

Analysis of products from breakdown of liquid benzene, toluene and cyclohexane caused by Nd³⁺:YAG pulsed laser irradiation

Kei Toyota, Tetsuya Tanaka, Shun-ichi Nishiwaki, Satoru Nakashima, Tadashi Okada*

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Osaka 560-8531, Japan

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Abstract

Products from liquid benzene, toluene and cyclohexane breakdown caused by strong Nd³⁺:YAG fundamental pulsed laser irradiation were analyzed. Under nanosecond laser irradiation, hydrogen, methane, acetylene, ethylene, biphenyl, phenanthrene, anthracene and amorphous carbon were detected from liquid benzene and the laser intensity dependence of their yield was investigated. From laser intensity dependence of absolute quantity, it is suggested that biphenyl is produced by simple mechanism, while anthracene and phenanthrene are produced by diffusional collision of some kind of radicals via multi step reaction. In picosecond laser irradiation, the kind of products is same as those in nanosecond laser irradiation for liquid benzene, however yields of the products were higher because of stronger electric field. While in toluene and in cyclohexane same gaseous products as in benzene were detected. In particular, ethane was detected only from cyclohexane. In ultrasonic irradiation that is known as high pressure and high temperature reaction into liquid benzene and liquid toluene, results were different from those of laser irradiation. We could conclude that the reaction caused by near-infrared laser-induced breakdown is basically different from the reaction induced by high pressure and high temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Near-infrared laser breakdown; Liquid benzene; Analysis of products

1. Introduction

Tight focusing of near-infrared pulsed laser induces breakdown of liquid benzene by a strong electric field [1] and the phenomenon is understood as avalanche multiplication of free electrons [2]. Collision between accelerated electrons and molecules in the photon field induces ionization of the molecule. Furthermore, new electrons ejected from the ionized molecules are accelerated in photon field to ionize other molecules. In this process, free electrons multiply drastically to induce breakdown. In our previous work [1], it was found that the multiphoton excitation of molecules is not main process. From measurement of emission spectrum of breakdown in liquid benzene C₂ radical and CH radical were observed. Precise product analysis has not been studied so far under near-infrared pulsed laser irradiation into liquid benzene.

Some product analytic studies were reported in UV laser irradiation into liquid benzene [3–5]. Ablation of liquid benzene caused by ultraviolet nanosecond laser irradiation (248 or 308 nm) was investigated by Srinivasan and Ghosh [3]. They observed the formation of biphenyl,

phenylcyclohexadiene, naphthalene and carbon as photoproduct. Naphthalene and carbon were produced when the laser intensity was higher than 0.3 J cm⁻². Their suggestion is that the ablation of liquid benzene is attributed to the absorption of more than two photons per molecule. Formation of graphitic and polymeric carbon was reported by Pola et al. [4]. They have analyzed the details of the carbon material that was produced by unfocused ArF laser (193 nm) exposure. Since the structure of carbon materials showed the feature of that produced under ambient temperature, they concluded that the reaction proceeds under the ambient temperature. In more recent work, Katoh et al. analyzed the photoproducts caused by ArF laser (193 nm) irradiation [5]. Their conclusion is that the thermal energy generated by the non-radiative inactivation processes from electronically excited state induces the C–H dissociation. Like this, the reaction of liquid benzene induced by laser irradiation is still under discussion.

On the other hand, few product analytic studies in visible and non-resonant laser irradiation are found in the literature. Kobayashi et al. reviewed the synthesis of a diamond with a pulsed ruby laser (694.2 nm, 20 J cm⁻² per pulse) focusing onto the surface of silicon plate steeped in liquid benzene [6]. From the detail investigation of the diamond formation in various conditions, they concluded that the cyclic structure

* Corresponding author. Tel.: +81-6-6850-6242; fax: +81-6-6850-6244.
E-mail address: okada@chem.es.osaka-u.ac.jp (T. Okada).

of six carbons kept its structure at the boundary of silicon surface and liquid, and was to be the seeds of the diamond formation.

In present research, our attention was directed to products in breakdown plasma. We will report the results of analysis of products from liquid benzene, liquid toluene and liquid cyclohexane breakdown caused by Nd³⁺: YAG fundamental pulsed laser (1064 nm) irradiation. As a reference experiment, analysis of products from ultrasonic irradiation (60 W, 20 kHz) that is known as high pressure and high temperature reaction [7] into liquid benzene and liquid toluene will be compared with the results of pulsed laser irradiation.

2. Experimental

The pulsed laser beam is focused into liquid [1]. Two types of Nd³⁺: YAG laser, Q-switched nanosecond laser (Spectra-Physics DCR-3, 1064 nm, fwhm = 10 ns, 10 Hz, 0.11–1.7 MJ cm⁻²) and mode-locked picosecond laser (EKSPLA PL2143A, 1064 nm, fwhm = 20 ps, 10 Hz, 0.11 MJ cm⁻²) were used. A 30 mm focal lens was placed just before the quartz cuvette (40 mm × 80 mm, ∅). After laser irradiation of 1000 pulses, gas phase components were sampled with a micro syringe and analyzed by Gas Chromatography (GC, Okura, model 103 for hydrocarbons (FID detection)) and Shimadzu, MODEL GC-2C for hydrogen (TCD detection). The amount of gas products was estimated from the peak area of sample gases and the ideal gas approximation at 273 K. Every each laser intensity, the measurements were carried out three times and the average value was calculated. The experimental error of the value was large (about 40%) in lower laser intensity and become to be smaller (finally about 10%) in higher laser intensity.

The non-volatile products were analyzed by the following method. After 1000 pulses laser irradiation, the sample liquid colored yellow. It was concentrated and the deposits were extracted with 10 ml CH₃CN/H₂O (62.5/37.5) mixed solvent. This extracted solution was filtered with 0.2 μm pore size and analyzed by high performance liquid chromatography (HPLC, Hitachi L-6200 pump system and L-4200 UV detector with silica based column Inertsil ODS-2), monitored at 255 nm. Reaction products separated by HPLC were collected with a fraction collector. The absorption and fluorescence spectra of each collected fraction was measured by a spectrophotometer Hitachi U-3500 and Hitachi E850, respectively. Assignment of the products was made by comparing the spectra with reference compounds to show the same retention time of HPLC chromatogram. The amount of non-volatile products was estimated by peak intensities of standard sample solutions. Amount of products will be described as yield (mol J⁻¹) and absolute quantity (mol per pulse) in present research. Yield is value of the absolute quantity divided by total energy of one laser pulse (Joule per pulse). Residual black solids after extraction of deposits with CH₃CN/H₂O (62.5/37.5) mixed sol-

vent was analyzed by Raman spectrometer with an Ar⁺:laser (514.5 nm).

The ultrasonic was irradiated into liquid directly for 45 min. It was oscillated from rod-shaped high power ultrasonic instrument (BRANSON SONIFIER 185, 60 W, 20 kHz). The experiment was performed in liquid benzene and liquid toluene, respectively. In order to avoid the vaporization of the liquid, the flask containing liquid was steeped in ice bath. Argon gas was flushing into the liquid during the ultrasonic irradiation. Non-volatile products were analyzed by the HPLC analysis. The analysis method was same as that in laser irradiation.

UV spectral grade benzene, toluene and cyclohexane (Wako Pure Chemical Industries 99%) were distilled carefully before using. Residual toluene as contamination in benzene was estimated to be about 0.02% by using HPLC. Before laser irradiation, the liquids were deaerated by flushing argon for 15 min.

3. Results and discussion

3.1. Laser irradiation

3.1.1. Benzene

GC chromatograms and the HPLC chromatogram of the sample obtained from nanosecond laser irradiation are shown in Fig. 1. GC chromatograms of Fig. 1(a) and (b) are samples of 1.1 MJ cm⁻² laser irradiation, and HPLC chromatogram (c) is sample of 0.74 MJ cm⁻² laser irradiation. Hydrogen, methane, acetylene, ethylene, benzene, toluene, biphenyl, phenanthrene and anthracene were assigned. The other small peaks could not be assigned. We took the HPLC chromatogram of biphenyl, 4-methylbiphenyl, phenanthrene, anthracene and 9-methylanthracene as a reference (Fig. 1(d)). It is found that the addition of methyl-group to the compound make its retention time delay about 5 min. Consequently, methyl product is unlikely contained at least in the peak of biphenyl and anthracene in Fig. 1(c).

Raman spectrum of black solids in the residue obtained at laser intensity of 0.74 MJ cm⁻² is shown in Fig. 2. Characteristic peak of 1583 cm⁻¹ agreed with Raman band of graphite [8] and peak of 1334 cm⁻¹ agreed with the Raman band of diamond [6,9]. The characteristic spectrum has been often reported in some studies [9–11]. Similarity of bandwidth and ratio of these peak heights made us conclude that the black solid is amorphous carbon [12]. We considered the amount of amorphous carbon is too little to influence the breakdown and reaction process during 1000 pulses irradiation.

The laser intensity dependencies of absolute quantity and yields for hydrogen, methane, acetylene and ethylene are shown in Fig. 3(a) and (b), respectively. When the laser intensity is lower than 0.14 MJ cm⁻², quantity of gas products is too little to be detected. Absolute quantity of hydrogen is

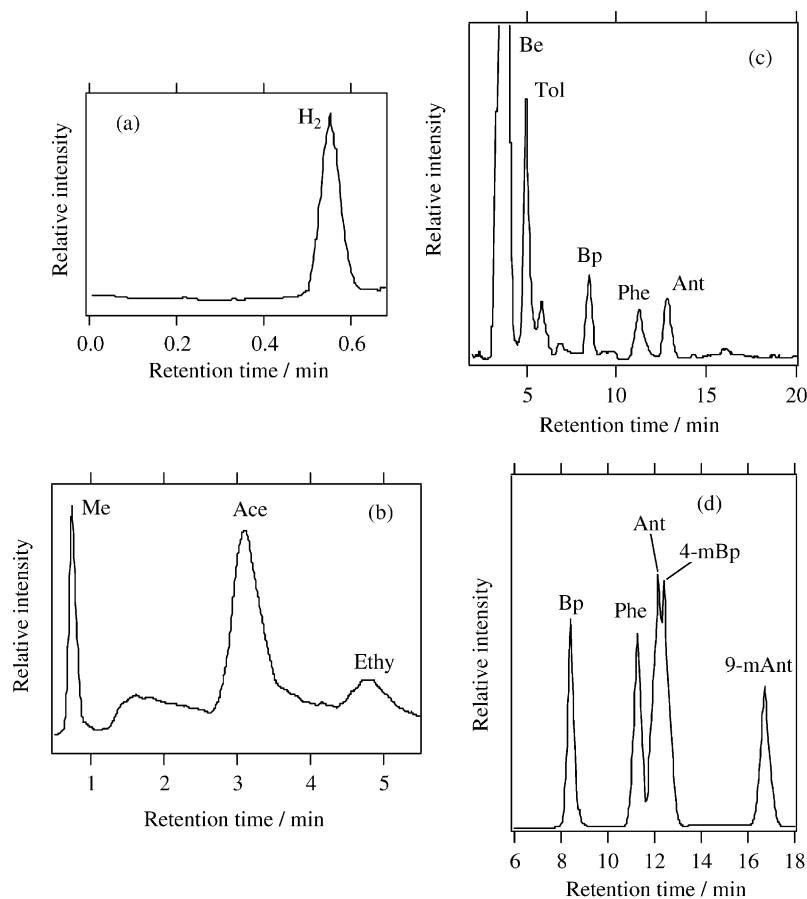


Fig. 1. Gas chromatogram (a), (b) and HPLC chromatogram (c) of products in nanosecond laser irradiation in liquid benzene. The laser intensity is 1.1 MJ cm^{-2} about (a), (b) and 0.74 J cm^{-2} about (c), respectively. H_2 : hydrogen, Me: methane, Ace: acetylene, Ethy: ethylene, Be: benzene, Tol: toluene, Bp: biphenyl, Phe: phenanthrene, Ant: anthracene (d) is HPLC chromatogram of standard sample. Bp: biphenyl, Phe: phenanthrene, Ant: anthracene, 4-mBp: 4-methylbiphenyl, 9-mAnt: 9-methylantracene.

the most among all detected gases, which is 10 times larger than that of the other hydrocarbons. Absolute quantity of all gases saturates in higher laser intensity range, and the yields of them decrease gradually from about 0.21 MJ cm^{-2} .

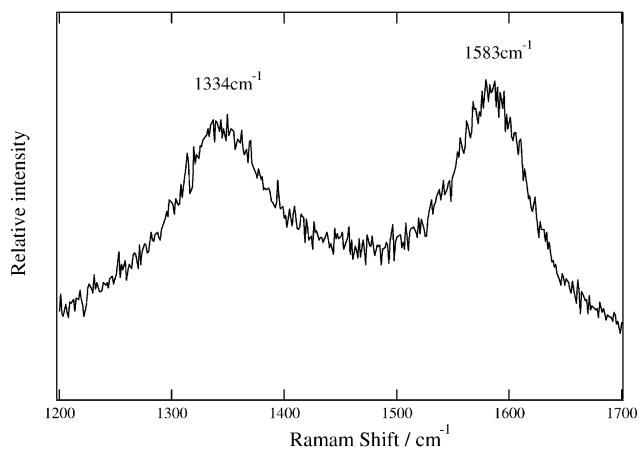


Fig. 2. The Raman spectrum of the black solid from liquid benzene in 0.74 MJ cm^{-2} nanosecond laser irradiation. The black solid is understood as amorphous carbon.

The non-linear behavior indicates that the reaction most likely proceeds with multi steps and these molecules are by-products. The reason of yields decreasing in higher laser intensity will be discussed later.

In Fig. 4, laser intensity dependence of absolute quantity for biphenyl (a), phenanthrene (b), anthracene (c) and laser intensity dependence of yields of those (d) are shown. The laser intensity dependence of absolute quantity of biphenyl shows linear profile above the threshold intensity of laser breakdown. This behavior can be explained by microwave breakdown theory. First we assumed that biphenyl is produced from a phenyl radical and a benzene molecule like as reported by Fujii and Asaba [13]. The kinetic energy of one electron in the photon field is more than $4 \times 10^{-19} \text{ J}$ [1], while a C–H bond dissociation in a benzene molecule needs $7 \times 10^{-19} \text{ J mol}^{-1}$ [14]. Since these two values are same order of magnitude, C–H bond dissociation can be induced by collision of accelerated electrons to produce a phenyl radical. C–H bond dissociation of linear alkane by collision of accelerated electrons was reported also in the study of breakdown caused by current pulse [15]. Moreover, the concentration of phenyl radicals in a shot of pulse must be proportional

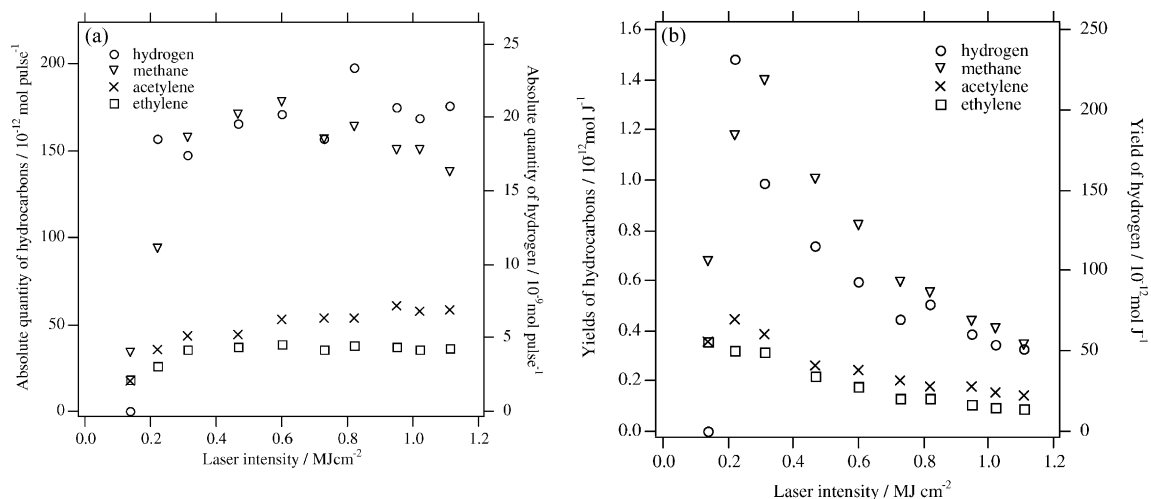


Fig. 3. The laser intensity dependence of the absolute quantity (a) and yields (b) of gas products.

to the laser intensity, because the energy that molecules acquire by collision of accelerated electrons is proportional to the laser intensity according to the microwave breakdown theory [1]. Therefore, the laser intensity dependence of absolute quantity of biphenyl shows linear behavior and it can

be concluded that a biphenyl molecule is produced from a benzene molecule and a phenyl radical.

As shown in Fig. 4(c) the laser intensity dependence of absolute quantity of anthracene does not show linear profile like biphenyl. Because various kinds of active species

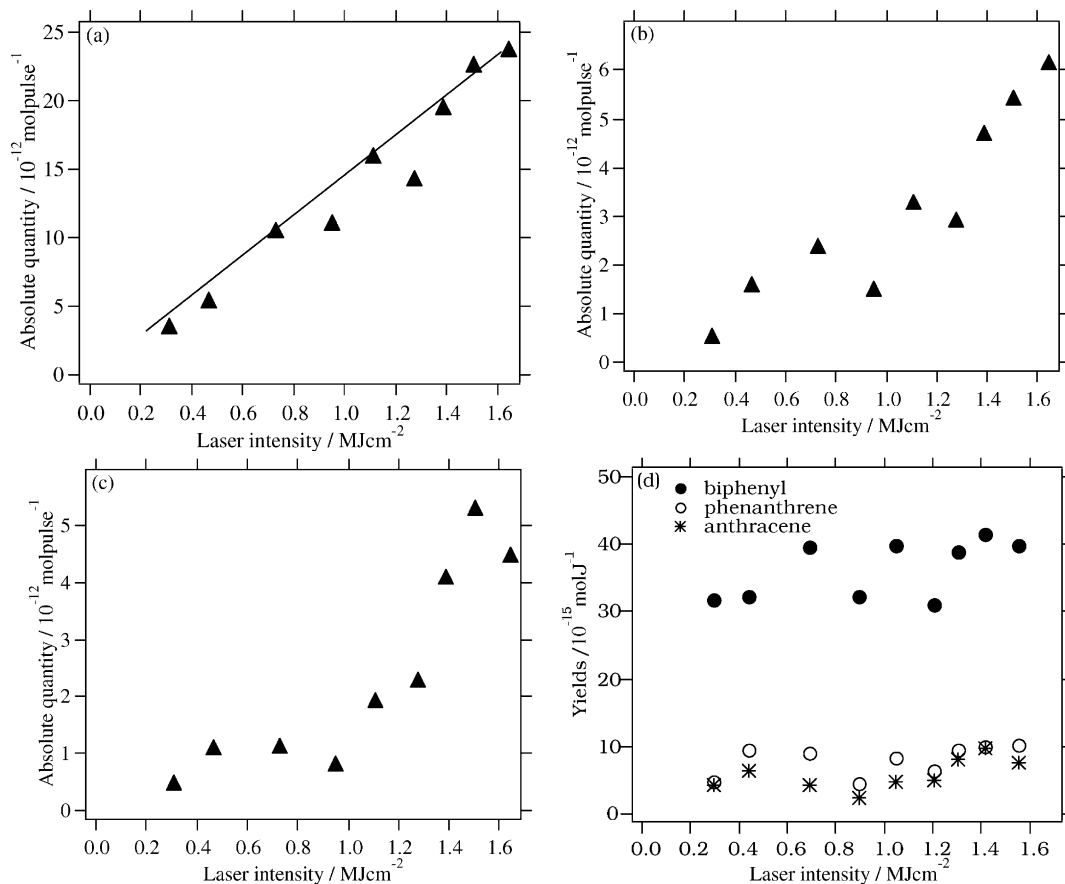


Fig. 4. The laser intensity dependence of absolute quantity of (a) biphenyl; (b) phenanthrene; (c) anthracene and the laser intensity dependence of yields of them (d).

are probably the source of one anthracene molecule and the mechanism of production is not so simple as that of biphenyl formation. In particular, absolute quantity of anthracene increases drastically from 0.95 MJ cm^{-2} . This increase is corresponding to the decrease of gas yields. At higher laser intensity, active species are consumed to produce large molecules because of high concentration and make absolute quantity of gas saturates (Fig. 3). That is to say, anthracene is produced by diffusional collision of active species. The active species can be thought C_2 radical [1], CH radical [1], phenyl radical, and so on. The same discussion can be applied for phenanthrene. Laser intensity dependence of yields of them is almost constant as shown in Fig. 4(d).

The analysis result obtained from picosecond laser (0.11 MJ cm^{-2}) irradiation was compared with that obtained from nanosecond laser (1.1 MJ cm^{-2}) irradiation. Fig. 5 indicates the HPLC chromatogram for products in picosecond laser irradiation. Benzene, toluene, biphenyl, phenanthrene and anthracene were assigned. The kinds of products are same with those in nanosecond laser irradiation. The difference between parameters of two lasers and amount of products is summarized in Table 1. Yields of products are much larger and the ratio of yield of biphenyl is obviously large in picosecond laser irradiation. Electric field of picosecond laser pulse is about 50 times higher than that of nanosecond laser pulse as shown in Table 1. Hence, the energy of accelerated electrons in picosecond laser pulse is also about 50 times higher. Consequently, probability of bond dissociation induced by collision of accelerated electron increases to increase concentration of radicals. Therefore, the products are formed more effectively. Since biphenyl is produced from one benzene molecule and one phenyl radical as discussed above, strength of electric field influences absolute quantity of biphenyl sensitively. In much higher electric

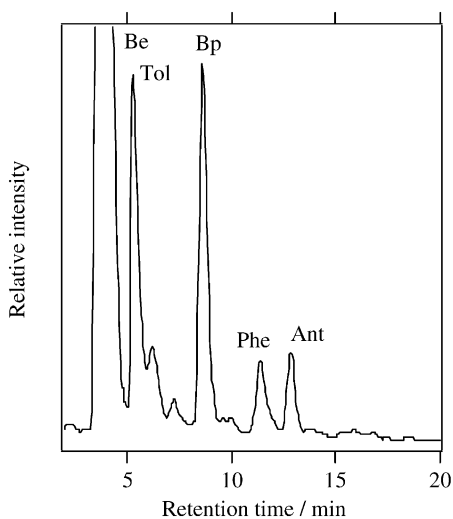


Fig. 5. The HPLC chromatogram of products in picosecond laser irradiation (0.11 MJ cm^{-2}). Be: benzene, Tol: toluene, Bp: biphenyl, Phe: phenanthrene, Ant: anthracene.

field under picosecond laser irradiation, concentration of phenyl radical become higher and it is thought that production from two phenyl radicals become effective. Therefore, comparing with nanosecond laser irradiation, the ratio of absolute quantity of biphenyl to those of phenanthrene and anthracene is higher in picosecond laser irradiation.

Some differences of products can be observed comparing with the study of 193 nm laser irradiation [5] and 248 nm laser irradiation [3] as summarized in Table 2. In 248 nm laser irradiation, they suggested that the ablation is induced by multi photon excitation of molecules. In this case, the photochemical reaction is a main factor of product formation. While in 193 nm laser irradiation, C–H bond dissociation proceeds by the heat generated from non-radiation of excited benzene molecules. While in present research, 1064 nm laser irradiation, C–H bond dissociation is caused by collision of accelerated electrons. These differences of initial process are thought to influence the distribution of kinds of radicals and to be revealed as differences of products in each case.

3.1.2. Toluene and cyclohexane

We have carried out the experiment about liquid toluene and liquid cyclohexane as well as about liquid benzene in nanosecond laser irradiation. In toluene, hydrogen, methane, acetylene and ethylene were produced, however non-volatile products as detected in benzene were not detected. While in cyclohexane ethane as well as hydrogen, methane, acetylene and ethylene were detected (Fig. 6). Also in cyclohexane, non-volatile products were not detected.

Production of benzyl radical was observed by Tsuboi et al. in excimer laser ablation (248 nm) of liquid toluene [16,17]. Benzyl radical is produced via photochemical reaction [18]. While in present research, the phenomenon is discharge and multi-photon process has been already denied in our previous study [1]. Analysis of the products from electric discharge of liquid toluene with graphite electrodes was reported by Beck et al. [19,20]. They suggested that toluene molecule is decomposed to phenyl radical and methyl radical but did not show the proof of production of benzyl radicals. Also in present research toluene can be thought to decompose to phenyl radical and methyl radical. Therefore, it is understood that products formed from benzyl radical are not detected.

In cyclohexane, the number of hydrogen atoms in a molecule is twice as those in a benzene molecule. Hydrogen can act as terminator of radical reaction. This is the reason why ethane is produced only from cyclohexane. Moreover, cyclohexane has no sp^2 orbital in its original structure. Thus, reasonably the aromatic compounds are difficult to be produced from cyclohexane. Reactions of these liquids seem to be very different from that of benzene.

Raman spectra of black solids obtained from toluene and cyclohexane are shown in Fig. 7. Also these black solids are understood as amorphous carbon. The peak at 1334 and 1543 cm^{-1} are known as D-band and G-band, respectively.

Table 1

Amount of products and status of two lasers. The character of “s” and “w” means strong and weak intensity of ns laser, respectively

	ns laser (s)	ns laser (w)	ps laser
Biphenyl yield ($\times 10^{-14}$ molJ $^{-1}$)	3.1	3.9	10 ⁵
Absolute quantity ($\times 10^{-11}$ mol per pulse)	1.6	0.36	3.9
Phenanthrene yield ($\times 10^{-14}$ molJ $^{-1}$)	0.82	0.47	6900
Absolute quantity (10^{-12} mol per pulse)	3.3	0.53	2.8
Anthracene yield ($\times 10^{-14}$ molJ $^{-1}$)	0.48	0.44	4300
Absolute quantity ($\times 10^{-12}$ mol per pulse)	1.94	0.49	1.7
Electric field ($\times 10^{10}$ V m $^{-1}$)	2.0	1.1	64
Out put power of one pulse ($\times 10^7$ W)	4.0	1.2	200
Total energy of one pulse (Joule per pulse)	0.4	0.15	0.04
Energy density of one pulse (MJ cm $^{-2}$)	1.1	0.32	0.11

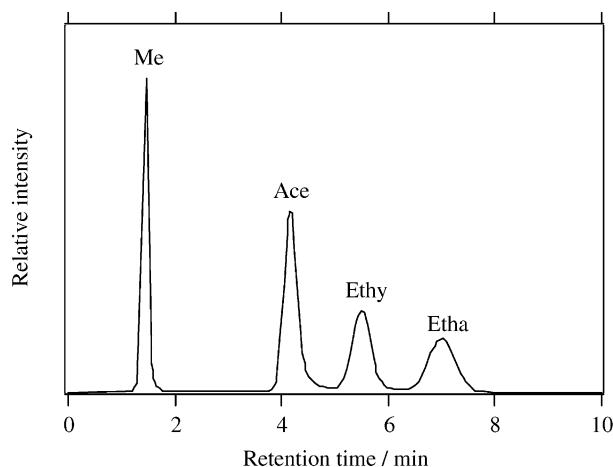
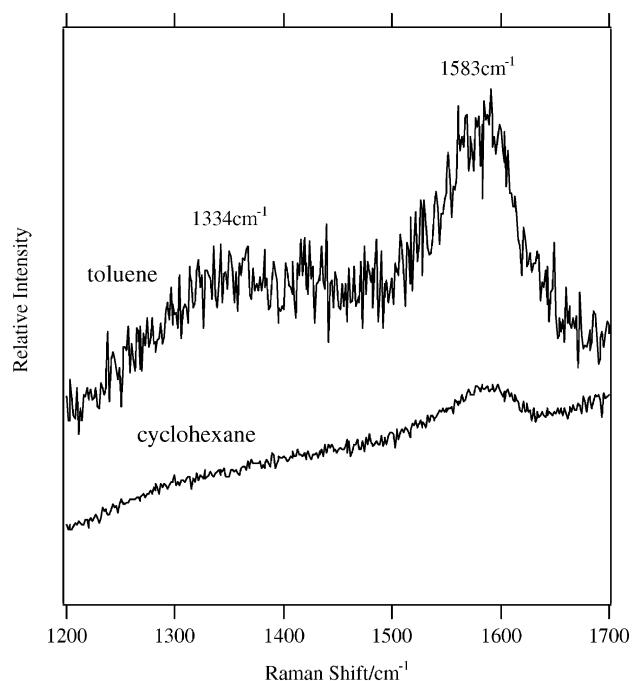
Table 2

The comparison of products with [3,5]^a

	248 nm	193 nm	1064 nm
Hydrogen	N	N	O
Methane	N	N	O
Acetylene	N	N	O
Ethylene	N	N	O
Naphthalene	O	X	X
Phenylcyclohexadiene	O	X	X
Biphenyl	O	O	O
Diphenyl acetylene	X	O	X
Phenanthrene	X	O	O
Anthracene	X	X	O
<i>o</i> -, <i>m</i> -, <i>p</i> -Terphenyl	X	O	X
Triphenyl	X	O	X
Carbon	O	O	O

^a O: produced, X: not detected, N: not measured.

The particle size of amorphous carbon becomes larger and larger, ratio of D-band intensity to G-band intensity becomes higher and higher [21]. From Figs. 2 and 7, it is indicated that particle size of amorphous carbon from liquid benzene is the largest and that from liquid cyclohexane is the smallest. The propagation of the amorphous carbon in

Fig. 6. The GC chromatogram in 1.1 MJ cm $^{-2}$ nanosecond laser irradiation in cyclohexane. Me: methane, Ace: acetylene, Ethy: ethylene, Etha: ethane.Fig. 7. The Raman spectra of the black solid from liquid toluene and liquid cyclohexane in 0.7 MJ cm $^{-2}$ nanosecond laser irradiation.

liquid cyclohexane is prevented because of many hydrogen atoms compared with benzene or toluene. This discussion does not contradict the ethane formation only from liquid cyclohexane.

3.2. Ultrasonic irradiation

HPLC analysis results of ultrasonic irradiation into liquid benzene and into liquid toluene are shown in Fig. 8(a), (b). In benzene, biphenyl was found as the main product, however phenanthrene and anthracene were not detected. While in toluene various products such as biphenyl, anthracene, 4-methylbiphenyl and pyrene were observed.

The reaction induced by ultrasonic irradiation is known as high pressure and high temperature reaction [7]. Ultrasonic irradiation into liquid benzene produced only biphenyl and

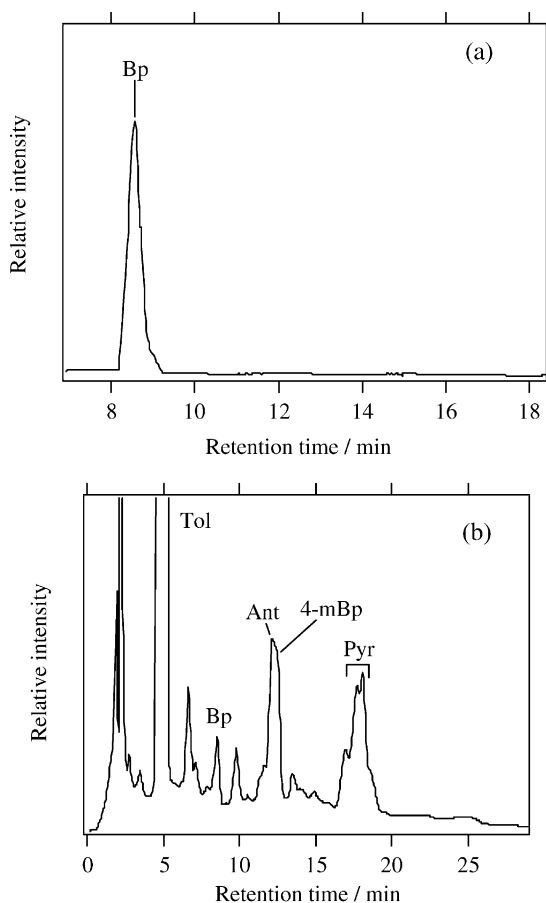


Fig. 8. The HPLC chromatograms of products from liquid benzene (a) and liquid toluene (b) in ultrasonic irradiation. Tol: toluene, Bp: biphenyl, Ant: anthracene, 4-mBp: 4-methylbiphenyl, Pyr: pyrene and other products.

laser irradiation into it produces many kinds of products. On the other hand the opposite tendency was observed in toluene. Consequently, the reaction induced by laser irradiation is not high pressure and high temperature reaction. We compared the yields of biphenyl in ultrasonic irradiation with that in laser irradiation in liquid benzene. Yield of biphenyl in ultrasonic irradiation was defined as the value of amount of biphenyl (4.4×10^{-7} mol) divided by total energy exposed from ultrasonic (162 kJ). In ultrasonic irradiation, it is 2.7×10^{-12} molJ $^{-1}$. In laser irradiation, about 3.5×10^{-12} molJ $^{-1}$ in nanosecond laser irradiation and 1.0×10^{-9} molJ $^{-1}$ in picosecond laser irradiation, respectively. We have no information ultrasonic intensity dependence of biphenyl yield, however, in picosecond laser irradiation, biphenyl is produced more effectively than in ultrasonic irradiation in present research.

4. Summary

Analysis of the products from breakdown of liquid benzene, toluene and cyclohexane with Nd $^{3+}$: YAG pulsed

laser having an ns- and ps-pulse was carried out. In benzene, hydrogen, methane, acetylene, ethylene, biphenyl, phenanthrene, anthracene and amorphous carbon were detected. In toluene, hydrogen, methane, acetylene, ethylene and amorphous carbon were detected. In cyclohexane, hydrogen, methane, acetylene, ethylene, ethane and amorphous carbon were detected. In benzene absolute quantity of gaseous products saturates at higher laser intensity, because active species that are source of gases are consumed to produce larger molecules like as phenanthrene or anthracene. Moreover, in picosecond laser irradiation, radicals are produced more effectively due to the higher electric field of ps-laser pulse, because the energy of accelerated electrons are higher to increase the probability of bond dissociation. Comparing with the study of excimer laser irradiation [3,5], some differences of kinds of products were observed in benzene. In 248 nm laser irradiation, the reaction proceeds with photochemical process and in 193 nm laser irradiation it was concluded that C–H bond dissociation proceeds by the heat generated by non-radiation of excited benzene molecules. While in our experiment, dissociation of C–H bond is induced by collision of accelerated electrons in a high electric field of laser. These differences of initial process are thought to influence the differences of products in each case. In ultrasonic irradiation into liquid benzene and liquid toluene, the results of analysis of products are largely different from that of laser irradiation. The reaction is not one that is proceeded only with high temperature and high pressure.

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