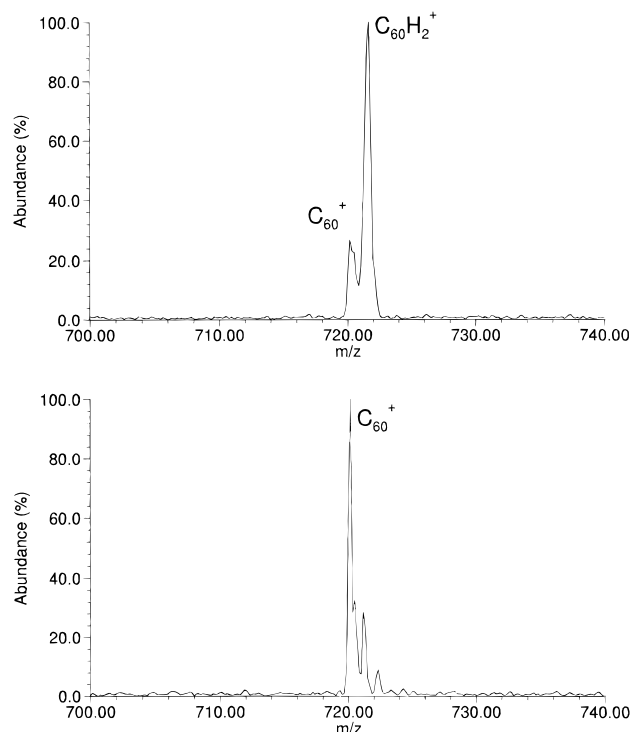


Figure 2. Positive ion laser desorption mass spectra of the reddish-brown powder, illustrating how the spectrum changes as the laser is repeatedly fired at the same spot on the sample. Upper panel: spectrum of first five laser shots on a new area of the sample. Lower panel: spectrum of the next four laser shots on the same spot on the sample. After several shots, the spectrum is similar to that of pure C_{60} .

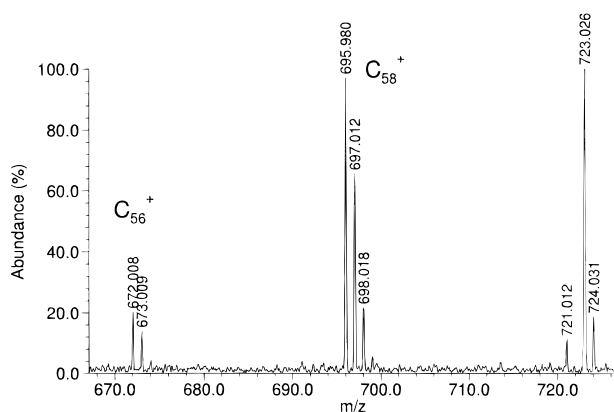


Figure 3. Mass spectrum of a sample prepared by sonicating a solution of C_{60} in deuterated decahydronaphthalene, revealing $C_{60}HD^+$ (m/z 723) as the product. See text for an extended discussion of this figure.

solvent left a reddish-brown powder which was then examined by laser desorption FT mass spectrometry. The positive-ion mass spectrum yielded an abundant peak at m/z 720 (which can only be $^{12}C_{60}^+$), as well as minor peaks at m/z 721–724. In order to more carefully examine the identities of these minor peaks, the abundant ion at m/z 720 was ejected prior to ion detection. The resulting spectrum, shown in Figure 3, provided some interesting and unpredicted results. Note that the abundant ion at m/z 720 is gone; however, ejection of this ion results in the formation of characteristic ions at m/z 696–698 ($^{12}C_{58}^+$ with its isotopes) and 672–674 ($^{12}C_{56}^+$ and its isotopes). These ions provide internal standards for verifying the mass calibration accuracy. Note that the most abundant ion in the higher mass region is m/z 723. The presence of this ion is somewhat surprising since only $C_{60}D_2^+$ (m/z 724) and $C_{60}D^+$ (m/z 722) were expected. Careful mass measurement of the m/z 723 ion revealed its identity to be $C_{60}HD^+$ (measured, m/z 723.026;

calculated, m/z 723.021) and not $^{13}C_3^{12}C_{57}^+$ (calculated, m/z 723.010). While the presence of this ion may be unexpected from the sonication of C_{60} in completely deuterated decahydronaphthalene, comparison of this product with other similar systems suggests that residual hydrogen/deuterium scrambling is not uncommon. Although the sonication was conducted in deuterated decahydronaphthalene, the resulting sample was exposed to normal glass surfaces, room air, and the stainless steel probe tip for the mass spectrometry experiments. Because $C_{60}H_2$ is suspected to be a moderately strong acid (based on the predicted²⁷ stability of $C_{60}H^-$), this compound may readily undergo proton exchange with residual hydrogen sources (such as moist air, etc.). For comparison, mass spectrometric examinations of pure D_2O often initially reveal the presence of HOD , due to rapid H/D exchange with background H_2O adsorbed onto walls of containers, vacuum chamber, etc. These results imply that sonication of C_{60} in deuterated decahydronaphthalene most likely generates $C_{60}D_2$, which rapidly undergoes H/D exchange prior to mass spectral examination to produce $C_{60}HD$. Also, the possibility cannot be ruled out that toluene trapped in the C_{60} is the actual source of hydrogen in these experiments.

During the course of the FTMS experiments, it was noticed that the mass peak at m/z 722 ($C_{60}H_2^+$) was quite broad and its ^{13}C isotopes were not resolved with the expected intensities, even though the peaks corresponding to C_{60}^+ could be measured in better detail, as shown in Figure 1 (lower panel). On the basis of FTMS ion-detection parameters, the expected resolutions for the ions in the m/z 720–725 region should be similar. One possible explanation for the decreased resolution of the $C_{60}H_2^+$ ions may be the recently discovered ion-coalescence effect, which occurs when the cyclotron motions of two ion packets of similar m/z couple together and rotate around their center-of-mass with an oscillating radius. This phenomenon is most prominent when a large number of ions with very similar masses are present in the FTMS ion cell and is evidenced by a single ion peak with no resolved isotopes.^{28,29} Under the experimental conditions used in the paper, we estimate that more than one million ions are generated per laser shot, which is sufficient to cause ion coalescence to occur at these mass-to-charge ratios. What is somewhat surprising is that the isotopes of the pure C_{60}^+ appear to be better resolved than the $C_{60}H_2^+$ peak. An alternate explanation for the observed peak broadening and loss of isotope resolution may be strong ion–neutral interactions. If there is a strong interaction between the $C_{60}H_2^+$ species and a neutral such as $C_{60}H_2$, then this “ion drag” may effectively alter the apparent mass (and hence m/z) and degrade the resolution of the ion-measurement process. In some cases, this effect complicates the ability to obtain definitive identity information by FT mass spectrometry. But, the observation of peak broadening in this particular experimental system may provide a unique test of the theoretical concepts of coupled ion–ion (or ion–molecule) motion in a magnetic field.

Although the formation of hydrogenated fullerenes by ultrasonic irradiation of C_{60} is not surprising in and of itself, it is surprising that $C_{60}H_2$ is apparently the only derivative being formed. To clarify the results, HPLC separations were performed, first on the toluene extract of the reddish-brown powders and then directly on the irradiated solutions. A typical chromatogram of an ultrasonically irradiated sample appears in Figure 4. The chromatograms are the same for the toluene extract of the powders and the solutions. The peaks at elution times of 6.15 and 8.93 min have retention times^{11–14} and UV–vis spectra^{11,12} that are consistent with C_{60} and $C_{60}H_2$, respectively (see Figure 5). For retention times between 6.7 and 8.7 min there are at least three separable—but as yet unidentified—

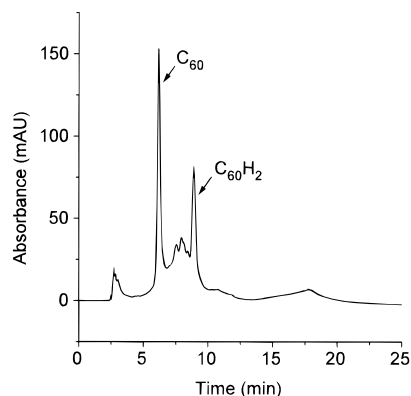


Figure 4. Typical chromatogram of an ultrasonically irradiated sample of C_{60} in decahydronaphthalene. The relative peak areas depend on the initial C_{60} concentration and irradiation time. The peaks for retention times between 6.7 and 8.7 min are completely reproducible, but the specific compounds which are being separated are not yet identified. Fractions were collected corresponding to the peaks labeled C_{60} and $C_{60}H_2$. See text for HPLC conditions.

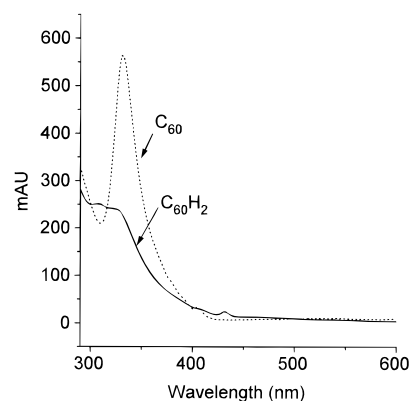


Figure 5. UV-vis spectra of the peaks labeled C_{60} and $C_{60}H_2$ in the chromatogram of Figure 4. These spectra support the present identification of the compounds.

compounds. It should be stressed that these small peaks between 6.7 and 8.7 min are completely reproducible. They have been observed using a wide variety of HPLC conditions and have even been observed using a different stationary phase.²⁶ HPLC-MS and NMR experiments are underway in order to try to identify these minor products.

Fractions were collected that correspond to the peaks at retention times of 6.15 (C_{60}) and 8.93 min ($C_{60}H_2$). When reinjected, the C_{60} fraction was found to be free of impurities, whereas the $C_{60}H_2$ fraction contained a trace amount of C_{60} . Positive-ion mass spectra were obtained on both the C_{60} and $C_{60}H_2$ fractions. The mass spectrum of the C_{60} fraction was the same as that obtained on a C_{60} standard, whereas the spectrum of the $C_{60}H_2$ fraction was similar to the spectrum of the reddish-brown powder discussed above.

It was difficult to estimate the yield of the reaction because all of the C_{60} could not be accounted for as the reaction progressed. This is illustrated in Figure 6, which consists of a plot of a time series of chromatograms obtained by periodically removing 200-mL aliquots from the reaction vessel. As shown in Figure 6, the concentration of C_{60} rapidly decreases with time as the sample is ultrasonically irradiated; the concentration of $C_{60}H_2$ increases fairly quickly at first, and then it, too, decreases. This is further illustrated in Figure 7, in which the peak areas of the C_{60} and $C_{60}H_2$ fractions are plotted as the reaction progresses. The important thing to note is that the increase in $C_{60}H_2$ is not only not proportional to the decrease in C_{60} but, after about 160 min, the concentrations of both C_{60} and $C_{60}H_2$

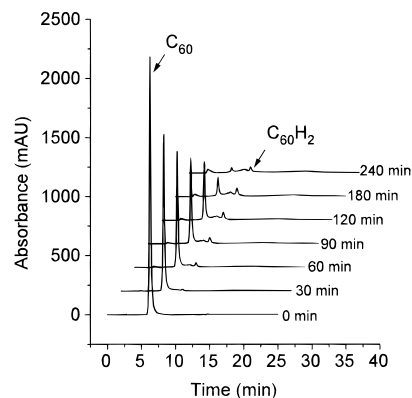


Figure 6. Series of chromatograms obtained on a fairly concentrated (1.9 mg/mL) solution of C_{60} in decahydronaphthalene for the irradiation times indicated. For clarity, the chromatograms have been displaced vertically by arbitrary amounts. See text for the HPLC conditions.

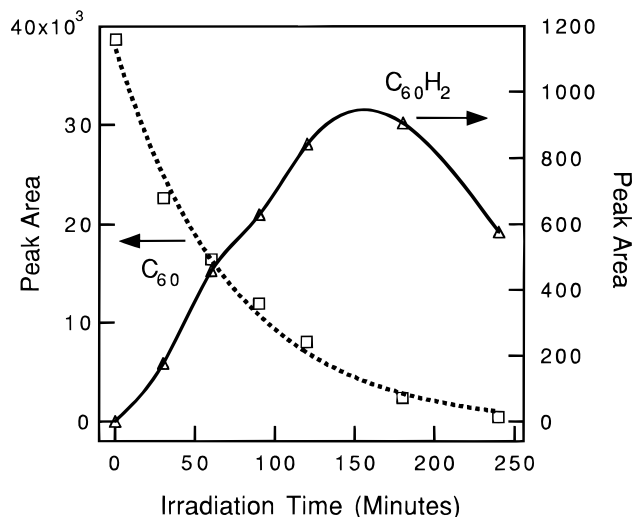


Figure 7. Peak area vs irradiation time for the peaks occurring at retention times of 6.15 (C_{60}) and 8.93 min ($C_{60}H_2$) in Figure 6. The dotted line represents a least-squares fit to the expression $A = Ce^{-t/\Delta}$, where A is the peak area, C is a constant, t is the irradiation time, and Δ is the $1/e$ time. The parameters of obtained from the fit were $C = 37,785$ and $\Delta = 71.2$ min. The solid line is a guide to the eye. Note that after ~ 160 min the concentrations of both C_{60} and $C_{60}H_2$ are decreasing with time.

are decreasing with time. Some estimate of the yield of the reaction can be made by dividing the maximum peak area of the $C_{60}H_2$ curve by the unirradiated C_{60} peak area. This gives a yield of about 2.5%, but because this analysis assumes that C_{60} and $C_{60}H_2$ absorb equally at 330 nm, it almost certainly underestimates the yield by a factor of 2 or 3. Unfortunately the molar absorptivity of $C_{60}H_2$ has not yet been determined, so a better estimate of the yield cannot be made at this time.

Figure 7 implies that if the sample is irradiated long enough, no C_{60} or $C_{60}H_2$ will be left in solution. Evidence that this is in fact the case can be found in Figure 8, in which successive UV-vis spectra of a dilute (0.1 mg/mL) sample of C_{60} in decahydronaphthalene are shown. After 30 min of ultrasonic irradiation, only a weak feature remains at 329 nm, and, after 90 min, no feature remains at all. Since in dilute solutions no precipitate forms, it is clear that—optically, at least—the C_{60} has disappeared.

In order to understand the sonochemistry of C_{60} , it is important to first understand the sonochemistry of the pure solvent. For alkanes (and, by extension, nonaromatic alkane-like compounds such as decahydronaphthalene), experiments on these compounds have been performed previously by Suslick

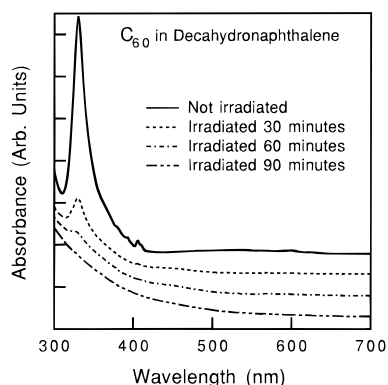


Figure 8. UV-vis spectra obtained on a dilute (0.1 mg/mL) solution of C_{60} in decahydronaphthalene irradiated for the times indicated. For clarity, the curves have been displaced vertically by arbitrary amounts. After 90 min of ultrasonic irradiation, no trace of C_{60} or of $C_{60}H_2$ is present.

*et al.*³⁰ In a careful series of experiments the following were shown: (1) the primary products of alkane sonolysis are H_2 , CH_4 , C_2H_2 , and smaller 1-alkenes; (2) these products are consistent with the Rice radical-chain mechanism proposed for alkane pyrolysis;³¹ and (3) as the solvent vapor pressure decreases, the intensity of cavitation collapse increases, which consequently increases the sonochemical reaction rate. On the basis of these and similar observations, Suslick proposed³² that "primary" sonochemistry takes place almost entirely in the vapor phase inside the bubbles and that reactions in the liquid phase are "dominated" by secondary reactions. In ref 32, Suslick estimated that the volume ratio of the gas to liquid reaction zones was 10^5 and that the liquid "shell" surrounding the cavitation bubbles was only 500 atoms thick. Recent thinking stimulated by the differences between single-bubble³³ and multiple-bubble¹ sonoluminescence, however, strongly implies that reactions in the liquid phase are an important aspect of sonochemistry. The key observation was that single-bubble sonoluminescence produces a blackbody spectrum, whereas multiple-bubble sonoluminescence produces a spectrum characteristic of highly excited molecules. In a recent paper, Matula *et al.*⁶ compare single-bubble and multiple-bubble sonoluminescence in the same 0.1 M NaCl solution. Whereas the single-bubble spectrum was characteristic of blackbody radiation, the multiple-bubble spectrum contained a prominent sodium D emission line near 589 nm. Because the sodium ions were definitely in the liquid, it is clear that the liquid itself, and not just the vapor, was subject to extreme conditions. Very recently, Crum⁴ proposed that, during multiple-bubble sonoluminescence, interactions between the bubbles can result in jets of liquid that are injected into the collapsing bubbles and then heated to incandescence. This proposal represents an advance over the liquid "shell" idea, which would not predict any difference in the spectra between single- and multiple-bubble sonoluminescence, but to the best of our knowledge, Crum's proposal has not yet been experimentally confirmed.

Certain aspects of the present experiments can be immediately understood on the basis of the observations of Suslick *et al.*³⁰ For example, since atomic hydrogen is produced by sonolysis of the solvent, it is not difficult to understand the formation of $C_{60}H_2$. Also, in experiments using alkanes with a high vapor pressure such as heptane, 2 h of ultrasonic irradiation produced virtually no effect. This can also be understood on the basis of the observations of Suslick *et al.*³⁰

Other aspects of the present experiments, however, are not so easily explained. Why, for example, is only $C_{60}H_2$ formed rather than a greater variety of hydrogenated derivatives? Are

the reducing conditions really so mild, and if they are, then why does the concentration of $C_{60}H_2$ decrease with further irradiation? What happens to the C_{60} —i.e., why is it disappearing, and where is it going? It is difficult to explain these observations given only the presence of atomic hydrogen. It is far more likely that the C_{60} experiences a high-energy environment during irradiation and that $C_{60}H_2$ is the only derivative sufficiently stable to survive these conditions. The C_{60} and $C_{60}H_2$ disappear because the integrity of the fullerene cage is destroyed, and they then fragment into smaller hydrocarbons. It is also possible that polyfullerenes³⁴ or C_{60} —alkane— C_{60} structures are being formed. More work is clearly necessary to understand these aspects of the sonochemical interactions.

In conclusion, $C_{60}H_2$ has been synthesized using ultrasonic irradiation. Although this synthesis can be understood as a secondary reaction arising from the production of atomic hydrogen during sonolysis of the solvent, it is argued that the C_{60} experiences a high-energy environment during ultrasonic irradiation. Like other high-energy synthetic tools such as pyrolysis and photolysis, ultrasonic irradiation can potentially yield exotic reaction products that are inaccessible by other methods. Fullerene sonochemistry appears to offer considerable promise for a rich and rewarding addition to more-mainstream fullerene chemistry.

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