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The 248-nm Excimer-Laser-Ablation Mechanism of Liquid Benzene Derivatives: Photochemical Formation of Benzyl Radical Leads to Ablation

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The mechanism underlying 248-nm laser ablation of liquid benzene derivatives (alkyl benzenes, benzyl chloride, benzyl alcohol) was revealed by means of transient absorption spectroscopy. One characteristic in the present liquid system is that the ablation threshold can be correlated not to the boiling point at all but to the photochemical reactivity of β-bond cleavage. In the spectroscopic measurement, the benzyl-radical formation was confirmed upon ablation, and its concentration was quantitatively evaluated at the threshold. The obtained value was ~0.05 M, which was almost common to all of the examined liquids. The result means that the present liquids, whose macroscopic physical properties such as surface tension do not differ too much from each other because of the analogous molecular structure, undergo the ablation when the radical concentration reaches the critical value of 0.05 M. This is the first demonstration for bridging a gap between microscopic photochemical process and macroscopic morphological change. The ablation behavior can be well interpreted in terms of the photochemical volume explosion.

Introduction

Since the pioneering studies by Srinivasan et al.[1] and Namba et al.,[2] the interest in the UV laser ablation of various materials has increased steadily in relation to nonlinear photophysics and photochemistry as well as numerous applications such as microfabrication, surface modification, thin-film deposition, surgery, and so on. The past numerous studies have revealed that laser ablation of most polymer films is initiated by photothermal temperature elevation.[3−5] For polymer films doped with laser-absorbing aromatic molecules, we have demonstrated how the absorbed energy is converted into a thermal one, the cyclic multiphotonic absorption of the laser light by excited and transient species.[6−9] Our time-resolved spectroscopic approaches to the doped polymer systems have revealed that the main transient species involved in the ablation are the lowest excited singlet (S_1) and triplet (T_1) states of dopants with excess vibrational energy (hot molecules). It is noteworthy here that the photothermal ablation model is applicable to the ablation of solution (for example, biphenyl in ethanol), in which explosive boiling leads to morphological changes.[10] In spectroscopic measurements of the ablation of these doped polymers and solutions, hot bands of the excited species have been clearly observed; however, bands due to neutral-radical species generated by bond ruptures have not been detected at all. On the other hand, photochemical ablation is rather limited to a polymer having a diazo group,[11] amorphous dye films,[12] and so on. Even in a polymer film doped with 5-diazo Meldrum's acid whose reaction yield of photochemical decomposition is quite high (almost unity), ablation proceeds photothermally through cyclic multiphotonic absorption.[7]

In addition to the above mechanistic controversy, there still remains a fundamental as well as crucial problem about what little is known. Namely, no detail information is available on the mechanisms whereby small molecular particles, fragments, and debris generated by bond scission are ejected instantaneously with supersonic velocity, and whether the mechanism is photothermal or photochemical. For addressing the subject, only one computational attempt was done by Srinivasan and Garrison to our knowledge;[13] however, further experimental approach seems to be necessary. Relevant to this issue, to understand the photochemical process, it is indispensable to detect fragmented molecules directly and to know the number of bond scissions, in other words, the radical concentration that induces ablation. We consider a molecular liquid is a promising prototype system for evaluating the number of bond scissions leading to ablation, since the liquids are simple compared to amorphous polymers. In the polymer films where ablation is brought about photochemically, the distribution of free volumes, glass−rubber transitions, and anisotropic and interpenetrating structures may not correlate ablation threshold directly with photochemical reaction yield.

Recently, we have found an interesting photochemical behavior in the ablation of liquid benzene derivatives by 248-nm pulsed-laser irradiation.[14,15] The ablation threshold decreases in accordance with an increase of the photochemical reactivity of bond cleavage (Ph−X or $PhCH_2$−X, Ph is phenyl) for benzene, chlorobenzene, toluene, benzyl alcohol, and benzyl

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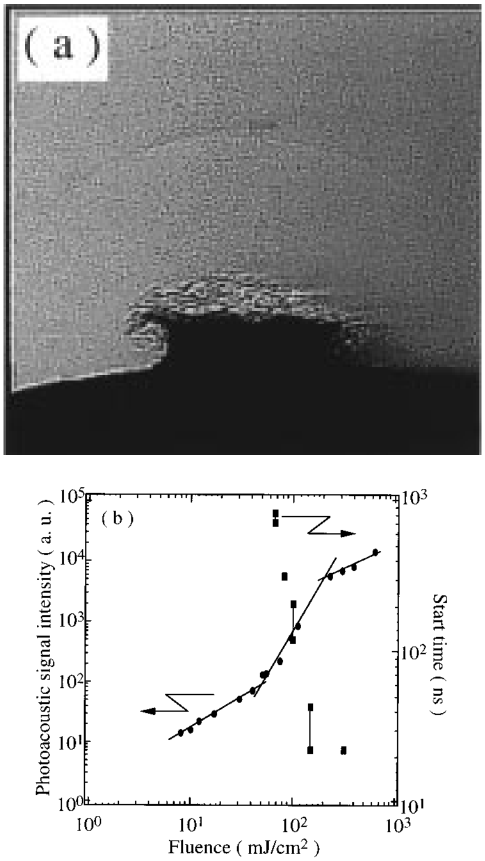

Figure 1. (a) Nanosecond ablation image of liquid ethylbenzene. The laser fluence is 150 mJ/cm^2, and the delay time is 5 μs. (b) Photoacoustic signal and ablation start time as a function of laser fluence in ethylbenzene (see text).

chloride. On the basis of this result, we have proposed photochemical ablation for the neat benzene system, where the following photofragmentation reaction plays a key role.

$$\mathrm{PhCH_2{-}X \xrightarrow{h\nu} PhCH_2 + X} \quad \mathrm{(X = H, OH, Cl)} \qquad (1)$$

In relation to this point, it should be mentioned that Srinivasan et al. have pointed out the importance of the photochemical reaction through two-photon absorption in 248-nm benzene ablation.[16]

In the previous study for the benzene-derivative systems,[15] we adopted time-resolved luminescence spectroscopy upon ablation. However, we failed in observing the benzyl radicals, which should be generated through reaction 1, around the ablation thresholds. Fluorescence of the benzyl radical was observed high above the ablation thresholds. For understanding the ablation process well, we have detected here successfully the benzyl radical at ablation thresholds by using nanosecond transient absorption spectroscopy, detailed results of which are now presented in this paper. By analyzing the absorbance of benzyl radicals, we have also succeeded in evaluating a critical value of benzyl-radical concentration to induce ablation. We believe that our spectroscopic approach is fruitful to bridge a gap between microscopic photochemical processes and macroscopic morphological changes.

Experimental Section

Benzene and toluene (Nacalai Tesque, HPLC grade of $>$99.5%) were used as received. Ethylbenzene, *n*-propylbenzene, benzyl chloride, and benzyl alcohol (Wako or Nacalai Tesque, GR grade of 99%) were distilled before use.

A KrF excimer laser (248 nm, fwhm $\approx$ 20 ns, Lambda Physik Lextra 200) was used as an excitation light source. The ablation threshold was determined by nanosecond imaging as well as by photoacoustic measurements in the same manner as in previous work.[14,15] Nanosecond transient absorption spectra above 300 nm were measured with a streak-camera system using a Xe lamp as a probe light.[8,15] The origin of the time axis was defined as the time when the excitation pulse reached its maximum. A quartz cell with an optical path length of 1 mm was filled with a neat liquid. The transient absorbance at 248 nm was also measured with two photodiodes and a digital oscilloscope as reported elsewhere.[6] In this case, sample liquids were measured as a liquid membrane (25% 2-propanol solution) with thickness of $<$10 μm. A transient-absorbance change at the excitation wavelength is often induced by intense laser-pulse excitation, which is due to depletion of the ground state, multiphoton absorption, and so on. The absorbance change should be measured for each experiment. Otherwise, correct estimation of absorbed energy, which is necessary to calculate the radical concentration, is impossible.[6] All the experiments were performed under a nitrogen atmosphere at room temperature.

Results and Discussion

Ablation Threshold. By means of the nanosecond imaging technique and photoacoustic measurements, the ablation threshold can be determined with high accuracy.[14,15] Although the thresholds of some liquids were determined in the preliminary work, here we newly measured the threshold of ethylbenzene and *n*-propylbenzene. As a representative example, a snapshot of the ablation, the fluence dependence of the ablation start time, and the photoacoustic signal intensity are shown in Figure 1 for neat ethylbenzene. In the photoacoustic signal as a function of laser fluence, we clearly observed two break-points. The fluence at the first (lower) point is regarded as the threshold, which was consistent with that estimated from the imaging study.[15] The increase of the photoacoustic signal became moderate beyond the second break-point around 200 mJ/cm^2. The time delay between the excitation pulse and the first onset of the plume ejection is named here as the start time, and it decreased with an increase of laser fluence. The ablation commenced within the excitation pulse when the fluence exceeded about 200 mJ/cm^2. Therefore, the second break-point is ascribable to the shielding effects by the ejected plume. When the ablation commences within the excitation pulse, the latter part of the pulse is scattered by the plume, leading to a decrease of the absorbed light energy and, consequently, to a decrease of the photoacoustic signal. Similar effects were confirmed also for all the other liquids examined here.

Incidentally, one of the most precise devices to determine ablation threshold is the quartz-crystal microbalance with nanogram weight resolution.[17] Application of the microbalance technique to the liquid benzene system may give lower threshold values compared to the present values and is very difficult because of rapid vaporization, which reduces the weight of sample liquids. Here, we term the apparent morphological change and the nonlinear increase seen in the Figure 1 the liquid ablation. The ablation-threshold values determined by the imaging and photoacoustic methods are summarized in Table 1. Inspection of the table reveals one characteristic feature; namely, the ablation-threshold value lies in the following order:

TABLE 1: Ablation Threshold (F_{th}), Boiling Point (bp), and Temperature Estimated at the Threshold (T_{th}) of Examined Liquid Benzene Derivatives (Ph; phenyl)[a]

	Ph−H	Ph−Cl	Ph−CH$_3$	Ph−CH$_2$OH	Ph−CH$_2$Cl	Ph−C$_2$H$_5$	Ph−C$_3$H$_7$
bp, °C	80	132	110	205	179	136	159
F_{th}, mJ cm^{-2}	100	60	35	60	30	50	40
T_{th}, °C	137	97	77	87	77	77	67

[a] By use of eq 4, absorption coefficients (α) are measured in our lab (see ref 15), and the specific heat (C) and density (ρ) are sited from the literature (i.e., *Handbook of Chemistry and Physics*; CRS Press).

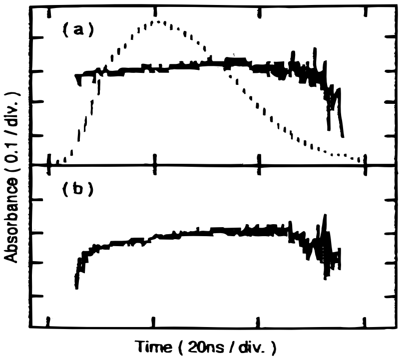

Figure 2. Transient absorbance at 248-nm excitation wavelength upon laser ablation for (a) toluene at 35 mJ/cm^2 and (b) ethylbenzene at 50 mJ/cm^2. Dotted line in (a) is a time profile of the excitation laser pulse.

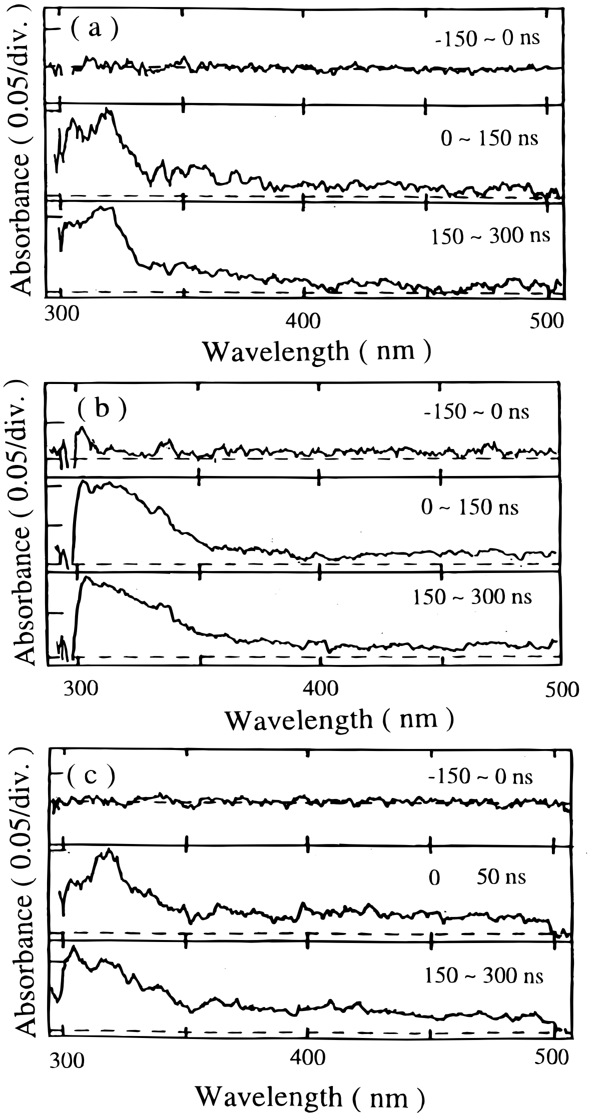

Figure 3. Nanosecond transient absorption spectra around ablation thresholds: (a) benzyl alcohol (60 mJ/cm^2); (b) benzyl chloride (30 m J/cm^2); (c) ethyl benzene (55 mJ/cm^2). Gate time is given in the figure.

$$\mathrm{PhCH_2{-}Cl < PhCH_2{-}H < PhCH_2{-}C_2H_5 < PhCH_2{-}CH_3 < Ph{-}H} \quad (2)$$

Although the photochemical reactivity of β-bond cleavage (PhCH$_2$−X) follows the order[18]

$$\mathrm{PhCH_2{-}Cl > PhCH_2{-}H > [PhCH_2{-}C_2H_5, PhCH_2{-}CH_3] > Ph{-}H} \quad (3)$$

Namely, the threshold decreases as the photochemical reactivity increases, on the basis of which we have proposed photochemical ablation. Only benzyl alcohol deviates from relations 2 and 3. This was ascribed to intermolecular hydrogen bonding, which tends to suppress ablation. Here, we have to remember that the photochemical reactivity cannot be correlated with the bond energy at the β-position while the photothermal reaction should be. The bond energy of PhCH$_2$−H (77.5 kcal/mol) is higher than that of PhCH$_2$−CH$_3$ (63 kcal/mol);[18] however, the threshold of the former is lower than that of the latter. The result clearly distinguishes the present behavior from the photothermal processes and supports the photochemical mechanism proposed.

Transient Absorbance at 248 nm within the Excitation Pulse. For ablation in liquid systems, a plausible as well as important mechanism is photothermal explosive boiling;[10] however, this is not for this case. We can numerically estimate the temperature at the irradiated surface at the ablation threshold by using the following equation[19] on the assumption that the light energy is entirely converted into thermal one (upper limit of temperature):

$$T_{th} = 20 + \frac{\alpha F_{th}}{\rho C} \quad (4)$$

where T_{th}, F_{th}, α, ρ, and C are the temperature at the threshold, threshold, absorption coefficient, density, and specific heat of the liquid, respectively. In using eq 4, we should pay attention to some changes of these parameters arising from high-power irradiation. In particular, it has been reported frequently that the absorption coefficient α could change considerably within an excitation pulse because of the absorption by densely generated transient species.[6] To examine this effect, we measured the transient absorbance of the excitation pulse around the threshold.

The transient absorbance in toluene and ethylbenzene are shown in Figure 2 as a representative example. One can clearly see that the absorbance keeps almost a constant value even during the excitation pulse. Similar behavior was confirmed also for other liquids; hence, we can use the ground-state absorbance at 248 nm to calculate the absorbed photon number upon ablation. In benzyl chloride and benzyl alcohol, slight increases (<20%) of transient absorbance were observed, which is taken into account in the following calculation and consideration. Using the effective absorbance confirmed here, we

TABLE 2: Absorption Maximum of Benzyl Radical at 318 nm ($OD_{radical}$) and Its Concentration at the Irradiated Surface Layer ($C_{radical}$) around the Ablation Threshold[a]

	$Ph-CH_3$	$Ph-CH_2OH$	$Ph-CH_2Cl$	$Ph-C_2H_5$	$Ph-C_3H_5$
st, dyn cm^{-1}	28.5	39.9	37.5	29.0	28.2
F, mJ cm^{-2}	40	60	30	55	40
$OD_{radical}$	0.1	0.16	0.17	0.14	0.14
$C_{radical}$, M	0.044	0.055	0.068	0.048	0.046

[a] Surface tension of liquids (st) and laser fluence (F) at which $OD_{radical}$ is measured are also listed. Ph = phenyl.

evaluated the temperature at the surface layer upon laser exposure by using eq 4. The evaluated values of T_{th} are also collected in Table 1. The estimated temperature rise was lower than the boiling point by a few tens of a degree; hence, we consider the photothermal effects should be minor. The explosive boiling hardly takes place in the present systems at the threshold.

Nanosecond Time-Resolved Absorption Spectroscopy upon Ablation. To prove the photochemical mechanism directly, the observation of benzyl radical, as expected from reaction 1, is indispensable especially at the ablation threshold. In Figure 3 are shown the transient absorption spectra of benzyl alcohol, benzyl chloride, and ethylbenzene around the ablation threshold. Although the S/N value is not good because of the single-shot measurement of a thin liquid layer, a band with a maximum around 305−320 nm was observed. This is obviously assigned to the benzyl-radical absorption spectrum in accordance with the literature value.[18,20,21] As stated already, the temperature at the thresholds did not reach the boiling point; hence, the bond rupture should be ascribed not to the thermal degradation but to photochemical fragmentation. As seen in the spectra, the first manifestation of benzyl radicals lie in the time region of 0−150 ns (gate time of streak camera). According to the results of nanosecond imaging,[14,15] ablation (plume ejection, see Figure 1) at the threshold commenced at several hundred nanoseconds after the excitation pulse. Moreover, absorbance due to the radicals does not decrease with the time evolution. Continuum bands seen at the late stages are ascribable to the scattering of probe light by microbubbles in the liquids. These results mean that the benzyl and other radicals (H, CH_3, Cl, etc.) are densely generated and did not decay through geminate recombination prior to ablation.

It is noteworthy here that the excited singlet and triplet states of benzene derivatives have broad tail-like absorption bands whose extinction coefficients are much less than 2000 M^{-1} cm^{-1} in the observed spectral region of 300−500 nm.[22,23] Owing to the relatively low extinction coefficient and to the spectral shape, it is rather difficult to confirm the S_1 and T_1 states of the liquid molecules unless they are produced sufficiently and comparably to the radical. We can readily estimate the number of photons absorbed per chromophore at a given fluence from the result of the analysis of the transmittance at 248 nm. For the present threshold of a few tens of millijoules per squared centimeter, only a few percent of the molecules is excited in the irradiated unit (number of absorbed photon per molecule is less than 0.1). Consequently, the bleaching of the ground-state chromophores hardly takes place. Therefore, the effects arising from the absorption by the other transient species should be neglected. For doped polymer ablation, we have revealed the importance of cyclic multiphotonic absorption as stated already. This is, however, not for the present case apparently. A key essence in the cyclic multiphotonic absorption mechanism is that a large number of chromophores (dopants) are excited to their transient states (i.e., S_1 and T_1) with the ground states appreciably bleached. This result clearly distinguishes the present ablation from the doped polymer ablation in which each dopant can absorb more than 10 photons.[6]

The present result that only the benzyl radical was observed clearly under ablation conditions indicates that the ablation is triggered by the dense photochemical generation of the radicals. We observed the absorption spectrum of the benzyl radical for a series of examined liquids at their thresholds. It should be pointed out that no absorption spectral measurement of radical formation leading to ablation has been reported until now regardless of the kinds of materials or lasers. In the case of benzene and chlorobenzene, generation of phenyl radicals would be expected as a result of photofragmentation. The phenyl radical, however, has a main absorption band around ∼250 nm[24] where the ground-state molecules can absorb the probe light efficiently; hence, it is impossible to measure the spectrum.

Photochemical Ablation Mechanism. Viewing the above experimental results, we consider that the benzyl radical plays a key role in the photochemical ablation. From the absorption spectra, we can evaluate the radical concentration near the irradiated surface readily at a given fluence by using Lambert−Beer's law, since the chromophore saturation and other nonlinear absorption hardly take place. The concentration of benzyl radical at the irradiated surface ($C_{radical}$) is expressed as follows:

$$C_{radical} = 2.303(\epsilon_{liquid}C_{liquid}/\epsilon_{radical})OD_{radical} \tag{5}$$

where ϵ_{liquid} and C_{liquid} are the molar absorption coefficient (M^{-1} cm^{-1}) at 248 nm and concentration of neat liquid (∼10 M), respectively. $\epsilon_{radical}$ is the molar absorption coefficient of the benzyl radical at 318 nm, which is 5500 cm^{-1} M^{-1}.[20] $OD_{radical}$ is the maximum of transient absorbance at 318 nm obtained by transient absorption spectroscopy.

$OD_{radical}$ and $C_{radical}$ values near the ablation threshold are listed in Table 2 together with the surface tension of the liquids. It is worth noting that the values of $C_{radical}$ are close to each other, although the threshold value and the molecular photochemical reactivity vary from system to system. It is considered that the common value of $C_{radical}$ (averaged, ∼0.052 M) is necessary for laser ablation. Namely, these liquids undergo macroscopic morphological changes when the quantity of radicals in a unit volume reaches a common critical point (0.05 M). In more detail, the $C_{radical}$ is classified into two groups: 0.046 ± 0.002 M for alkyl derivatives of benzene and 0.055−0.068 M for benzyl compounds. The difference of radical concentration may be due to macroscopic properties of liquids. One candidate property is the surface tension of liquids, since the increase of surface area is necessary for the macroscopic morphological changes. As seen in the table, the slightly higher $C_{radical}$ for benzyl compounds may be related to their higher values of surface tension (∼37 dyn/cm) compared with those of alkyl derivatives of benzene compounds (∼29 dyn/cm). This supports the idea that photochemical formation of radical initiates laser-ablation dynamics.

Here, we briefly discuss the mechanism by which the liquids undergo laser ablation. When an efficient β-bond scission takes place as described above, in addition to the benzyl radical, a vast number of small radicals, H, Cl, CH_3, etc., with low vapor pressure should be generated instantaneously in a confined volume. Since the benzyl radical absorption band did not decay significantly prior to the ablation, the effect of geminate recombination processes should be negligible. Therefore, the total concentration of these small radicals is estimated to be ~0.05 M. Since these small molecules are gaseous, about 1.2 L of gas will appear instantaneously within a unit volume of 1 L upon laser irradiation. Since the liquids were saturated with nitrogen gas prior to the experiment, we consider the 1.2 L value is large enough to induce the volume explosion leading to ablation. Indeed, the volume-explosion model has been regarded as one candidate for the ablation mechanism.[13]

Note that the above mechanistic argument holds only for the ablation around the threshold. As the laser fluence increases greatly above the threshold, various nonlinear effects such as multiphoton absorption are involved in ablation. Indeed, it has been reported that alkylbenzene in the gas-phase decomposes by UV multiphoton excitation.[25] In addition, Srinivasan et al. has revealed peculiar chemical reactions by two-photon absorption in the case of 248-nm ablation of liquid benzene above ~300 mJ/cm^2 of laser fluence. Presumably, the multiphoton processes as well as photothermal effects are not negligible when the fluence exceeds the ablation thresholds. The abrupt nonlinear increases of the photoacoustic signal above the thresholds may reflect such multiphoton absorption.

Summary

In this study, we investigated the 248-nm excimer-laser ablation of liquid benzene derivatives mainly by means of nanosecond transient absorption spectroscopy. The ablation threshold value can be correlated not with the boiling point of the liquid but with the photochemical reactivity of the β bond. The temperature at the irradiated surface evaluated using the effective absorption coefficient obtained by the transient absorbance measurement did not reach the boiling point. Hence, the photothermal mechanism (explosive boiling) is rejected for the present systems. In addition, the cyclic multiphotonic absorption hardly took place. The nanosecond absorption spectroscopy confirmed that the main transient species involved in ablation was the benzyl radical, which was expected to be generated through the β-bond scission. Moreover, we have succeeded in the direct evaluation of the transient-radical concentration upon ablation, information of which has never been reported in past studies.

Thus, the photochemical ablation mechanism is verified for the ablation of liquid benzene derivatives. The present photochemical ablation falls in a new category and is distinguishable from other liquids ablation induced by explosive boiling or intense photoacoustic wave.[26] Relevant to the present study, we have reported recently the mechanistic switching for solutions of benzene derivatives.[27] In this case, as the concentration of benzene derivatives decreases, the benzyl radicals work as an energy converter to heat through cyclic multiphotonic absorption. Thus, the benzyl radicals play a quite important role in the ablation phenomena of benzene derivative systems.

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