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Formation of 1,3-hexadiene-5-yne by two-photon chemistry of benzene via hot molecule

Yasuko Honjo, Takamasa Kinoshita, Tomoyuki Yatsuhashi, Nobuaki Nakashima*

Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585, Japan

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Abstract

The two-photon chemistry of gaseous benzene was studied by laser flash photolysis using an ArF laser (193 nm) pumping to the S_2 state. The major product was assigned to 1,3-hexadiene-5-yne, and one of the minor products was the phenyl radical. The formation mechanism is suggested to be as follows: hot benzene (S_0^{**}) is formed by internal conversion from the S_2 state, and hot benzene with two-photon energy (S_0^{***}) is formed from an excited state of S_0^{**}. S_0^{***} is produced by a two-photon process, and its internal energy reaches 1243 kJ/mol. 1,3-Hexadiene-5-yne can form at rates much faster than the collision frequency ($\sim 10^{10}\,s^{-1}$) under benzene 0.53 kPa in the presence of 51 kPa of propane. Collisional cooling is expected to quench the slow processes from S_0^{**} as well as the decomposition of 1,3-hexadiene-5-yne. 1,3-Hexadiene-5-yne and the phenyl radical can be the primary products of the two-photon fragments, which have been found by a multimass ion imaging technique.

Keywords: Two-photon chemistry; Benzene; Laser flash photolysis; ArF laser; 1,3-Hexadiene-5-yne; Phenyl radical; Hot molecule

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1. Introduction

Vacuum ultraviolet photochemistry, in which molecules are excited to high electronic states but at energy levels below the ionization potential, is an interesting subject. If molecules are pumped to a highly electronically excited state in the gas phase, internal conversion is efficient and finally leads to a highly excited vibrational state in the electronically ground state. Rapid intramolecular vibrational redistribution takes place in the ground state, forming "hot" molecules called S_0^{**}. The equivalent temperature of S_0^{**} is quite high; for example, 3400 K at the 193 nm excitation of benzene. Therefore, chemical reactions are easily induced. Laser chemistry via S_0^{**} for many molecules has been studied, and the related reviews are available [1,2]. S_0^{**} photochemistry is also of interest. The second photon in a nanosecond laser pulse can excite S_0^{**}, in which case S_0^{**} is immediately converted to a hot molecule with two-photon energy; that molecule is denoted here as S_0^{***}. The S_0^{***} of benzene produced by a 193 nm laser pulse has the equivalent temperature of 5900 K. Recently, two-photon excitation products of d_6-benzene were found by the newly developed multimass ion imaging techniques [3]. The major channel for the reaction of S_0^{***} is the elimination of two D atoms, that is C_6D_4 formation. Two ring-opening dissociation channels, $CD_3 + C_5D_3$ and $C_2D_3 + C_4D_3$, have been found.

In 1988, the first examples of reactions from S_0^{***} were reported in the dissociation of toluene and alkylbenzenes to benzyl radical [4], and in azulene isomerization to naphthalene [5]. The two-photon laser chemistry via S_0^{***} is commonly observed in alkylbenzenes [4], azulene [5,6], cycloheptatrienes [7], naphthalene [8], cyclophanes [9], diazabenzenes [10], coumarine [11], biphenylene [12], and so on. Three or more photons can be absorbed and form hot molecules with multi-photon energy. The hot C_{60} with multi-photon energy dissociates to C_{60-2n} ($n = 1$–14) [13], and triphenylmethane with three-photon energy dissociates to the triphenyl radical [14,15].

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* Corresponding author. Tel.: +81 6 6605 2552; fax: +81 6 6605 2552.
E-mail address: nakashim@sci.osaka-cu.ac.jp (N. Nakashima).

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The one-photon chemistry of benzene S_n ($n = 2, 3$) is already established. In the 1960s, photoproducts by the Hg resonance line excitation at 184.9 nm were reported to be fulvene and 1,3-hexadiene-5-yne. The intermediate of the products was suggested to be S_0^{**} [16,17]. In 1983, S_0^{**} was detected in the transient absorption spectra by laser photolysis at 193 nm [18]. The disappearance rate constant of the S_2 state was measured in 1995 with 170 fs pulses at 200 nm as $2.5 \times 10^{13}\,s^{-1}$, strongly supporting the efficient formation of S_0^{**} [19]. Using an F_2 laser (158 nm), a rate constant of $2.3 \times 10^{7}\,s^{-1}$ from benzene to the phenyl radical was derived [20], and an ArF laser was used to measure this rate constant as $1.0 \times 10^{5}\,s^{-1}$ [21]. These observed values are in agreement with the statistical reaction rate constant at each internal energy. The kinetic energies of the H atom elimination were measured and clearly indicated that the reaction occurs from hot benzene, S_0^{**} at both of F_2 and ArF laser energies [22]. The two-photon chemistry of d_6-benzene forms the fragments of C_6D_4, $CD_3 + C_5D_3$, and $C_2D_3 + C_4D_3$ in a beam under collision-free conditions [3].

In this paper, two-photon chemistry is studied in the presence of a foreign gas at several tens of kPa. The primary products from S_0^{***} and/or intermediates for the fragments can be obtained. The reaction rate constants at the energy of the two photons of the ArF laser wavelength are expected to be so high that the products would form before the quenching reactions by the collisional relaxation and would then be stabilized by collisional cooling before subsequent reactions. The slow processes from S_0^{**} are completely quenched because the reaction rate constant to the phenyl radical is much slower than the rate of collisional relaxation. The hot molecule itself has a high internal energy, but the buffer gas is cold. This characteristic enables us to observe thermally unstable primary products via hot molecules such as 1,3-hexadiene-5-yne and the phenyl radical. These products can be intermediates of the two-photon fragments.

2. Experimental

2.1. Time-resolved absorption spectra

A conventional method of nanosecond laser photolysis was applied to gaseous benzene in a quartz cell irradiated by an ArF excimer laser (Lambda Physik COMPex102, 193.3 nm, fwhm 14 ns, maximum energy 200 mJ/pulse). The method was primarily the same as that previously described [23,24]. The size of the laser irradiation was typically a 0.5 cm × 3 cm area. The laser fluence was controlled by NaCl solution filter, while the fluence was measured by Genetec ED 200 and ED 500 power meters. Transient species were monitored by an EG&G FX425 Xe flash lamp and monochromators connected to Hamamatsu Photonics R758 photomultiplier tubes. The transmitted light through two slits with 1 mm wide was separated by a thin-beam splitter made of quartz and focused into a monochromator (Jovin-Yvon HR320, $\Delta\lambda = 1.3$ nm); the reflected light was focused into another monochromator (Jovin-Yvon UV10, $\Delta\lambda = 2.5$ nm). The signal at 230 nm through the latter monochromator was used for normalization of signals through the former monochromator, where the monitoring wavelengths were changed step by step. The sample had to be renewed for each shot under high laser intensity experiments, because benzene was very reactive. In order to average data of individual several shots, the normalization procedure was effective to compensate the ±10% signal fluctuation. Data were collected with a Tektronix TDS 620 oscilloscope.

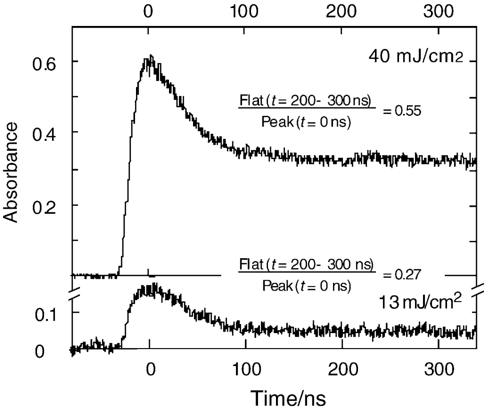

Fig. 1. Time profiles of transient signals observed at 230 nm at a high laser fluence of 40 mJ/cm² (a) and a low fluence of 4 mJ/cm² (b), for 0.53 kPa of benzene in the presence of 0.1 MPa of nitrogen. The initial decay component is due to the collisional relaxation of hot benzene S_0^{**} by the addition of another gas, in this case nitrogen. The remaining component with a constant absorbance after 100 ns is ascribed to photoproducts. The ratio of the absorbance at $t = 300$ ns/$t = 0$ ns is 0.27 at 13 mJ/cm² and increases to 0.55 at 40 mJ/cm².

The typical time profiles are shown in Fig. 1. Time $t = 0$ ns was defined at the peak absorbance as indicated in the figures. The time did not mean the end of the laser pulse. For the case of 0.1 MPa of nitrogen, 90% of the laser energy has reached the sample cell and the 10% tail follows after the 0 ns. Therefore, the data were corrected by multiplying the nitrogen raw data $t = 0$ ns by a factor of 1.1 (Fig. 2). The normalization factor was 1.4 at $t = 0$ ns in Fig. 3. Data for the power-dependence experiments were taken only with the first shot because the photoproducts were highly photoreactive; the second shot caused a very different time profile.

A sample was prepared by filling gaseous benzene through a vacuum line and adding nitrogen or propane gases into the sample cell. The cell was left for a couple of hours in order to complete mixturing before laser irradiation. The sample cell after irradiation was cleaned in the furnace at 770 K for several hours. Benzene and nitrosobenzene were purchased from Aldrich Chem. Co. with stated purities of 99.9 and 97%, respectively. Nitrogen and propane gases were purchased from Osaka Sanso with stated purities of N_2 99.999% and C_3H_8 99.9%. Nitrogen monoxide was obtained from Takachiho Sangyo with a stated purity of 99.9%.

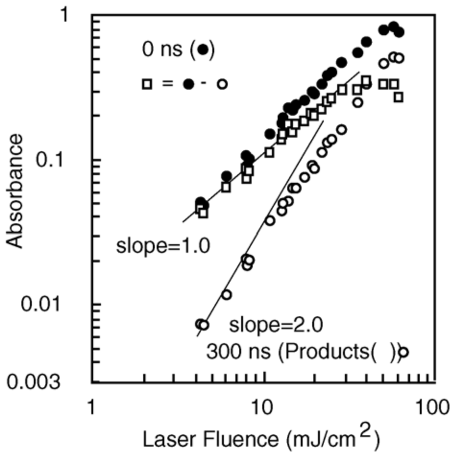

Fig. 2. The correlation between laser fluence and transient absorption of benzene at 0 (●) and 300 ns (○) for 0.53 kPa of benzene in the presence of 0.1 MPa of nitrogen observed at 230 nm. The symbols of square (□) indicate the difference between ● and ○. The lines with slopes of 1.0 and 2.0 indicate that the species □ are produced by a one-photon process and that the products (○) are formed by a two-photon process.

2.2. *1,3-Hexadiene-5-yne and nitrosobenzene*

1,3-Hexadiene-5-yne was synthesized in the manner previously described [25,26]. NMR data on Bruker Avance 600 showed a mixture of *cis* and *trans* 1,3-hexadiene-5-yne, pentane, and 1,5-hexadiyne. The ratio of *cis* to *trans* was 5:8 and that of 1,3-hexadiene-5-yne to pentane to 1,5-hexadiyne was estimated to be 16:1.7:1 on the basis of the proton intensity ratio. 1,3-Hexadiene-5-yne has the specific NMR coupling constant, which originates from the end of the triple bond. The coupling constants of *cis* and *trans* 1,3-hexadiene-5-yne were 2.37 Hz at 3.03 and 3.23 ppm, respectively. The chemical shifts originating from conjugated bonds were recognized in the spectral regions of 5.3–5.6 and 6.3–6.9 ppm. The UV of the mixture were measured on a spectrophotometer (Shimadzu UV-2550). The molar extinction coefficient of 1,3-hexadiene-5-yne was $2.6 \times 10^4\ M^{-1}\ cm^{-1}$ at 239 nm. The absorption spectra of 1,5-hexadiyne and pentane showed a negligible contribution to the spectrum of 1,3-hexadiene-5-yne (less than $0.03 \times 10^4\ cm^{-1}$ in the 200 nm region). The molar extinction (see Section 3.3) has been corrected to account for the pressures of the other two mixtures.

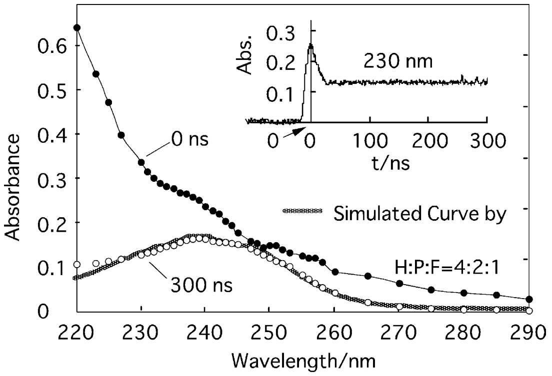

Fig. 3. Transient absorption spectra at 0 (●) and 300 ns (○) for 0.53 kPa of benzene in the presence of 51 kPa of propane are observed by irradiation with an ArF laser at 10 mJ/cm^2. The thick mesh line on the 300 ns data (○) was constructed with the absorption spectra of 1,3-hexadiene-5-yne (H), the phenyl radical (P), and fulvene (F) at a concentration ratio of 4:2:1. The definition of 0 ns is indicated in the inserted data.

Photoproducts of benzene were accumulated by irradiating the ArF excimer laser at 10 Hz at 30 mJ/cm^2 for 3 h while the benzene flowed continuously. The products were transferred under vacuum and then measured immediately with the NMR spectrometer. The nitrosobenzene absorption spectrum in the gas phase was re-measured, and the molar extinction coefficient was confirmed to be $1.0 \times 10^4\ M^{-1}\ cm^{-1}$ at the peak of 271 nm.

3. Results

3.1. *Higher laser fluence gives a higher yield of products*

Fig. 1 shows typical time profiles of transient signals observed at 230 nm at high and low laser fluences. Obviously there are two components; one of them shows fast (100 ns) decay, and the other has longer-lasting absorbance. In a previous study, the fast-decay component has been assigned to the collisional cooling process of S_0^{**} in the presence of 0.1 MPa of nitrogen [18]. The decay time becomes shorter in the presence of higher nitrogen pressure and in the presence of efficient energy-transfer molecules, like propane compared with nitrogen. After the initial decay, the flat component lasts more than a few microseconds. This was assigned to photoproducts in the laser fluence range below 10 mJ/cm^2 [18,27]. The formation efficiency of the photoproducts is higher at a higher laser fluence. This finding is manifested by comparing the ratio of absorbance between the flat part (photoproducts) and the peak (S_0^{**}). The ratio 0.27 at 13 mJ/cm^2 increases to 0.55 at 40 mJ/cm^2.

The correlations between laser fluence and transient absorption of benzene indicate that the photoproducts are produced by a two-photon process as shown in Fig. 2, because the slope of the photoproducts at 300 ns (○) is close to 2.0.

The absorbance (abs.) differences were plotted as square symbols (□) in Fig. 2 based on the following equation:

$$\text{Difference abs.}\ (\square)$$

$$= \text{abs.}\ (t = 0, \bullet) - \text{abs. photoproducts}\ (t = 300\ \text{ns}, \bigcirc).$$

The species at 0 ns are composed of the component S^{**} and photoproducts ($t = 0$), when the reactions are very fast. In order to extract the component S^{**} from $t = 0$ ns abs. data, the abs. differences were obtained by subtracting the photoproducts under the assumption of abs. photoproducts ($t = 0$, ●) ≈ abs. photoproducts ($t = 300$ ns, ○). Since the photoproducts just after formation would have large internal energy, the spectra of photoproducts $t = 0$ ns would be broad compared with those at 300 ns, where they are in a collisionaly relaxed state; nevertheless, the above assumption is expected to be fairly good at 230 nm. At a high temperature, an absorption spectrum changes broad; the peak absorption is suppressed and the absorption at valley is higher. The absorption spectrum of the products is broad as shown in Fig. 3 and the observed point at 230 nm is located in the middle between the peak and valley. Therefore, the absorption coefficient at 230 nm is not expected to be changed largely by the internal energy of the products, in other words, the above assumption is acceptable. The difference abs. denoted by □ in Fig. 2 can be regarded as that of hot benzene S_0^{**}, because the reactions to the product are very fast as discussed below.

The hot benzene (S_0^{**}, □) has a slope close to 1.0, whereas a deviation from the ideal slope of 1.0 for S_0^{**} is seen in a intensity region higher than 20 mJ/cm^2. The photoproducts show a slope smaller than 2.0 in a higher-intensity region. The photoproducts could be photo-decomposed because the probable product 1,3-hexadiene-5-yne has a high molar extinction coefficient of several thousands in a unit of $M^{-1}\,cm^{-1}$ at 193 nm (see Section 3.3). As a conclusion, S_0^{**} is produced by a one-photon process and that the products are formed by a two-photon process.

Transient absorption spectra at 0 ns (●) and 300 ns (○) in the presence of 51 kPa of propane were obtained by irradiation with an ArF laser at 10 mJ/cm^2 as shown in Fig. 3. The short-lived component (S_0^{**}) showed a decay faster than that for nitrogen, because propane has a 18 times greater efficient deactivation ability than nitrogen [18]. As a result, the short-lived component (S_0^{**}) would have a lifetime of several nanoseconds, and the shape becomes similar to the excitation laser pulse.

This spectrum has a small hump around 239 nm and other structures around 247 and 259 nm. These are explained in terms of spectral overlap and depletion on the monotonous spectrum of S_0^{**}. The hump would be due to a photoproduct (239 nm), while the structures result from the benzene absorption in the ground state (247 and 259 nm). The depletions have been interpreted in terms of bulk heating effects [18,24,27].

3.2. Identification of three products

The formation of 1,3-hexadiene-5-yne was confirmed in the NMR spectra of photolysed mixtures; the peaks were the same as those of synthesized 1,3-hexadiene-5-yne. The reaction mixture had the same coupling constant ($J = 2.4$) as that of synthesized 1,3-hexadiene-5-yne at 3.2 ppm. This observation indicates a proton peak at the end of the triple bond. The chemical shifts originating from conjugated bonds were also recognized in the spectral regions of 5.3–5.6 and 6.3–6.9 ppm. The irradiation laser energy was 30 mJ/cm^2, where the relation between the products and the laser fluence deviated from the slope of two as seen in Fig. 2. Photoproducts could be partly photolysed by the laser light at this laser fluence; however, the major product was considered to survive to a great extent.

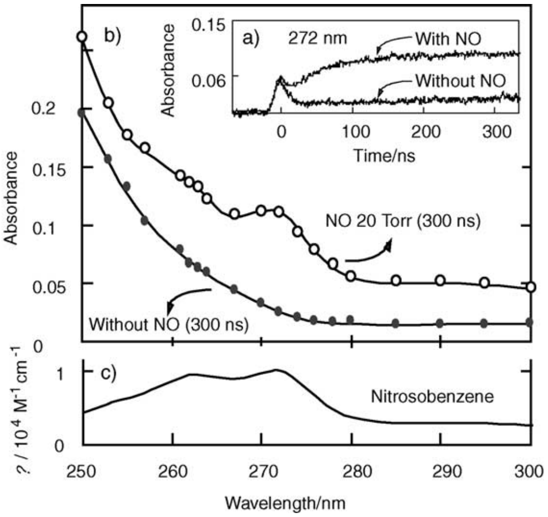

Fig. 4. Trap of photoproducts by nitrogen monoxide. (a) The time profiles of transient absorption in the cases of including and excluding 27 kPa of NO at 272 nm in the presence of 51 kPa of propane at a laser fluence of 15 mJ/cm^2. The formation process of the phenyl radical is considered to be completed within the laser pulse. The slowly rising process in transient absorption by the addition of NO is indicated as the formation process of nitrosobenzene. (b) The products' spectra observed at 300 ns in the presence (○) of 27 kPa of NO and in the absence (●) of NO at a laser fluence of 15 mJ/cm in the presence of 51 kPa of propane at a laser fluence of 15 mJ/cm^2. The shoulder around 272 nm is assignable to nitrosobenzene. (c) Absorption spectrum of nitrosobenzene as a reference [29].

As one of the current authors previously demonstrated, the phenyl radical can be trapped by NO by measuring the absorption spectrum in the UV region [28], as follows.

NO gas does not have absorption at 193.3 nm, and the product nitrosobenzene has absorption with the molar extinction coefficient of $1.0 \times 10^4\,M^{-1}\,cm^{-1}$ at a broad peak around 271 nm [29]. Mixtures of 0.53 kPa of benzene, 27 kPa of NO, and 51 kPa of propane were irradiated at a laser fluence of 15 mJ/cm^2. Fig. 4 inset shows the time profiles of transient absorptions for cases including or excluding NO at 272 nm. The rise time of sub-100 ns was observed with NO similar to that observed for the phenyl radical and NO reaction [28]. In fact, a rising time of 73 ns at 2.67 kPa of NO is expected for the phenyl radical and NO reaction, based on the reaction rate constant of $2.09 \times 10^{-1}\,cm^3\,molecule^{-1}\,s^{-1}$ [30]. The phenyl radical would be formed by two-photon absorption because the one-photon process is slow and quenched completely by the foreign gas, propane. The formation should be completed in the laser pulse; therefore, the rise of transient absorption after the excitation pulse is attributed to the formation of nitrosobenzene. Fig. 4 shows the transient absorption spectra at 300 ns in the NO trap for samples that included (○) or excluded (●) NO gas. A shoulder was observed at 261 nm and a broad peak at 271 nm. These features are attributed to nitrosobenzene by comparing them to the lower spectrum of nitrosobenzene. It should be noted that the absorbance versus

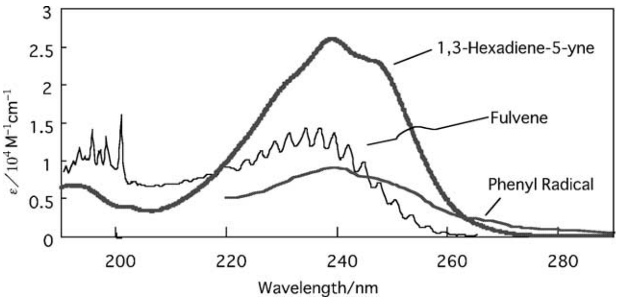

Fig. 5. The absorption spectra of 1,3-hexadiene-5-yne, the phenyl radical [30], and fulvene [31]. The vertical axis shows the molar extinction coefficient.

laser power at 261 nm showed a slope of 2.0, suggesting that nitrosobenzene and its precursor, the phenyl radical, were produced by a two-photon process.

The absorption spectrum of fulvene shows featured peaks in the UV region, and these peaks can be easily detected. In fact, the corresponding peaks were seen in the UV spectrum after a sample was photolysed. The fulvene intensity was low, and the present study did not clarify the laser fluence dependence.

3.3. Reconstruction of the transient absorption spectrum

Three species—1,3-hexadiene-5-yne, phenyl radical, and fulvene—were identified. Although other products may have been formed, we tried to reconstruct the photoproduct spectrum in Fig. 3 at 300 ns using the three reference spectra. Fig. 5 shows the absorption spectra of 1,3-hexadiene-5-yne, the phenyl radical [30], and fulvene in the gas phase [31]. 1,3-Hexadiene-5-yne has a broad peak around 240 nm and a shoulder around 250 nm. The molar extinction coefficient of the peak is measured at $2.6 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$, which is close to that in isooctane solution $\varepsilon = 2.55 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 250 nm [26]. The 10 nm blue shift is often seen when a molecule is placed into a solvent.

The thick mesh line on the 300 ns data (○) in Fig. 3 was composed of the absorption spectra of 1,3-hexadiene-5-yne (H), the phenyl radical (P), and fulvene (F) with a concentration ratio of 4:2:1. It should be noted that the major part of the thick mesh line can be simulated without the spectrum of fulvene. We included fulvene because it was detected in the stationary-state spectrum of the photoproducts.

The apparent formation yield of a product was defined as the ratio of the concentration of 1,3-hexadiene-5-yne to the absorbed photon number, assuming that one-photon absorption would take place. The yield of 1,3-hexadiene-5-yne was estimated to be 0.05, where the $t = 0$ ns spectrum was assumed to represent the number of photons absorbed. The molar extinction coefficient of hot benzene (S_0^{**}) has been determined to be $3500\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 230 nm [18]. The yield was calculated using the coefficient of 1,3-hexadiene-5-yne of $2.6 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 239 nm and those of the two other minor products in Fig. 5. The value of 0.05 at 10 m/Jcm^2 is smaller than the yield (0.24) of the benzyl radical formation from toluene with the same two-photon mechanism at a fluence of 11.5 mJ cm^2 [4]. The reason is presumably due to the benzene's smaller molar extinction coefficient of the intermediate (S_0^{**}). The coefficient of hot benzene (S_0^{**}) at the ArF laser wavelength is $8300\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ [18], lower than the $20000\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ for hot toluene [4].

4. Discussion

4.1. Two-photon products

Photofragments by two-photon excitation have been detected under jet-cooled d_6-benzene by the multimass ion imaging technique at 193 nm [3]. In that study, the authors observed the elimination of two D atoms and the formation of C_6D_4, and two ring-opening channels, $C_6D_6 \rightarrow CD_3 + C_5D_3$ and $C_6D_6 \rightarrow C_2D_3 + C_4D_3$. Based on their observations of the small kinetic energy release in the ring-opening dissociation channels and in the elimination channel of the two D atoms, those authors suggested that internal conversion also occurred after the second photon absorption by S_0^{**} and that the dissociations occur in the electronically ground state through the hot molecule S_0^{***}. The reactions at 193 nm are listed below. They include one-photon reactions at 184.9, 193, and 158 nm, which are isomerization, and hydrogen-atomic and molecular-dissociation reactions.

$C_6H_6\ (S_0^{**}) \rightarrow C_6H_6$ (isomers)	(1)	[16,17]
$C_6H_6\ (S_0^{**}) \rightarrow C_6H_5 + H$	(2)	[20,21]
$C_6H_6\ (S_0^{**}) \rightarrow C_6H_4 + H_2$	(3)	[21]
$C_6H_6\ (S_0^{***}) \rightarrow C_6H_4 + 2H$	(4)	[3]
$C_6H_6\ (S_0^{***}) \rightarrow CH_3 + C_5H_3$	(5)	[3]
$C_6H_6\ (S_0^{***}) \rightarrow C_2H_3 + C_4H_3$	(6)	[3]
$C_6H_6\ (S_0^{***}) \rightarrow C_6H_6$ (isomers)	(7)	This Work
$C_6H_6\ (S_0^{***}) \rightarrow C_6H_5 + H$	(8)	This Work

The present experiment was performed in the presence of a foreign gas, propane (51 kPa), in which the collisional relaxation takes place with a collision frequency of $8. \times 10^9\ \mathrm{s}^{-1}$. According to our analysis [18], propane takes away energy of about 14 kJ/mol by the collision at an internal energy of 624 kJ/mol. The collisional cooling can easily quench slow-rate-reaction channels; in other words, the cooling mechanism can trap thermally unstable products. The reaction rate constants from S_0^{***} can be evaluated on the basis of the RRKM theory. For the case of the phenyl radical formation, the transition state of the vibrational frequency of the phenyl radical was assumed to be 84% of those in the ground state of benzene. The C–H dissociation energy of 464.3 kJ/mol was used, though the somewhat higher value was also reported (475 kJ/mol) [32,33]. The calculated results fit the two observed values of $1 \times 10^5\ \mathrm{s}^{-1}$ at 193 nm [3] and $2.3 \times 10^7\ \mathrm{s}^{-1}$ at 158 nm [20]. The rate constant at 1243 kJ/mol (2 × 193 nm + energy at room temperature) was predicted to be $3.4 \times 10^{11}\,s^{-1}$. Some unimolecular reaction pathways from benzene to 1,3-hexadiene-5-yne have been suggested [34]. The transition state is predicted to have 463.2 kJ/mol, which is reached after the hydrogen atoms are rearranged before the carbon bond dissociates [34]. The extension to an internal energy of 1243 kJ/mol predicts the RRKM rate constant to 1,3-hexadiene-5-yne to be $2.1 \times 10^{11}\,s^{-1}$. The rate constants in reactions (7) and (8) are far above the collisional rate constant of $8.0 \times 10^{9}\,s^{-1}$.

Slow processes would be completely quenched. Isomerization by the one-photon process of reaction (1) and the hydrogen-dissociation of reaction (2) are quenched in the presence of 51 kPa of a foreign gas. The molecular hydrogen elimination process, reaction (3), would be quenched, because a slow reaction rate is predicted based on the height of the transition state; this height is predicted to be 26 kJ/mol higher than the transition state of $C_6H_5 + H$ [34].

1,3-Hexadiene-5-yne can be a good intermediate for the ring-opening reaction of reactions (5) and (6), and the phenyl radical could be a candidate for the precursor to reaction (4) for the elimination of two hydrogen atoms. The phenyl radical has an energy of 771 kJ/mol at most for the two-photon chemistry. 1,3-Hexadiene-5-yne has the heat of energy of 270 (*cis*)/253 kJ/mol (*trans*) from the benzene ground state; [35] its internal energy just after isomerization would be 973 (*cis*)/990 kJ/mol (*trans*). The dissociation rate constants from the phenyl radical and 1,3-hexadiene-5-yne to the fragments in (4)–(6) would be slower than the present collisional cooling, and the three two-photon-channels (4)–(6) could be quenched under the present collision conditions with the rate of $8.0 \times 10^{9}\,s^{-1}$.

4.2. Comments on fragments and benzene cation

It should be noted that the present flash photolysis did not extract a conclusion whether fragment species from reactions (3)–(6) were included in the transient spectra. The absorption spectra of C_6H_4, C_2H_3, CH_3 and so forth have been reported; the benzene spectrum appears in the spectral range between 233 and 263 nm [36], and C_2H_3 has a monotonous spectrum shorter than 237 nm [37]. A deviation from the absorption simulation based on the spectra of 1,3-hexadiene-5-yne, phenyl radical, and fulvene can been seen in the wavelength region shorter than 225 nm in Fig. 3. This could be an indication of the absorptions of those species by reactions (3)–(6).

Benzene and its fragment ions have been detected in the mass spectra by multi-photon excitation of a 193 nm nanosecond laser [38–40]. Benzene cation is expected to be a dominant ionic species by extrapolating the data in Ref. [38]. The ionization efficiency of the benzene ion can be read as 0.5×10^{-5} at 15 mJ/cm^2 from the estimation in Ref. [40] The cation would be transformed to benzene dimer cation by association with the unexcited state benzene and the dimer cation has a strong absorption in the visible–near-infrared region. The authors did not detect the corresponding absorptions of benzene and/or benzene dimer cation. The benzene cation absorption should appear around 500 nm with the large molar extinction coefficient of 5700 M^{-1} cm^{-1} [41]. The formation efficiencies of the benzene and its dimer cation were too low to be detected by the present apparatus, i.e. the efficiency was less than 0.005.

4.3. Comments on the previous flash photolysis experiments

One of the authors (N.N.) attempted to observe the phenyl radical by NO trap experiments, but no peak of nitrosobenzene was observed. In the early experiment [18], no rise was observed due to nitrosobenzene formation. The most probable reason is that the laser fluence at that time was 6 mJ/cm^2, which has simply not enough power to induce two-photon reactions, unlike the 15 mJ/cm^2 used in the present study.

The photoproduct spectra had been obtained in the presence of 33.3 kPa of nitrogen by irradiating 0.53 kPa of benzene with 6–9 mJ/cm^2 at 193 nm [27]. They thought that the product was fulvene, but the major product should be revised to 1,3-hexadiene-5-yne.

5. Summary

Fig. 6 summarizes the two-photon chemistry of benzene via hot benzenes (S_0^{**} and S_0^{***}) in the gas phase at 193 nm in the presence of a few tens of kPa (a few hundreds of Torr) of a foreign gas. Benzene is pumped to the S_2 state at the fourth vibrational peak with a molar extinction coefficient of 4650 M^{-1} cm^{-1}. Fast internal conversion (IC) finally leads to a highly vibrationally excited but electronically ground state, followed by rapid intramolecular vibrational re-distribution (IVR) which is defined as S_0^{**} with the equivalent temperature of 3400 K. The S_0^{**} is predicted to have a high molar extinction coefficient of 8300 M^{-1} cm^{-1} ($\sigma = 3.2 \times 10^{-17}$ cm^2) at the 193 laser wavelength. This value was calculated on the basis of the modified Sulzer–Wieland model for explaining an absorption spectrum at high temperature [18]. The S_0^{**} readily absorbs the second laser photon in the excitation pulse and is eventually converted to hot benzene S_0^{***} with the internal energy of the two photons. The reaction rate constant of S_0^{***} is estimated to be on the order of $10^{11}\,s^{-1}$, which is faster than the collision rate, and the S_0^{***} is transformed to 1,5-hexadieneyne with a minor product of a phenyl radical. Fulvene was also detected. The collision quenches the process from S_0^{**} and stabilizes the products from S_0^{***}. The yield of 1,3-hexadiene-5-yne was estimated to be 0.05 at 10 mJ/cm^2 based on the transient absorbance. The collision rate is presumably faster than the further decomposition of the products to C_6H_4, C_5H_3, CH_3, C_2H_3, and C_4H_3, which are products via S_0^{***} [3]. In other words, 1,3-hexadiene-5-yne and the

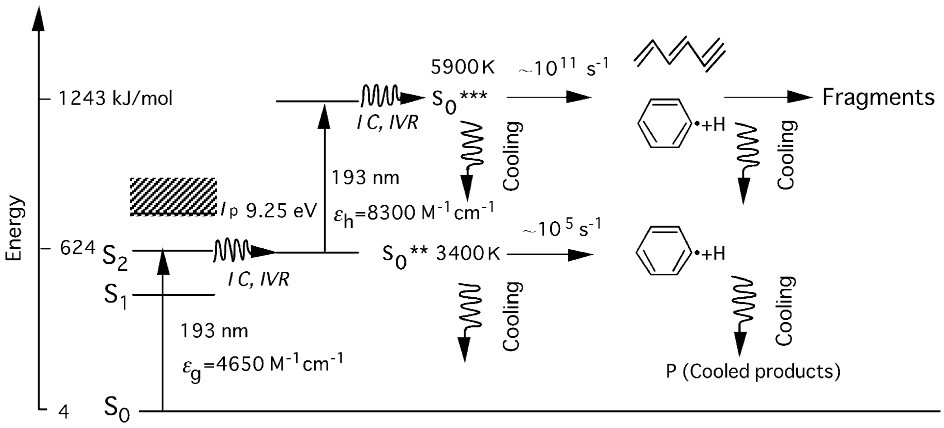

Fig. 6. Benzene laser chemistry in the gas phase at 193 nm in the presence of a few tens of kPa of a foreign gas proceeds via hot benzenes (S_0^{**} and S_0^{***}) (see text). The vertical scale indicates the internal vibrational energy. I_p is the ionization potential. Some of the values and species are for the ones under collision free conditions. They are the molar extinction coefficient of S_0^{**}, the equivalent vibrational temperatures, the rate constants, and the fragments. "Cooling" indicates collisional relaxation with the foreign gas. Isomers [16,17] by one-photon chemistry are not shown.

phenyl radical could be intermediates of those fragmented products.[1]

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