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Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 481–487

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Single-, two- and three VUV photon reactions of a series of alkylarenes in the gas phase

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Received 4 August 2003; received in revised form 12 September 2003; accepted 20 September 2003

Abstract

A series of alkylarenes (AR) was excited by an ArF excimer laser in the gas phase. The neutral radical was observed by transient absorption spectroscopy without traces of emission, triplet state, or cation radical. Single and multiphoton (up to three-photon) processes were observed even though molecules have similar structures. This presents a quite different feature from ordinary photochemistry in the condensed phase. Neutral radical production was explained well by the hot molecule mechanism and compared with statistical reaction theory. The differences between multiphoton reactions in the condensed phase and those in the gas phase were discussed.

Keywords: Hot molecule; Multiphoton reactions; ArF excimer laser; Alkylarenes; VUV photochemistry; Vibrationally excited state

1. Introduction

Vacuum ultraviolet photochemistry, excitation of molecules to higher electronic states but at an energy below the ionization potential, is very interesting subject to explore and holds great potential for the field of radical chemistry. In the condensed phase, collisional relaxation occurs efficiently and draws excited molecules down to the lowest excited state, in other words, to the reactive state where photochemical reaction are dominant. However, there is another possible reactive state if molecules are excited to high electronic states in the gas phase under collision-free conditions. Such a state can be described as vibrationally excited levels in the electronic ground state of molecules, which are known as “hot molecule”. In the case of aromatic hydrocarbons, as the excitation wavelength becomes shorter, the internal conversion rate becomes faster in the gas phase [1]. For example, the rate of internal conversion of benzene from the S_2 state is on the order of tens of femtoseconds measured by VUV ultrafast spectroscopy [2]. Such a high internal conversion rate results in a high yield of hot molecule formation. This behavior is very different from ordinary photochemistry in the condensed phase. Hot molecules react from a state with extremely high vibrational temperatures with a specific reaction rate constant, which can be compared with that obtained by statistical reaction theory [3]. One of the most important differences from ordinary thermal reactions at the same temperature is that the products can be cooled down by collisional relaxation. Therefore, thermally unstable products can be obtained without undergoing secondary reactions and could be used for further studies. Production of neutral radicals instead of ion radicals is another application of hot molecule reactions. Generally, photolysis is thought to be the easiest way of radical production. However, it is not easy to produce neutral radicals by short wavelength laser light in the condensed phase. Instead, a cation radical is formed due to multiphoton ionization in the condensed phase. Subsequent absorption of photons by radicals results in fragments, which induce complex reactions and finally result in soot formation [4]. Although alkylarenes (AR) could be decomposed with the multiphoton process both in the condensed and in the gas phase, the decomposition mechanisms are very much different (Scheme 1). The formation of radicals was explained by the deprotonation (R: H) of radical cations in polar solvent, which were formed by the second photon absorption by the electronic excited state in the condensed phase (Scheme 1a). In the non-polar solvent with 266 nm laser excitation, further photon absorption was not necessary and diphenylmethane (DPM) radical formation through a triplet state was reported [5]. On the other hands, the radicals were formed from hot molecule (S_0^{**}) which was produced by the second photon absorption by hot molecules (S_0^*) in the gas phase (Scheme 1b) [6]. The difference between S_0^* and S_0^{**} is the degree of internal energy accumulated in the

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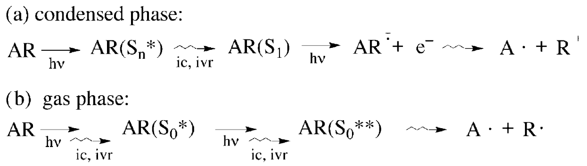
doi:10.1016/S1010-6030(03)00389-7



Scheme 1.

molecule. In the case of hot molecule, it is not necessary for R to be hydrogen. Interestingly, the second photon is not always necessary if the internal energy is sufficient to produce a reaction rate faster than the collisional relaxation rate. Therefore, single and multiphoton reactions could be observed simultaneously.

Multiphoton hot molecule chemistry was found in 1987 for the dissociation of toluene [7] and isomerization of azulene [8]. The second photon was easily absorbed by hot molecules because hot molecules have relatively long lifetimes and large molar extinction coefficients in the VUV region. We have investigated a few examples of multiphoton hot molecule chemistry [9]. An accumulation of knowledge on multiphoton hot molecule chemistry is necessary in order to explore new photochemical reaction pathways of photo-inert molecules , such as biphenylene [10] and also to study radicals.

In this study, VUV photochemistry of a series of alkylarenes was studied in the gas phase by an ArF excimer laser excitation. The radicals were formed by multiphoton processes without emission, triplets state or cation radicals. The transient spectra within the laser pulse duration were well-simulated by the Sulzer–Wieland model for hot molecule spectra. The multiphoton process via hot molecules in all alkylarenes were observed and were compared with reaction rate theory.

2. Experimental

2.1. Materials

Diphenylmethane (DPM, Aldrich) and 1,3-diphenylpropane (DPP, Nacalai) were purified by a trap-to-trap distillation. 1,2-Diphenylethane (DPE, TCI) was purified by sublimation. Triphenylmethane (TPM, Nacalai) was purified by recrystallization from ethanol with charcoal followed by sublimation. Nitrogen gas was purchased from Osaka Sanso and the stated purity was 99.9999%.

2.2. Measurements

Absorption spectra were measured by a spectrophotometer (Shimadzu UV-2400). The details of transient absorption spectra in the gas phase at high temperature was described previously [11]. Gaseous sample was irradiated by an ArF excimer laser (Lambda Physik COMPex 102, 193.3 nm, FWHM 20 ns, 200 mJ/pulse). Laser fluence was controlled by a NaCl aqueous solution filter, and by adjusting the applied voltage of the laser. Laser fluence was monitored by a pyroelectric Joule meter (Genetec ED 200 and ED500). Transient species were monitored by a pulsed Xe flash lamp (EG&G FX 425) with a perpendicular beam against the laser beam. The transmittance light was focused into a monochromator (Jobin-Yvon HR320) which was connected to a photomultiplier tube (Hamamatsu Photonics R758). Data were collected by a digital oscilloscope (Sony Tektronix TDS 620B), and analyzed on a Power Macintosh. The sample and cell was renewed at every laser shot in order to avoid effects due to the accumulation of photoproducts. Data were not averaged, and a single shot measurement was carried out. Datum was corrected with the datum observed at fixed wavelength at the same time for normalization. A typical spracil gas cell was placed in a home made hot cell. The temperature was controlled by a chromel–alumel thermocouple and a 400 W heater combination. The reaction cell was kept for over 30 min at the experimental temperature for the complete vaporization and complete mixing with foreign gas.

3. Results and discussion

3.1. No triplet state, no emission, no radical cation but neutral radicals in the transient absorption spectra

Fig. 1 shows the transient absorption spectra of alkylarenes in the presence of nitrogen as a foreign gas. Spectra were taken at 0 s (filled circle) and 400 ns (open circle). The 0 s was defined as the peak of the sharp hump appearing in the transient time profiles in the presence of nitrogen at 230 nm as shown in Fig. 1e. As clearly shown in the spectra, absorption in the visible region was negligible. The absence of absorption in the visible region indicates that the formation of triplet states and cation radicals of alkylarenes were negligible. Absorption of cation radicals in the visible region have already been reported for the 1,3-diphenylpropane radical cation [12] and the triphenylmethane radical cation [13]. Triplet state absorption of diphenylmethane [14] also appears in the visible region. By analogy, the absorption of other radical cations and triplet states of alkylarenes were expected to appear in the visible region. Instead, the absorption spectra after the sharp hump were clearly identified as well-known benzyl-type radicals. These spectra were essentially identical to the diphenylmethyl radical [15], benzyl radical [16], and tripehylmethyl radical [17] measured in the condensed phase. All the results indicated that C–C bond cleavage occurred in DPE and DPP. The C–H bond was dissociated in DPM and TPM. The products and dissociation reactions are reasonably explained in view of bond dissociation energy. Thermolysis of alkylarenes [18] has been studied well for DPM [19], DPE [20], and DPP [21]. Based on the transient absorption spectra, it is concluded that the neutral radical was formed by VUV laser photolysis in the gas phase as in the case of thermolysis. However, it should be

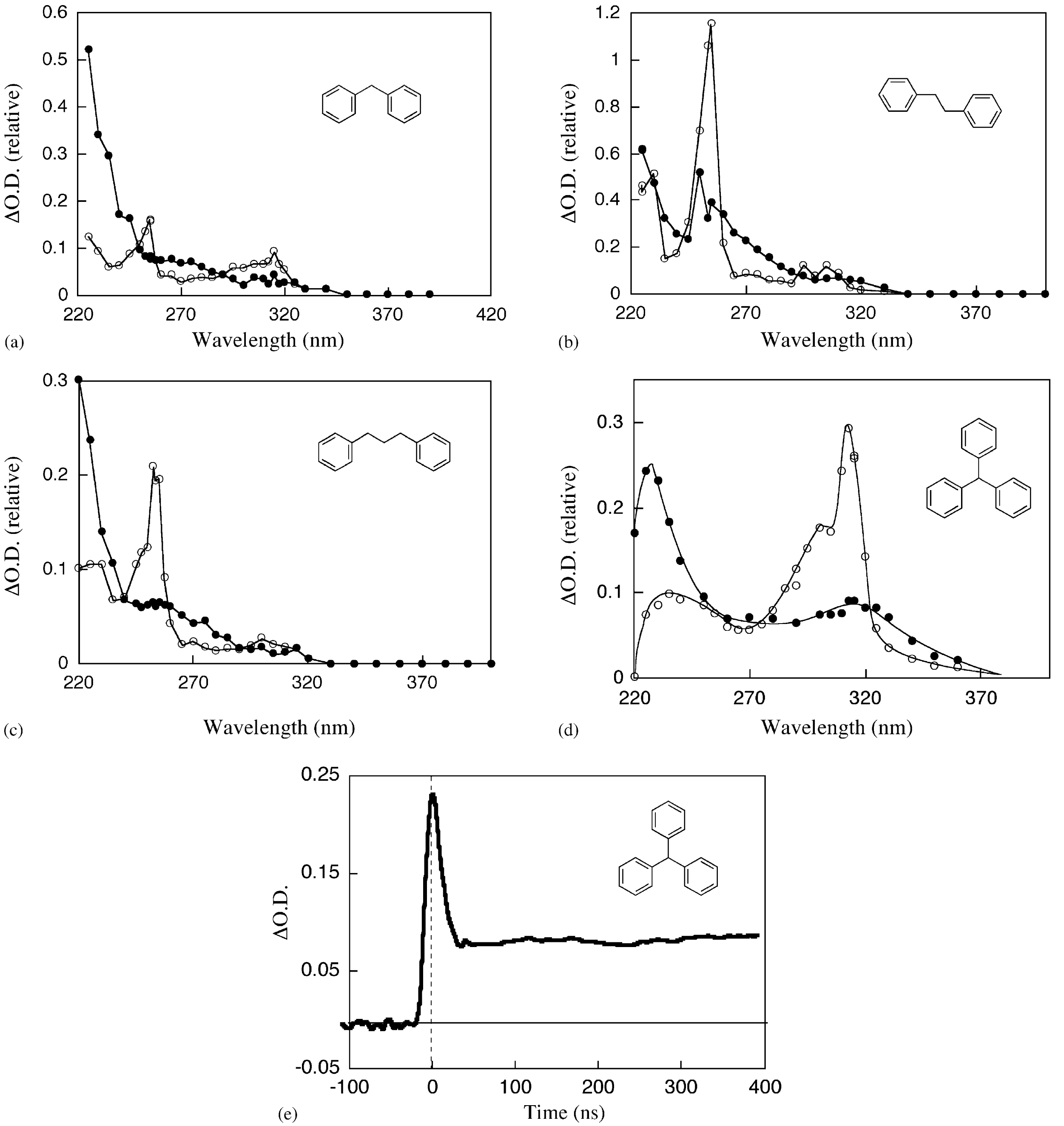


Fig. 1. The transient absorption spectra of alkylarenes in the presence of nitrogen observed at 0 s (●) and 400 ns (○) after the laser pulse. (a) DPM (373 K), Spectra were taken in the presence of 504 Torr nitrogen. Laser fluence was $9.5 \pm 0.3\,\mathrm{mJ\,cm^{-2}}$. (b) DPE (423 K), Spectra were taken in the presence of 544 Torr nitrogen. Laser fluence was $8.8 \pm 0.4\,\mathrm{mJ\,cm^{-2}}$. (c) DPP (423 K), Spectra were taken in the presence of 544 Torr nitrogen. Laser fluence was $9.6 \pm 0.3\,\mathrm{mJ\,cm^{-2}}$. (d) TPM (433 K), Spectra were taken in the presence of 585 Torr nitrogen. Laser fluence was $16.0 \pm 0.1\,\mathrm{mJ\,cm^{-2}}$. (e) Time evolution of the transient absorption of TPM (230 nm, 433 K, 585 Torr of nitrogen).

noted that the formation of radicals by VUV laser irradiation was completed within 100 ns and remained constant as shown in Fig. 1e.

3.2. Spontaneous formation of hot molecule

Transient absorption spectra of gaseous alkylarenes in the absence of nitrogen are shown in Fig. 2. Again, no absorption was apparent in the visible region. The solid line in Fig. 2 is the simulated spectrum of a hot molecule by modified Sulzer–Wieland model [22]. The absorption spectrum of a hot molecule has a broad shape and is red-shifted compared with its cold molecule. All the spectra except TPM can be assigned to those of hot molecules of the reactants. In the case of TPM, the absorption was reasonably assigned to the hot triphenylmethyl radical (also compare the spectra in

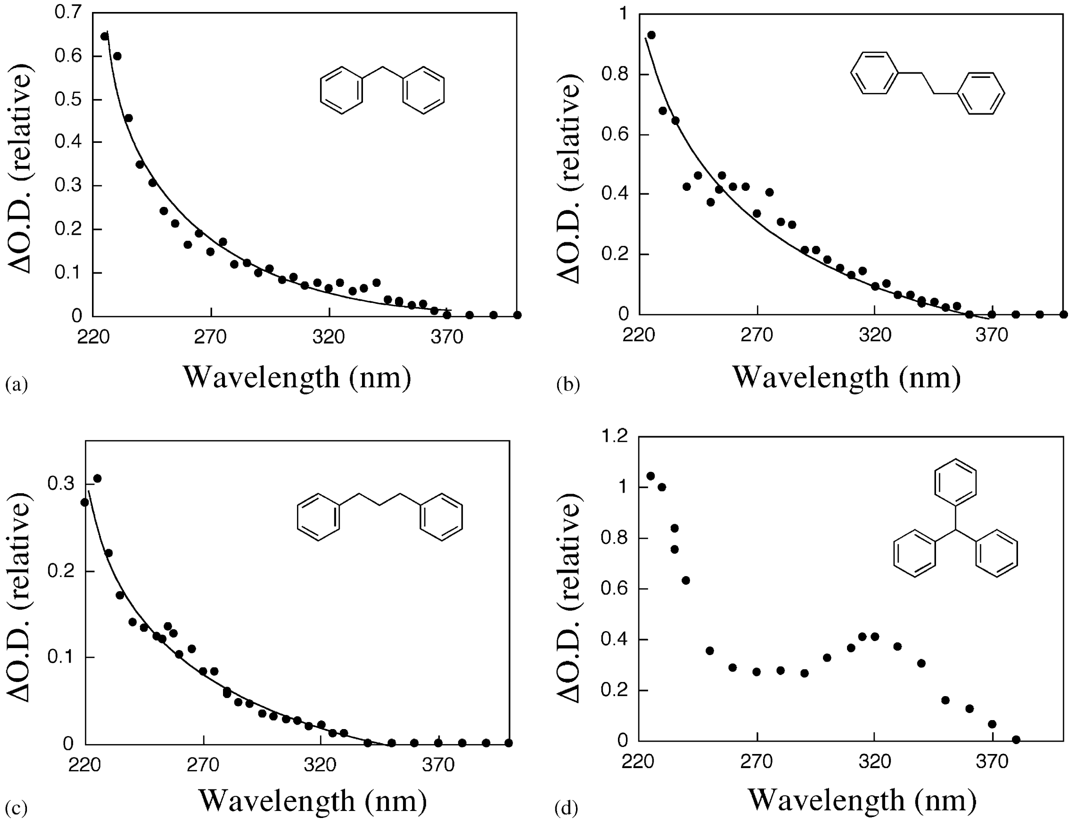


Fig. 2. The transient absorption spectra of alkylarenes in the absence of nitrogen observed at 0 s after the laser pulse. (a) DPM (373 K), laser fluence was 9.5 ± 0.5 mJ cm^{-2}. (b) DPE (423 K), laser fluence was 8.7 ± 0.4 mJ cm^{-2}. (c) DPP (423 K), laser fluence was 9.7 ± 0.3 mJ cm^{-2}. (d) TPM (433 K), laser fluence was 16.0 ± 0.1 mJ cm^{-2}.

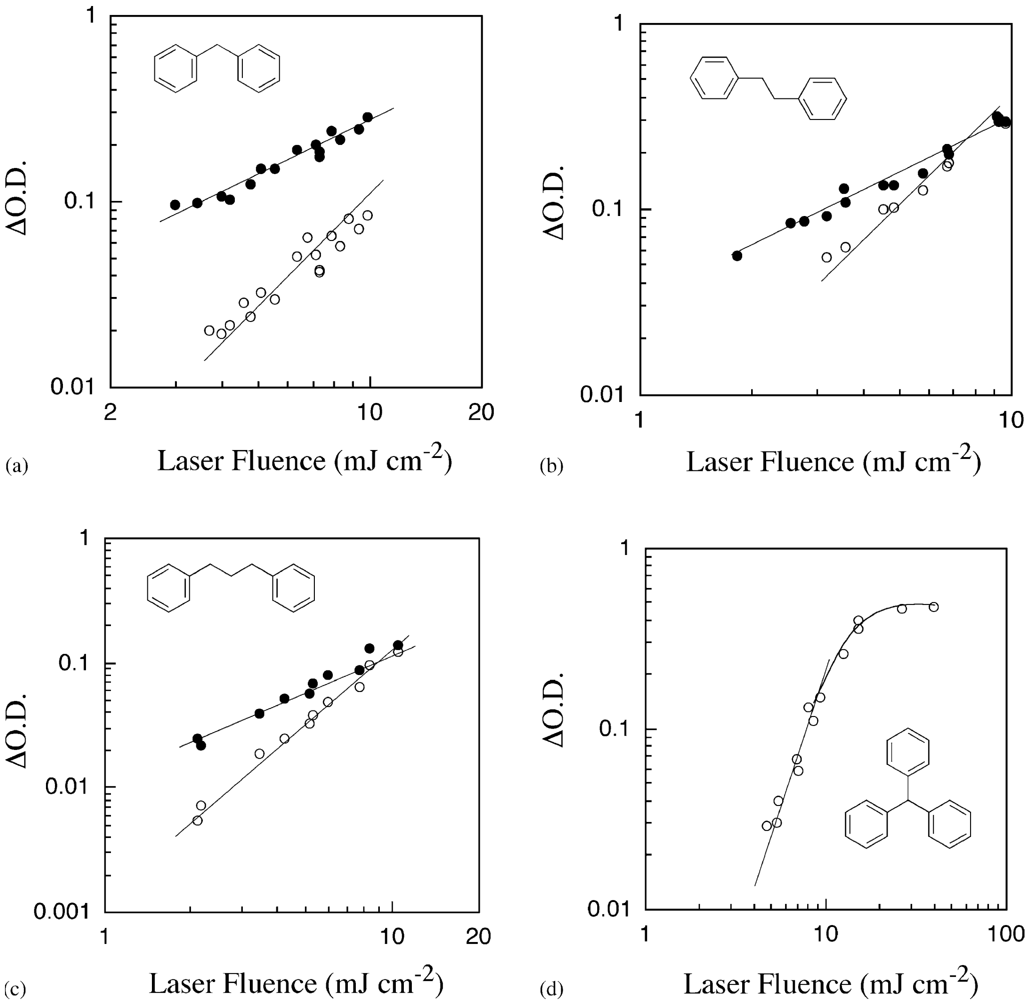
Fig. 1d) instead of hot TPM. The absence of hot TPM means that the formation of triphenylmethyl radical is very fast and the molar extinction coefficient of radical is larger than hot TPM. All the results indicated that an initial intermediate is a hot molecule of reactant formed by a rapid internal conversion within the resolution time of 10 ns.

Hot molecules in a highly vibrationally excited state are deactivated by collision with a foreign gas. If a hot molecule is a source of radicals, the foreign gas will significantly suppress the formation of radicals. In fact, the Stern–Volmer constants (Torr^{-1}) obtained by the correlation between the reciprocal of optical density of the radicals and nitrogen gas pressure were 3.1×10^{-3} (DPM, 315 nm), 1.9×10^{-3} (DPE, 253 nm), 7.5×10^{-3} (DPP, 252 nm), and 4.9×10^{-3} (TPM, 310 nm). While the slow (single-photon) reaction of a hot molecule is suppressed by collision with a foreign gas, the fast reaction (multiphoton reaction) of a hot molecule survives. At a nitrogen pressure of 400 Torr, the formation of radicals was still significant. These results indicated that the radical formation reaction rate competes with the collisional deactivation rate with nitrogen. For example, the radical formation rate is calculated as 2×10^{10} s^{-1} assuming a collisional rate constant of 5×10^{7} Torr^{-1} s^{-1} [23] and nitrogen gas pressure of 400 Torr.

3.3. Radical formation by single-, two-, or three-photon hot molecule mechanism. Comparison with statistical reaction theory

The single-photon hot molecule reaction of toluene is a typical example which has been studied well. The dissociation reaction rate constant of toluene with single 193 nm photon excitation is 2.4×10^{6} s^{-1} [24]. Interestingly, under the collision-free condition, both single- and two-photon reactions were observed. Toluene dissociated by the two-photon mechanism with rate constants faster than instrumental response (>10^{8} s^{-1}). Recently, photoisomerization of toluene was found by Ni and co-workers [25]. Due to the large molar extinction coefficient of radicals, it is difficult to observe isomerization by transient absorption spectroscopy.

Fig. 3 shows the correlation between the absorbance of transients and laser fluence. The initial (hot reactant) absorption (filled circle, 0 s) was linearly proportional to the laser fluence, while radical absorption (open circle, 400 ns) was proportional to the square (DPM, DPE, DPP) or cubic (TPM) of laser fluence. The absorption of both hot reactant and radical should be overlapped. However, the molar extinction coefficient of hot reactant is larger than that of radicals at shorter wavelength region and the relative ratio of



(a) (b) (c) (d)

Fig. 3. The correlation between absorbance and laser fluence at 0 s (●) and 400 ns (○) after the laser pulse in the presence of nitrogen. (a) DPM (230 nm, 373 K), Spectra were taken in the presence of 504 Torr nitrogen. The solid line has a slope of 1.0 (●) and 2.0 (○). (b) DPE (230 nm, 423 K), Spectra were taken in the presence of 544 Torr nitrogen. The solid line has a slope of 1.0 (●) and 2.0 (○). (c) DPP (230 nm, 423 K), Spectra were taken in the presence of 544 Torr nitrogen. The solid line has a slope of 1.0 (●) and 2.0 (○). (d) TPM (315 nm, 433 K), Spectra were taken in the presence of 585 Torr of nitrogen. The solid line has a slope of 3.0.

the concentration of hot reactant is larger than that of radical at 0 s as clearly seen in Figs. 1 and 2. Therefore, we obtained the different power dependencies for hot reactant (0 s) and radical (400 ns). The saturation of the triphenylmethyl radical formation under a high laser fluence region was observed (Fig. 3d). This saturation indicated the depletion of the ground state of reactants or the decomposition of radicals by further photon absorption [7]. The photofragmentation of the benzyl radical has been discussed [26].

Hot molecules have large molar extinction coefficients in the VUV region; thus, the second photon is easily absorbed. However, the absence of cation radicals meant that the intermediate in multiphoton processes was not the electronic excited state but the electronic ground state formed by ultrafast internal conversion. As a result of internal conversion and photon absorption sequence, photon energy was accumulated as vibrational energy. For example, if DPE absorbed two 193 nm photons without collisional deactivation, it was equivalent to the vibrational temperature of 2770 K.

The statistical reaction rate theory can predict the specific dissociation rate constant of the molecules. Assuming that the internal energy consists of the photon energy of 618.8 kJ mol^{-1} (193.3 nm) and vibrational energy at the experimental temperature. Bond dissociation energy (kJ mol^{-1}) values were taken from the literature as follows: 343 (C–H, DPM) [27], 339 (C–H, TPM) [27], 277 (C–C, DPE) [28], and 301 (C–C, DPP) [29], respectively. The vibrational energies and the eigenvalues of vibration which was required for RRKM calculation were obtained by Gaussian’94 (HF, 6-31G(d, p)) [30]. The scaling factor of 0.91 was used for adjusting the calculated data to the experimental data. The vibrational frequencies of the activated complex were assumed to be reduced to 90% of those in the ground state. Fig. 4 shows the correlation of the calculated dissociation rate constant and internal energy for DPM,

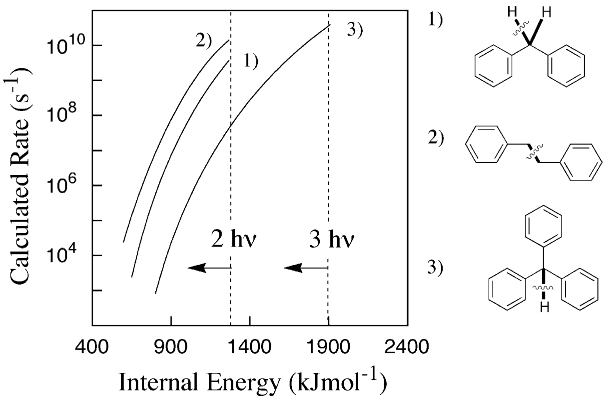
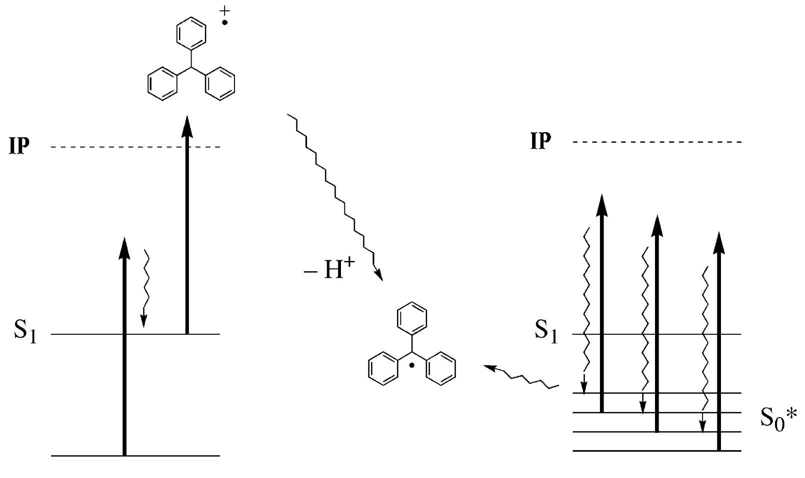


Fig. 4. Dissociation rate estimated by RRKM theory for DPM, DPE and TPM (see Section 3.3). The dashed lines indicate the maximum internal energy accumulated in the molecule by two- or three-photon absorption. Suppose the collisional deactivation was not considered, the crossing points between calculated curves and dashed lines give the maximum reaction rates. Wavy lines on the molecules indicate the dissociative bond considered in the calculation.

DPE and TPM. The dashed lines in Fig. 4 indicate the maximum internal energy accumulated in the molecule by two- or three-photon absorption. Suppose the collisional deactivation was not considered, the crossing points between calculated curves and dashed lines give the maximum reaction rates. The results indicate that energy corresponding to at least two-photons was necessary to decompose DPM, DPE and also DPP in the presence of several hundred Torr of nitrogen. Three-photon energy was required in the case of TPM. Single-photon absorption is not sufficient for the dissociation reaction of any of the alkylarenes under the experimental conditions. Unfortunately, the reaction rate of neither single nor multiphoton reactions was not accessible in this experiment because our observable reaction rate was between 10^6 and $10^8\,\mathrm{s}^{-1}$. It is possible to measure reaction rates on the order of 10^4–$10^5\,\mathrm{s}^{-1}$ with the multimass ion imaging technique [31] and the time-of-flight technique [32]. We need a picosecond VUV system to measure the range above $10^8\,\mathrm{s}^{-1}$. Nonetheless, qualitative agreements between theory and experiment were confirmed. However, we and other groups have succeeded in observing reaction rates of similar molecules and found fairly good agreements between experimental results and theoretical calculations [3,33,34]. The internal energy of S_0^* was dependent on how many photoabsorption, internal conversion cycles were achieved. Single-photon hot molecule reactions (from S_0^*), two-photon hot molecule reactions (from S_0^{**}) and further multiphoton hot molecule reactions occurred at the same time though reaction rate constants were quite different. It is quite different features of hot molecule reactions compared with ordinary photochemical reactions.

3.4. Hot molecules in the gas phase and radical cation in the condensed phase

Multiphoton chemistry of alkylarenes has been studied also in the condensed phase. The neutral radicals of DPM [35] and TPM [17] were formed by two-photon ionization followed by deprotonation. Cation radicals were formed as an intermediate in the condensed phase. However, we have shown that the hot molecule mechanism was major reaction pathway when gaseous molecules were excited (below the ionization potential) by a VUV laser light. There was no trace of cation radical. Why were neutral radicals but not ion radicals formed by the hot molecule mechanism? In the condensed phase, an internal conversion followed by intramolecular vibrational redistribution (IVR) and collisional deactivation is dominant. Finally, S_1 acted as the main reactive state in the condensed phase. During the relaxation from the initial excited state, the internal energy was taken by surrounding molecules by molecular collisions. However, S_1 has a long enough lifetime to absorb a second photon and molecule was ionized (Fig. 5a). On the other hand, the situ-



(a) (b)

Fig. 5. Reaction scheme of triphenylmethyl radical formation. (a) Typical photochemistry in condensed phase. (b) Hot molecule chemistry in the gas phase.

ation was quite different in the gas phase. The vertical axis in Fig. 5 shows the sum of electronic and vibrational energy of a single vibrational mode. In this picture, the simple sum of photon energy exceeds ionization energy, however, photon energy was converted to vibrational energy by fast internal conversion and distributed over all the vibrational modes (99 in the case of TPM). If the photon energy was distributed equally to each vibrational mode, the energy was only 6.9 kJ mol^{-1} per mode. As a result, the absorption of a second photon by a hot molecule does not provide enough electronic energy for ionization (Fig. 5b) because molecules stay in the electronic ground state even though the total (sum of all the vibrational modes) internal energy is quite high. Conical intersection plays an important role in such a fast internal conversion; to access the conical intersection more easily, it is necessary to excite molecules to higher state. Excitation energy-dependent internal conversion is important and a key factor in the difference between hot molecule reactions and reactions in the condensed phase, as mentioned in the introduction.

Formation of hot radicals is expected if radicals in the gas phase are excited again by a VUV laser. In the gas phase, interference from surroundings , such as a solvent does not exist. Therefore, the thermal reaction of a radical [36] can be studied by virtue of the hot molecule mechanism. This is a great advantage for studying combustion chemistry without interference from surroundings. Successive and complicated reactions occurring in ordinal thermal reactions can be separated and studied as independent reactions using hot molecules, a feature that points to important applications of hot molecule chemistry.

Acknowledgements

The present research was partially supported by a grant-in-aid from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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