Laser-Initiated Chemical Reactions in Carbon Suspensions

Thomas E. McGrath and Gerald J. Diebold*

Department of Chemistry, Brown University, Providence, Rhode Island 02912

David M. Bartels and Robert A. Crowell

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

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We report on laser-initiated chemical reactions in colloidal carbon suspensions. Irradiation of carbon particles ranging in size from 13 to 75 nm in diameter suspended in water, toluene, and benzene with high power nanosecond, picosecond, and femtosecond laser pulses leads to the formation of a number of gaseous hydrocarbons as well as a series of liquid-phase products. In the product gas above irradiated carbon suspensions in water, H_2 and CO, the main reaction products of the carbon-steam reaction, and numerous hydrocarbons ranging from C_1-C_4 were detected. Irradiation of particulate carbon in toluene and benzene gave H_2 as the main gas product with small amounts of C_1-C_3 hydrocarbons. Bibenzyl and biphenyl were found as the main liquid products produced in toluene and benzene suspensions, respectively, but with numerous polycyclic aromatic hydrocarbons in smaller concentrations. The amount of products generated by pulsed laser irradiation is shown to depend on particle size and concentration, as well as the laser fluence and pulse width. The chemical reactions reported take place under conditions characterized by extremely high temperatures and pressures of short duration.

I. Introduction

One of the consequences of the large optical absorption cross sections characteristic of particulate carbon in liquid suspensions[1,2] is that on irradiation of a suspension with a high power, pulsed laser, the particles can be driven to temperatures sufficiently high to initiate chemical reactions.[3] In addition to the synthesis of a number of gases,[3] the production of diffuse white light,[4] the generation of an anomalously large sound wave referred to as the "Giant" Photoacoustic effect,[5] the production of shock waves,[6,7] and the formation of bubbles around carbon particles,[8,9] which, under a controlled excitation geometry, results in sonoluminescence[10] have been reported in aqueous carbon suspensions. Other effects that take place when pulsed lasers irradiate suspensions include optical limiting,[4] and, in the case of metal colloids, the formation of metal ions, and the reduction in the diameter of the particles.[11,12]

In experiments with carbon suspensions,[3,13] it was found that both the formation of gases and the intensity of the light emitted by the suspension increased as the diameter of the particles increased. It was subsequently found that ethyne formation increased with increasing carbon particle size. Light scattering measurements carried out on the carbon suspensions have also shown a significant reduction in the agglomerated particle diameters as a result of the irradiation, although electron micrographs taken of the carbon particles after only a few firings of the laser revealed the formation of nearly spherical, shell-like structures several times the size of the original particles. Continued irradiation was shown to lead to an overall reduction in the size of the particles through chemical reaction to a point where the temperature rise of the particle is so limited that no further reaction follows on subsequent laser irradiation. The optical energy delivered to the carbon particles by the laser beam provides the enthalpy for the carbon-steam reaction, which, with some certainty, can be taken as the first step in a sequence of reactions that lead to the formation of hydrocarbons. The brevity of the Q-switched laser pulse, coupled with the high endothermisity of the carbon-steam reaction and the high rate of cooling from heat conduction and thermal radiation, results in rapid quenching of the temperature at the sites of the particles.

Although bubble formation[8] and permanent gas generation[3,5,10] have been previously reported in laser-irradiated aqueous carbon suspensions, no detailed analysis of the composition of the reaction products or the dependence of gas composition on irradiation conditions has been carried out. In Section II, we describe experiments where suspensions of carbon particles in water, toluene, and benzene are irradiated with the outputs of high power, pulsed lasers. In Section III, the results of experiments to determine the effects of laser power and pulse width on product gas generation are reported. The synthesis of several hydrocarbons not found in previous experiments is reported. Sections IIIA and IIIB give the results of experiments with aqueous carbons suspensions; Sections IIIC and IIID give corresponding experimental data for carbon suspensions in toluene and benzene. Section IV, the discussion section, gives comments on the experimental data, and identifies the unusual reaction conditions leading to the formation of the observed products.

II. Experiments

Carbon suspensions in water, toluene, and benzene were made up and irradiated in a 10 mL glass hypodermic syringe fitted with a connector that housed a rubber septum from which samples could be taken for chromatographic analysis. Suspensions of 200 mg/L carbon black were made in the glass syringe by adding 1.5 mg of carbon particles to 7.5 mL of solvent. All visible air was forced from the syringe using the plunger before

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* Corresponding author.

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the connector was attached. Prior to irradiation, the loaded syringe was placed in an ultrasonic cleaner for approximately 60 s to disperse the particles. Insonicating the carbon particles in water resulted in the generation of an optically thick carbon suspension, completely opaque to the eye. The suspension of carbon in the syringe was then irradiated with the 1064 nm output of a Q-switched Nd:YAG laser. The laser delivered 650 mJ in a 10 ns pulse and was fired at a repetition rate of 10 Hz. An unfocused laser beam approximately 1 cm in diameter was used in all experiments. During irradiation of a carbon suspension, extremely fine bubbles of permanent gas are produced after only a few firings of the laser. Over the course of the experiment, irradiation of the suspension was stopped a few times and the syringe shaken to ensure that all the suspension was exposed to the radiation. The irradiation of the suspension was terminated when no more gas was generated. Carbon suspensions in water were also irradiated with the 1064 nm unfocused and focused output of a 100 ps Nd:YAG laser and the 780 nm, unfocused output of a 40 fs Ti:Sapphire laser.

The carbon particles were supplied by Cabot Inc. whose numbering code of “Black Pearls” 1300, 470, and 130 refers to three different particle diameters, specified as 13, 25, and 75 nm. Elemental analysis of the particles showed them to contain less than 1% H, and 0.5% N. Isotopic ^{13}C amorphous carbon (99 atom % ^{13}C) was obtained from Aldrich Chemical Co. Distilled, deionized water was used to make the carbon suspensions. Toluene (99.8%) and benzene (99.8%) were obtained from Aldrich and used without further purification. Product gas analysis was carried out using on a Varian 6000 gas chromatograph (GC) equipped with a Spherocarb 100/120 packed column using thermal conductivity and flame ionization detectors, and on a Hewlett-Packard 5890A gas chromatograph−mass spectrometer (GC-MS). Helium was used as the carrier gas for experiments where CO, CO_2, N_2, and O_2 were detected. Nitrogen was used as the carrier gas when H_2 and the C_1-C_4 hydrocarbons were detected. The Hewlett-Packard 5890A gas chromatograph−mass spectrometer equipped with a Carboxen 1006 Plot capillary column was used to detect and identify the full range of C_1-C_4 hydrocarbons. Liquid-phase products after irradiation were probed using the GC-MS, a UV−visible spectrophotometer, a ^{13}C nuclear magnetic resonance (NMR) spectrometer, and a liquid chromatography−mass spectrometer (LC-MS).

Irradiation of particulate carbon in water, toluene, and benzene with the high power optical pulses gave an audible photoacoustic effect, produced an easily observable diffuse white light in the portion of the syringe traversed by the laser beam, and generated bubbles around the sites of the particles that led to the accumulation of permanent gas above the suspensions as has been previously reported. The shock wave generated by the irradiation was sometimes strong enough to fracture the wall of the glass syringe.

III. Experimental Results

A. Gaseous Species from Aqueous Carbon Suspensions. Three carbon suspensions (20 mg/L) were made up using carbon particles with diameters of 13, 25, and 75 nm, respectively. The optical absorption spectra of a suspension made from 75 nm particles is shown in the inset in Figure 1. Of the three particle diameters used, the largest particles had the largest extinction coefficient at 1064 nm. For a fixed irradiation time, the optical absorption of the carbon suspensions were found to be smallest for the largest diameter particles, indicating that the amount of carbon consumed during irradiation is largest for the largest particles. Figure 2 (upper section) is a photograph of a carbon suspension made up in water taken before and after irradiation with 6000 laser pulses. The change in the absorption spectra shown in Figure 1 caused by laser irradiation is evidenced by the striking change in the appearance of the sample of the suspension before and after irradiation shown in Figure 2 (upper section).

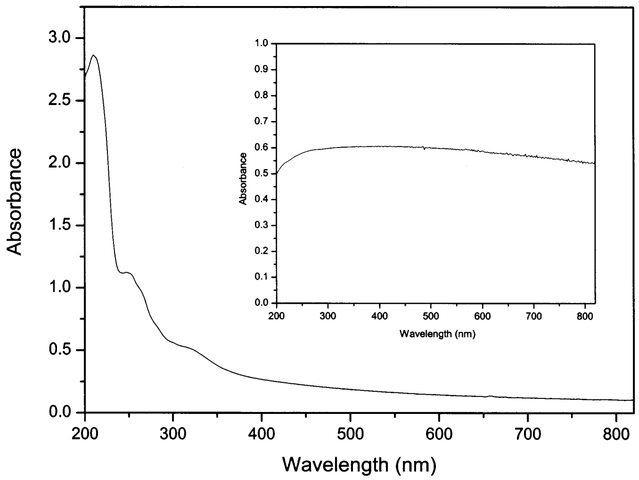

Figure 1. Spectrophotometer recording of absorbance versus wavelength for a 750 mg/L suspension 75 nm diameter carbon in water after irradiation for 4 h at 10 Hz by 330 mJ pulses of 532 nm radiation (used in this experiment only) from the 10 ns laser. The solution was originally dilute, and carbon was periodically added to give the equivalent of 750 mg/L. Inset: Absorbance versus wavelength for a 20 mg/L suspension 75 nm diameter carbon in water before irradiation.

To determine the effect of laser pulse width, or, equivalently, peak laser power on the formation of gases, aqueous carbon suspensions were irradiated using several laser powers using nanosecond, picosecond, and femtosecond pulsed lasers. The volume ratios of C_2H_2 and C_2H_4 to CH_4 as a function of laser fluence (energy per area) and intensity are given in Table 1. The first experiments were carried out using an unfocused 10 ns Q-switched Nd:YAG laser. The second set of experiments was carried out using unfocused and focused 100 ps Nd:YAG laser beams, while the third experiment was carried out using the output of an unfocused 40 fs Ti:Sapphire laser. Note that self-focusing of the femtosecond laser pulses cannot be ruled out. A 200 mg/L carbon suspension made from 25 nm diameter particles was used in all of the experiments shown in Table 1. Table 1 shows that, as the laser fluence is increased with the laser pulse width fixed, the ratio of volumes of C_2H_2 to CH_4 increases dramatically, while the volume ratio of C_2H_4 to CH_4 increases only slightly.

The gases detected above the suspension using GC and GC-MS include the main products of the carbon−steam reaction, H_2 and CO, along with numerous hydrocarbons ranging from C_1 to C_4. Additionally, O_2, N_2, CO_2, and COS were detected in smaller amounts. The detection of N_2 can be attributed to its presence in solution, whereas COS is assumed to arise from S impurities in the carbon. The amount of each product gas generated in a suspension of 25 nm diameter carbon particles in water irradiated with the nanosecond laser, expressed as a percentage of the total amount of gas produced was determined to be CO (68%), H_2 (25%), C_1 (2.0%), C_2 (4.4%), C_3 (0.2%), and C_4 (0.4%). GC-MS was used to detect individual hydrocarbons which were determined to be *methane* (CH_4), ethane (C_2H_6), ethene (C_2H_4), *ethyne* (C_2H_2), propene (C_3H_6), 1,2-propadiene (C_3H_4), *1-propyne* (C_3H_4), 1-buten-3-yne (C_4H_4), and *1,3-butadilyne* (C_4H_2). The main product in each hydrocarbon

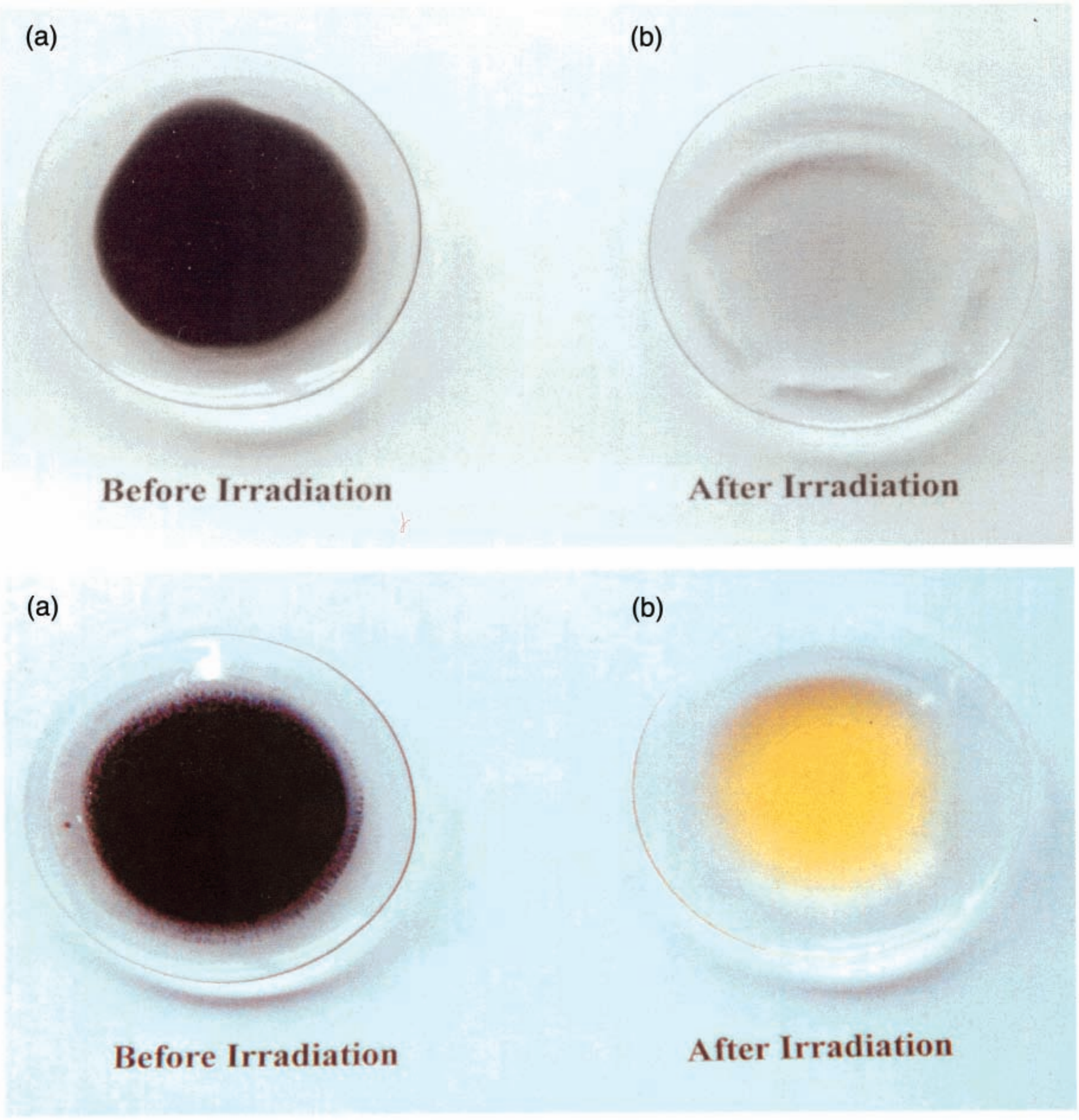

Figure 2. (Upper photograph) Watch glass filled with an aqueous carbon suspension (a) before irradiation, and (b) after irradiation with 6000 firings at 650 mJ with the 10 ns output of the1064 nm laser. Lower photograph: Watch glass filled with a carbon suspension in toluene (a) before irradiation and (b) after 6000 firings of the laser.

TABLE 1: Laser Power Influence on Gaseous Products

laser		product gas ratio[a]		
fluence ($J\ cm^{-2}$)	intensity ($10^8\ J\ cm^{-2}\ s^{-1}$)	CH_4	C_2H_2	C_2H_4
10 ns pulsed Nd:YAG laser[b]				
0.19	0.12	1.0	**0.6**	0.2
0.38	0.23	1.0	**1.3**	0.3
0.83	0.52	1.0	**2.3**	0.4
100 ps pulsed Nd:YAG laser[b]				
0.16	16	1.0	**3.9**	0.2
0.86[c]	85	1.0	**6.2**	0.2
40 fs pulsed Ti:Sapphire laser[d]				
0.02	4780	1.0	**1.5**	

[a] Ratio of C_2H_2 and C_2H_4 gases to CH_4. [b] Laser excitation wavelength = 1064 nm. [c] Laser beam focused. [d] Laser excitation wavelength = 780 nm.

group is highlighted in italics. The production of CO, H_2, C_1, and C_2 as a function of particle size has been reported in ref 3.

B. Liquid-Phase Species from Aqueous Carbon Suspensions. Liquid-phase products generated from the irradiation of the carbon suspensions with the nanosecond laser were also investigated. The post-irradiated aqueous carbon suspension was filtered using a 0.2 μm filter and a UV−Visible absorption spectrum taken. Light scattering experiments after filtration gave a mean particle diameter of 40 nm. It is thus possible that the absorptions recorded could be assigned to chromophores bound to particulate carbon. The filtered, irradiated water contained three main absorption peaks with maxima at 210, 250, and 330 nm as shown in Figure 1. To find the chromophores associated with these peaks, a ^{13}C-labeled carbon suspension in deuterated water was made up and irradiated. The irradiated labeled suspension was filtered as before and a ^{13}C NMR spectrum recorded. The main ^{13}C shifts occurred at 187, 163, 127, 82, 75, and 69 ppm. The ^{13}C NMR lines at 187 and 163 ppm are characteristic of chemical shifts from carbonyl carbons in carboxyl (R−COOH) and ester (R−COO−R) functional groups, respectively. The ^{13}C NMR line at 127 ppm is characteristic of

TABLE 2: Product Gases: Carbon Suspensions in Toluene

part. dia.[a] (nm)	vol. gen.[b] (mL)	product gases					
		H_2 (mM/g)[c]	CH_4 (mM/g)[c]	C_2H_2 (mM/g)[c]	C_2H_4 (mM/g)[c]	C_2H_6 (mM/g)[c]	C_3H_8 (mM/g)[c]
		Irradiation at 650 mJ per pulse					
13	1.8	27 *(89.6)*	2 *(6.6)*	1 *(3.3)*	0.1 *(0.3)*	0.02 *(0.1)*	0.01 *(0.1)*
25	1.8	29 *(90.2)*	2 *(6.2)*	1 *(3.1)*	0.1 *(0.3)*	0.03 *(0.1)*	0.02 *(0.1)*
75	2.4	41 *(88.6)*	3 *(6.5)*	2 *(4.3)*	0.2 *(0.4)*	0.03 *(0.1)*	0.03 *(0.1)*
		Irradiation at 300 mJ per pulse					
13	1.2	16 *(91.6)*	0.9 *(5.1)*	0.5 *(2.8)*	0.05 *(0.3)*	0.01 *(0.1)*	0.01 *(0.1)*
75	1.8	29 *(91.8)*	1.5 *(4.8)*	0.9 *(2.9)*	0.1 *(0.3)*	0.03 *(0.1)*	0.01 *(<0.1)*

[a] Individual particle size. [b] Total volume of gas generated. [c] Millimoles of gas produced per gram of carbon; the percentage of each product gas is given in parentheses.

a chemical shift from an arene carbon and the ^{13}C NMR lines at 82, 75, and 69 ppm are characteristic of chemical shifts from alkenes and alkynes.[14] Solvent extractions, LC-MS, and high performance liquid chromatography (HPLC) were carried out on the post irradiated filtered water but the concentrations of the chemical species in solution were so small that each technique failed to identify any organic liquid-phase compounds. The peaks present in the UV−Visible spectrum above can also be tentatively assigned to the functional groups identified by NMR spectroscopy. The absorption peak at 210 nm is characteristic of a COO chromophore in an organic acid, the peak at 250 nm is characteristic of a C═C bond in an arene ring, and the peak at 330 nm is consistent with a C═O chromophore in a quinone-type structure.[14] It should be noted that similar pendant functional groups are generated when coal is heated in steam[15] at 900 °C.

The presence of hydrogen peroxide in the liquid products was confirmed using an analytical detection procedure based on horseradish peroxidase[16] (HRP), which is a hemoprotein readily oxidized in the presence of H_2O_2. The oxidized form of HRP has a broad absorption that peaks at 460 nm. Here, 2 mL of an irradiated, filtered carbon suspension (0.2 μm filtered) was added to 2 mL of HRP and an UV spectrum taken after 15 min. With the use of a calibration plot, the number of moles of H_2O_2 generated per gram of carbon in the pre-irradiated suspension was determined to be 1.3 mM/g.

C. Gaseous Species from Carbon Suspensions in Organic Liquids. In a similar set of experiments, suspensions of carbon particles in toluene and benzene were irradiated with the 1064 nm output of the Q-switched Nd:YAG laser. Again, the solutions were irradiated with the laser operating at a repetition rate of 10 Hz until all visible carbon was consumed. Irradiation of these suspensions induced effects similar to those seen in aqueous carbon suspensions: on irradiation of the suspension, tiny bubbles of permanent gas formed, luminescence was observed, and a large audible photoacoustic effect was produced. Both the brightness of the luminescence and the amplitude of the photoacoustic effect were greatest for carbon suspensions in benzene. Although the carbon in the organic liquids is consumed during irradiation, the suspensions did not gradually become clear as in the case of the aqueous carbon suspensions. The originally black, opaque suspensions appear dark brown-yellow immediately after irradiation. Figure 2 (lower section) shows the appearance of a carbon suspension made up in toluene before and after irradiation with 6000 laser shots. If the suspensions are allowed to stand for a few minutes after irradiation, black carbonaceous material rapidly precipitates from the solution.

When a carbon suspension in toluene was irradiated, H_2 was found to be the major gaseous product. Small amounts of CH_4, C_2H_2, C_2H_4, C_2H_6, and C_3H_8 were found as well. The amounts of each gas detected following irradiation of carbon suspensions made with 13, 25, and 75 nm diameter particles irradiated at 650 and 300 mJ per pulse are given in Table 2, with the quantity of each gas expressed in millimoles of gas produced per gram of carbon in the preirradiated suspension. The data in Table 2 show that the absolute amount of each product gas increases with an increase in carbon particle size, irrespective of the laser power. Reducing the laser power by roughly 50% (from 650 mJ to 300 mJ), reduces the absolute amounts of each product gas by approximately 50%. The amount of each product gas, expressed as a percentage of the combined total amount of gas produced is given in Table 2. It can be seen that although there are variations in the yield of each gas as the laser fluence changes, the composition of the gases remains relatively constant irrespective of carbon particle size or laser fluence when compared with the results for aqueous suspensions. Surprisingly, no significant change in the yield of C_2H_2 with particle size or laser fluence is found for carbon suspensions in toluene.

Experiments were also carried out with carbon particles suspended in liquid benzene. It was found that at a carbon concentration of 200 mg/L, the amount of gas generated during irradiation was always greater than the 4 mL of gas the syringe was capable of holding. The irradiation was therefore terminated before all the carbon in the suspension could be consumed. The increased gas formation can possibly be attributed to reaction of additional carbon generated by the thermal cracking of benzene vapor on the hot surface of the carbon particles. Suspensions were thus made up and irradiated using a carbon concentration of 133 mg/L. The total amount of product gas generated from a suspension with this carbon concentration was 1.4 ± 0.1 mL. The products detected in the gas generated above the suspension followed by their molar amounts produced per gram of carbon in the suspension were H_2 (26 mM/g), CH_4 (0.6 mM/g), C_2H_2 (0.8 mM/g), and C_2H_4 (0.1 mM/g). The amount of each product gas expressed as a percentage of the total amount of moles formed is H_2 (94.6%), CH_4 (2.2%), C_2H_2 (2.9%), and C_2H_4 (0.3%).

For comparison purposes, a carbon suspension in toluene was made up with a carbon concentration of 133 mg/L and irradiated. The quantity of gas generated above the suspension was measured to be 1.1 ± 0.1 mL; the amount of each product gas produced, expressed as a percentage of the total amount, was H_2 (92.6%), CH_4 (4.9%), C_2H_2 (2.2%), C_2H_4 (0.2%), and C_2H_6 (0.1%). As can be seen in Table 2, the percentages of gaseous hydrocarbons produced from irradiated carbon suspensions in liquid toluene are almost independent of the laser power, carbon concentration, or carbon particle size.

D. Liquid-Phase Species from Carbon Suspensions in Toluene and Benzene. After irradiation, carbon suspensions in toluene and benzene were filtered and their respective liquid-

TABLE 3: Liquid Products: Carbon in Toluene and Benzene

liquid-phase products	
C/C_6H_6 suspension	C/C_7H_8 suspension
1-methylene,H-indene	1,2-dimethylbenzene
naphthalene	1-methylene-2-propenybenzene
biphenyl	1-propynylbenzene
biphenylene	1-methylnaphthalene
acenaphthylene	naphthalene
1-methytriphenylene	2-ethenylnaphthalene
	biphenyl
	1,1′-methylenebisbenzene
	4-methyl-1,1′-biphenyl
	biphenylene
	bibenzyl
	2,2′-dimethylbiphenyl
	9H-fluorene

phase products were analyzed using a GC-MS. The post-irradiated filtered toluene and benzene solutions were found to contain a wide distribution of polycyclic aromatic hydrocarbons (PAHs). The dominant PAH species present in irradiated carbon suspensions in toluene and benzene were found to be bibenzyl and biphenyl, respectively. Other PAH species found but in much smaller amounts are listed in Table 3.

IV. Discussion

As can be seen in the first entries in Table 1 describing the results of irradiation of the carbon suspensions in water with nanosecond laser pulses, the amount of C_2H_2 produced relative to CH_4 and C_2H_4 increases with increasing laser fluence. Although the assumption of thermodynamic equilibrium is not warranted, the formation of C_2H_2 is favored by a Gibbs standard free energy of formation that decreases with increasing temperature. Previous experiments[3] have shown that C_2H_2 formation increases when large particles are irradiated, and that an increase in particle size also favors high-temperature production for a fixed laser fluence.

Comparison of the ratio of hydrocarbon gases produced by the nanosecond and picosecond lasers at fluences of approximately 0.2 and 0.8 J cm^{-2}, respectively, i.e., comparison of row one with row four, or row three with row five in Table 1, shows that for a fixed laser fluence the fraction of C_2H_2 in the gas relative to CH_4 is significantly higher for picosecond pulse irradiation than for irradiation with nanosecond pulses, indicating that for a fixed laser fluence, the shorter the laser pulse the more C_2H_2 is produced. The increased production of C_2H_2 with the short pulses is evidence that high-temperature coupled with very fast quenching time provides a favorable environment for C_2H_2 formation and survival. The effect of pulse width on temperature and the formation of hydrocarbons can be understood from a rudimentary examination of thermal diffusion of heat from the particles. The thermal diffusion time characterizing the cooling of a spherical particle is given by $\tau = r^2/2D$, where D is the thermal diffusivity of the liquid, assumed to be identical to that of the particle. In the present case, for a 25 nm diameter particle, the thermal diffusion time is 13 ps, which is short compared with the 10 ns long laser pulse period. Thus, during the 10 ns irradiation period, heat is continuously conducted away from the particle through thermal diffusion resulting in a low efficiency for heating the particle. The picosecond pulse, on the other hand, delivers its energy to the particle on a time scale commensurate with, but still longer than, the thermal diffusion time for the particle, so that a greater fraction of the pulse energy is available for heating. Since the rate of thermal diffusion is proportional to the temperature gradient at the particle surface, the higher particle temperature produced by the picosecond laser also results in a faster quenching of the temperature. Since the rate of energy loss from the particles through thermal radiation also increases with temperature, the quenching rate is also expected to be highest for particles driven to the highest temperatures. It is noteworthy that ethyne is also the main hydrocarbon gas generated from the plasma pyrolysis of coal,[15] a process like laser irradiation of colloidal suspensions, that involves chemical reaction at extremely high temperatures followed by rapid quenching of the temperature.

The last entry in Table 1 for the femtosecond laser shows that the amount of C_2H_2 relative to the other light hydrocarbon gases is not critically dependent on laser intensity; that is, the remarkably high peak power in the femtosecond pulses does not translate into a correspondingly high efficiency for formation of C_2H_2. It follows again from elementary considerations of heat diffusion that once the pulse duration is less than the time for thermal diffusion from the particle, further reduction in the pulse length should produce no increase in temperature, and insofar as the present experiments are concerned, no further increase in the relative formation of ethyne. The second entry in Table 1 shows that the nanosecond laser gives roughly the same C_2H_2-to-CH_4 ratio as the femtosecond laser, but surprisingly with a fluence of only 0.02 J cm^{-2} compared with a fluence of 0.38 J cm^{-2} for the nanosecond laser. As discussed below, the high efficiency for C_2H_2 formation by the femtosecond laser is probably explained by the heat deposition on such a short time scale giving the most efficient delivery of energy for producing high temperatures. The important point, however, with regard to the use of femtosecond laser pulses for formation of hydrocarbon gases is that if the process involved a mechanism dependent on peak power, such as multiphoton absorption, then the C_2H_2-to-CH_4 ratio in the product gases would be far greater than the corresponding ratios for the picosecond and nanosecond laser pulses since the femtosecond pulses have peak powers far in excess of that for any of the nanosecond or picosecond pulses used in the experiments. We note parenthetically that similar experiments in colloidal Au and Ag again did not point to multiphoton processes in the size reduction of particles composed of these elements.

With regard to the formation of H_2O_2 in the liquid phase, its presence can be attributed to the recombination of OH radicals generated by the high temperatures that exist at the sites of the carbon particles. Note that H_2O_2 is one of the two principal products, with H_2 an additional product, formed from the high-intensity ultrasonic irradiation of water[17] where similar extreme reaction conditions exist on cavitational collapse of vapor bubbles. It is likely that the H_2O_2 produced during irradiation oxidizes the carbon particles, which leads to the formation of the functional groups identified in the UV−Visible and ^{13}C NMR spectra.

The hydrocarbons detected in the gas generated above irradiated carbon particles suspended in liquid toluene and benzene are similar to those produced from laser photolysis experiments. The formation of H_2, CH_4, C_2H_2, and C_2H_4 from the laser photolysis of liquid toluene and benzene has also been reported by Pola et al.[18] Surprisingly, the ratios of hydrocarbon gases reported in the laser photolysis of toluene and benzene are similar to those reported here. Sonochemical reactions[17] and high-temperature gas-phase pyrolysis of these two neat organic liquids also produce light hydrocarbon gases as well, which are predominantly H_2 and CH_4 in the case of toluene, and H_2, CH_4, and C_2H_2 in the case of benzene. However, the species produced by irradiation of suspensions of carbon in toluene and benzene are seen to be more numerous than those produced by sonochemical reactions, even though the reactions in sonochemical production of hydrocarbons in neat toluene and benzene also take place at the high temperatures and pressures produced by the collapse of vapor bubbles. The similarity of the main reaction products in laser irradiation of colloidal carbon in toluene, and the sonolysis and photolysis of toluene can most likely be ascribed to reactions 1 and 3 (see below) that are possibly the first steps in each case, and which dictate to a large extent which products are ultimately formed.

Insofar as the liquid-phase products seen in carbon suspensions in toluene and benzene are concerned, the species found here are similar to those reported from the laser photolysis of the neat organic liquids[18] but are more numerous than those reported in sonochemical reactions.[17] In the cited laser photolysis and sonochemical experiments, bibenzyl and biphenyl were also the dominant species produced in liquid toluene and benzene, respectively.

The formation of bibenzyl and biphenyl almost certainly involves the initial generation of benzyl and phenyl radicals from the fission of $C(sp^3)-H$ and $C(sp^2)-H$ bonds, respectively. The radicals then recombine primarily with each other to from bibenzyl and biphenyl, respectively, according to the reaction sequences in toluene,

$$C_6H_5-CH_3 \rightarrow C_6H_5-CH_2 + H \tag{1}$$

$$2C_6H_5-CH_2 + 2H \rightarrow C_6H_5-CH_2-CH_2-C_6H_5 + H_2 \tag{2}$$

and in benzene,

$$C_6H_6 \rightarrow C_6H_5 + H \tag{3}$$

$$2C_6H_5 + 2H \rightarrow C_6H_5-C_6H_5 + H_2 \tag{4}$$

The formation of a wide distribution of minor PAHs in the experiments reported here indicates that a variety of other reactions take place that must involve the cleavage of C−H and C−C bonds followed by a host of reactions that are known to occur during high-temperature reactions of hydrocarbons.[18]

The formation of a number of PAH species common to both of the irradiated carbon suspensions in toluene and benzene points to $C-CH_3$ bond cleavage in toluene prior to the formation of the species listed in Table 3, although the small amounts of 1-methyl-naphthalene, 2-ethenyl-naphthalene, 4-methyl-1,1′-biphenyl detected in the toluene suspensions indicate that some $C-CH_3$ bonds remain intact.[21] The formation of CH_4, C_2H_2, C_2H_4, C_2H_6, and C_3H_8 suspensions of carbon in toluene could be facilitated through either the formation of CH_3 radicals followed by a number of subsequent H-abstractions and recombination reactions, or via another H-abstraction route starting with C, CH, or CH_2 species.[19] The formation of CH_4, C_2H_2, and C_2H_4 from irradiated carbon suspensions in benzene points to an H abstraction mechanism as well.

It is possible to estimate the pressure rise in the particle when the laser pulse is shorter than the transit time of sound across the particle. Of course, values of thermodynamic parameters at the temperatures generated by the laser are not available, but for a carbon particle with a diameter of 25 nm, the transit time of sound across the particle is 10 ps. Thus, only for the 40 fs pulses does heat deposition in the particle increase the particle temperature in an essentially constant volume process. In such a process, when the laser pulse width is shorter than the transit time of sound across the particle, there is no significant motion of the particle as a result of the heating, and the pressure can be determined[20] through use of the relation $p = \alpha T$ where α is the pressure coefficient of expansion given by $\alpha = \rho\beta c^2/\gamma$, where ρ is the density, β is the volume expansion coefficient, and γ is the heat capacity ratio. For parameters measured at 300 K and 1 atm., α is found to be 1 atm/K so that for a temperature[21] of 3000 K, a rudimentary estimate of the peak pressure in the particle is 3000 atm. For the femtosecond pulses, the full energy of the laser pulse thus goes to heating and the subsequent production of high pressure, without the effects of heat diffusion or diminution of the pressure as a result of expansion. Of course, this primitive calculation does not take into consideration phase transitions or changes in thermodynamic parameters that can significantly change the results of the calculation.

The experiments reported here show that the rapid heating and subsequent cooling of colloidal carbon particles by pulsed lasers gives a high-pressure, high-temperature environment. The combination of the strong optical absorption coefficients found for submicron particles with the high intensity and short pulse lengths characteristic of pulsed lasers yields a short burst of high temperature and pressure at the sites of the particles. As has been shown in the case of colloidal metals as well as in the experiments reported here, the extreme conditions produced by absorption of large amounts of optical energy in a short time result in unique reaction conditions that produce not only unusual acoustic and optical effects, but also a surprising series of chemical reactions.

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