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Decomposition of Gaseous Phthalic Anhydride from a Vibrationally Hot Molecule Formed by ArF Laser Irradiation

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The photodecomposition of gaseous phthalic anhydride (PA) has been studied by ArF laser photolysis. The transient absorption profiles were strongly dependent on the concentration of the ground-state PA, the foreign gas pressure, and the laser fluence. Both biphenylene and triphenylene were detected as the final products. These results clearly indicated that benzyne (1,3-cyclohexadien-5-yne) was formed during the photolysis. The quenching of biphenylene formation by a foreign gas clearly showed that biphenylene was derived from a highly vibrationally excited (hot) intermediate. The hot PA and benzyne were found to be intermediates of the PA decomposition reaction.

Introduction

Benzyne, a very important intermediate in organic synthesis processes,[1] has attracted much attention for about 60 years since the first demonstration of its existence.[2] The existence of benzyne was well proved by synthetic methods including isotope labeling.[3] The properties of benzyne were experimentally examined and also discussed using theoretical calculations. Numerous theoretical studies were carried out to investigate the properties of benzyne, such as structure,[4] aromaticity,[5] thermochemistry[6] and the isomerization reaction.[7] Moreover, not only *o*-benzyne but also *p*-benzyne[8] and *m*-benzyne[9] were regarded as remarkable intermediates. Recently, the observation of benzdiyne (tetradehydrobenzene) was successful.[10] Benzyne was formed by the flash vacuum pyrolysis (FVP)[11] or photolysis[12] of the parent molecule, and then isolated in the cold matrix for direct observations.[13] In these cases, benzyne was characterized by steady-state spectroscopic methods such as IR spectroscopy,[14] photoelectron spectroscopy,[15] microwave spectroscopy,[16] and NMR spectroscopy.[17] However, time-resolved spectroscopy was reported only in the 1960s for TOF−MS,[18] and UV−vis absorption spectroscopy.[19] The observation of benzyne and its dimerization process was successful in the microsecond region, but flash photolysis in the nanosecond region was not achieved.[18] The UV−vis absorption of benzyne was reinvestigated using a steady-state matrix isolation technique.[20] For the matrix isolated condition, the photoirradiation of phthaloyl peroxide, benzocyclobutenedione,[14b] and phthalic anhydride (PA)[21] resulted in the formation of benzyne, and an interconversion among intermediates was observed. The matrix isolation is an effective method for isolating and characterizing the active intermediate, but the photoirradiation of matrix isolated materials may be complicated because reactants were closely packed in the matrix.[20] In the case of FVP, a very high-temperature condition, benzyne was also detected as an intermediate, but the interconversion among intermediates never occurred. Biphenylene and triphenylene were formed as final products by the FVP of PA.[22]

The other very high-temperature condition, namely vibrationally hot molecule formation, is achieved after a rapid internal conversion from an electronically excited state in the gas phase.[23] A hot molecule carries a very high vibrational energy that nearly equals the absorbed photon energy. The equivalent vibrational temperature is around 2000−4000 K for the benzene derivatives. Many molecules such as aromatic hydrocarbons,[24] olefins,[25] and aliphatic hydrocarbons[26] form hot molecules during UV−VUV light irradiation. The hot molecule mechanism for the chemical reactions has, however, been explored for only a small variety of molecules. An accumulation of knowledge of hot molecule chemistry will be a great help in understanding high-temperature chemistry. In this study, decomposition of gaseous PA was studied by ArF laser flash photolysis. The influence of various experimental conditions such as the concentration of PA, the laser fluence, and the inert gas pressure on the transient species revealed that benzyne was formed from vibrationally hot PA whose vibrational temperature was calculated to be 2700 K (Figure 1).

Experimental Section

Phthalic anhydride (PA, 99+%) was purchased from Aldrich and purified by sublimation. Phthalic anhydride-*d4* (PA-d_4) was synthesized by refluxing phthalic-d_4 acid (Aldrich, 98% D) in acetic anhydride, and then purified by recrystallization followed by sublimation.[27] Nitrogen gas was purchased from Osaka Sanso, and the stated purity was 99.99%.

Crystals to be photolyzed were dissolved in benzene which could be easily removed. About 100 μL of liquid was deposited onto the bottom of the sample tube. The solvent was then pumped carefully away until the background pressure was less than 10^{-3} Torr, and the tube was sealed. No residue of benzene was detected in the absorption spectra. The PA was vaporized at 423 K in a homemade hot cell (temperature was controlled by a chromel−alumel thermocouple and a 400 W heater). The concentration of PA was 2.5×10^{-4} M (6.6 Torr). The accuracy of the concentration was ±5% because of the uncertainly of the cell volume which was sealed off by hand. The maximum concentration of PA in this experiment was well below the calculated vapor pressure, at 423 K (18 Torr).[28] A linear correlation between the absorbance and the concentration of PA was satisfied under the experimental condition. The ground-

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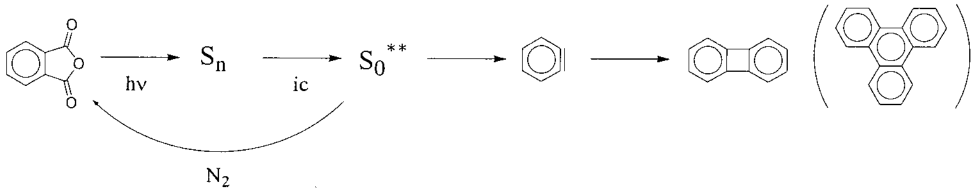

Figure 1. Schematic description of the photodecomposition reaction of PA via hot state (S_0**).

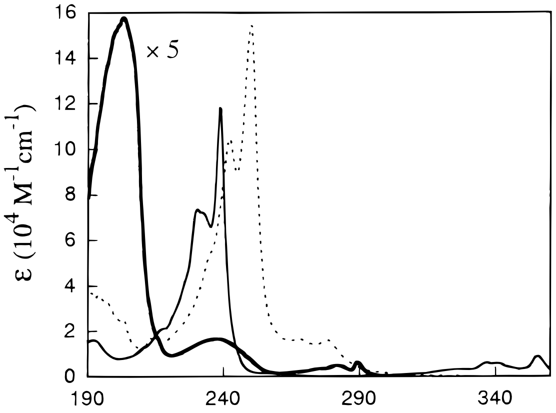

Figure 2. Absorption spectra of gaseous PA (423 K, 570 Torr N_2, thick line), biphenylene (423 K, 570 Torr N_2, thin line), and triphenylene (493 K, 650 Torr N_2, dotted line). The absorption spectra of PA were multiplied (× 5) to provide a clearer presentation.

state absorption of PA is too strong to observe the transient absorption between 270 and 300 nm; therefore, the spectra of this region were measured at a half-concentration of PA to obtain the intensity of light transmittance. The reaction cell was kept for over 30 min at the experimental temperature for the complete vaporization of PA. The decomposition of PA was not observed for several hours under this condition.

The absorption spectra were measured by a spectrophotometer (Shimadzu UV-2400). Gaseous PA was irradiated by an ArF laser (Lambda Physik LPF 205, 193.3 nm, fwhm 20 ns, 150 mJ/pulse) in an area of 0.5 cm × 3.0 cm. Laser fluence was controlled by a NaCl aqueous solution filter and by adjusting the applied voltage of the laser. Laser flurence was monitored by a pyroelectric joule meter (Genetec ED 200). 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 (Acton Research SpectraPro 150) 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 were renewed at every laser shot, so the error in the optical density may be relatively large because of the difference in the cells. Data were not averaged, and a single shot measurement was carried out.

Results and Discussion

Laser Flash Photolysis of PA and Final Products. The absorption spectra of gaseous PA (423 K, thick line) and biphenylene (423 K, thin line) are shown in Figure 2. PA has a strong absorption at the laser wavelength. An ArF laser (193.3 nm) pumps PA to the S_3 state. The photolyzate was dissolved in acetonitrile, and the absorption spectra of biphenylene and a small amount of triphenylene were clearly observed. The formation of biphenylene and triphenylene is strong evidence of benzyne formation as an intermediate during the photodecomposition process of PA. We may first point out some difficulty in transient absorption measurement of gaseous PA due to the significant influence of photoproducts on transient time profiles even in the second laser shot. The transient decay profiles of the first and second laser shots were dramatically different. A significant difference in the decay profiles was clearly observed at 230 and 260 nm. The sample and cell were then renewed for every laser shot in order to obtain results in this study. However, successive laser irradiations were also tested. After tens of laser shots, no transient was observed because of the consumption of vapor material under the experimental conditions. The pale yellow products, which were insoluble in acetonitrile, were observed on the wall of the cell. These insoluble materials were not analyzed, but would be a high polymer of benzyne or secondary products of biphenylene.

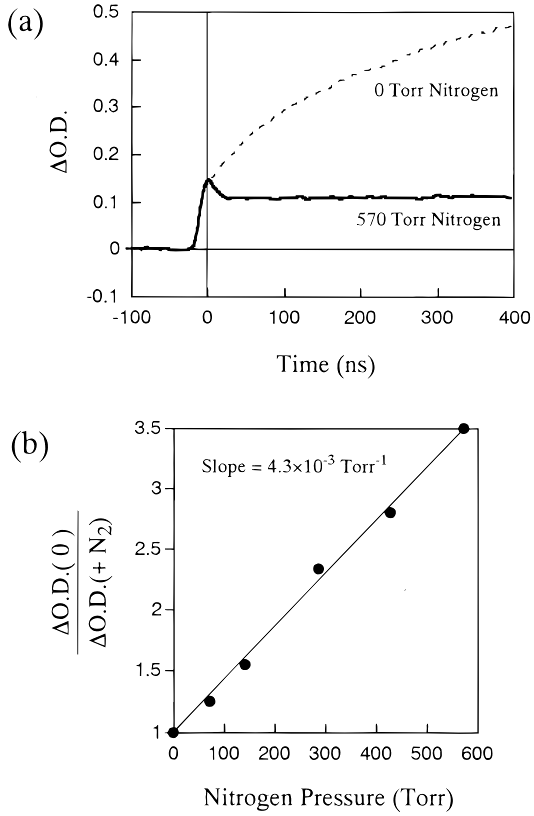

Figure 3. (a) Transient decay profiles of PA observed at 260 nm in the absence of nitrogen (dotted line) and in the presence of 570 Torr of nitrogen (solid line). Laser fluence was 15 mJ cm^{-2}. (b) Stern−Volmer plot of the transient absorption at 400 ns after the laser pulse observed at 355 nm in the presence of 570 Torr of nitrogen. Laser fluence was 14.8 ± 0.4 mJ cm^{-2}.

Foreign Gas Pressure and Concentration Effects. The effects of foreign gas and the concentration of the ground-state PA on the transient absorption were examined. Both factors were found to be very important. Figure 3a shows the effect of the addition of nitrogen as the foreign gas. Zero s was defined as the time where the transient absorption at 260 nm in the presence of 570 Torr of nitrogen has a sharp hump as shown in Figure 3a. In the absence of nitrogen, the transient profile at 260 nm

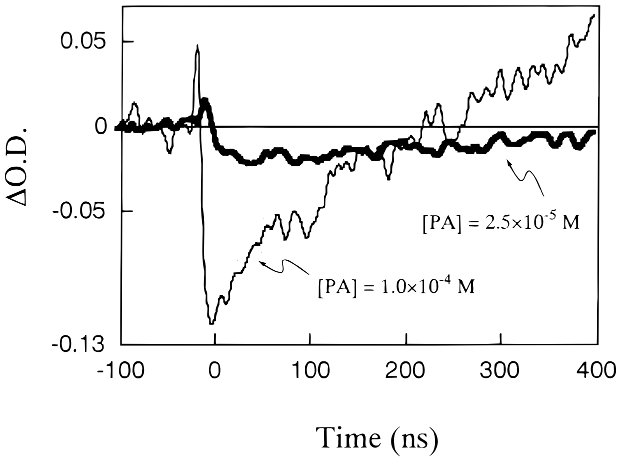

Figure 4. Transient decay profiles at relatively low (thick line, [PA] = 2.5 × 10^{-5} M) and high (thin line, [PA] = 1.0 × 10^{-4} M) concentrations of PA observed at 230 nm. Laser fluence was 15 mJ cm^{-2}.

consisted of two rise components. The fast-rise component appearing before 0 s was identical whether the nitrogen gas was added or not. On the contrary, the slow-rise component appearing after 0 s was very much suppressed with nitrogen, and a stable transient was observed over several hundreds of nanoseconds. The fast-rise component would correspond to the excited singlet state of PA and the formation of vibrationally hot PA. The slow-rise component would imply (1) a relaxation process of vibrationally hot PA and hot benzyne in the early stage, and (2) a dimerization or trimerization process of benzyne in the latter stage. Even in the absence of a foreign gas, the collisional relaxation of hot molecules will occur because the concentration of the ground state of PA is high enough (6.6 Torr). Assuming that the collisional frequency is 5 × 10^{7} Torr^{-1} s^{-1}, PA collides every 3 ns.

The sharp decay, which appeared in the presence of sufficient nitrogen, would originate in the collisional deactivation of the vibrationally hot molecules (PA and benzyne) and the stable absorption appearing after a sharp hump would be that of benzyne. The decarbonylation and decarboxylation reaction of hot PA would compete with the collisional deactivation rate by nitrogen due to sufficient initial internal energy, unconfined conditions, and a large enthalpy change during the decomposition reaction.[29]

The quenching of product by a foreign gas was then examined. Figure 3b shows the Stern−Volmer plot of the transient absorption with nitrogen. Biphenylene would be the only observable product at 400 ns after the laser pulse observed at 355 nm. The formation of biphenylene was significantly suppressed by the addition of a foreign gas, and a fairly linear Stern−Volmer plot was obtained. The Stern−Volmer constant was 4.3 × 10^{-3} Torr^{-1}. The dimerization of benzyne may occur by a three-body collision mechanism. The increase of foreign gas will enhance the dimerization reaction if the benzyne formation was not affected by foreign gas. However, the yield of biphenylene decreases with increasing nitrogen gas pressure due to the collisional deactivation of vibrationally hot phthalic anhydride, the source of benzyne. All the results indicate that the biphenylene should be derived from the vibrationally excited molecule.

Figure 4 shows the transient absorption profiles at 230 nm obtained at relatively low (thick line, 2.5 × 10^{-5} M) and at high (thin line, 1.0 × 10^{-4} M) concentrations of PA. In the presence of 570 Torr of nitrogen, the frequency of collision was calculated to be 2.9 × 10^{10} s^{-1}, assuming the collisional rate constant of 5 × 10^{7} Torr^{-1} s^{-1}.[30] Therefore, a hot molecule should not live for a long time. The influence of the concentration on the transient profiles, even in the presence of nitrogen, clearly shows the involvement of the intermolecular process in the transient profiles. The transient decay profile at 230 nm looks complicated, but it can be easily explained. The fast rise and decay around 0 s would imply at least three processes, such as (1) the depletion of the ground-state PA, (2) the formation of vibrationally hot PA, and (3) the collisional deactivation of the vibrationally hot PA with N$_2$. The shape of the hump depends on the molar extinction coefficient of these related species. As clearly shown in Figure 4, the subsequent slow rise was strongly dependent on the concentration of PA. At 230 nm, the dominant species at 400 ns after a laser pulse would be biphenylene, which has a strong absorption, as shown in Figure 2. The rise was attributed to the dimerization process of benzyne, and the initial concentration of benzyne was proportional to that of PA. On the contrary, a significant concentration effect was not observed at 290 nm (not shown), where the ground-state PA has a strong absorption. These results indicate that the dimerization of benzyne, rather than the reaction between PA and benzyne, is important.

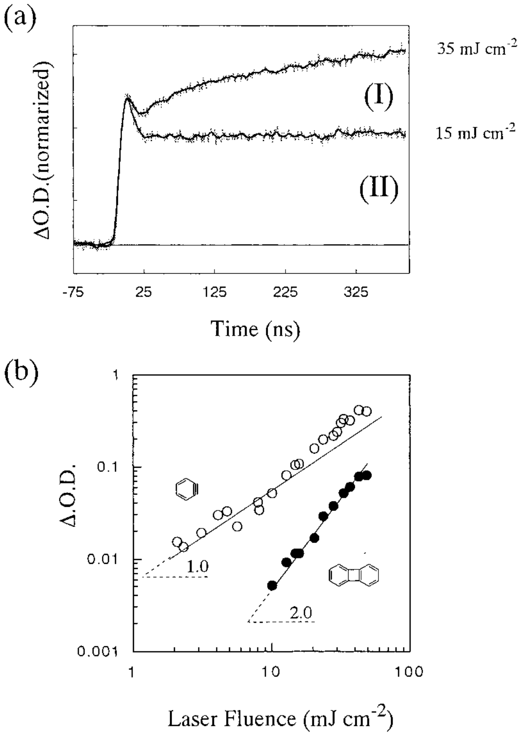

Figure 5. (a) Normalized transient absorption profiles at different laser fluences. Trace (I) was measured at 35 mJ cm^{-2}; trace (II) was observed at 15 mJ cm^{-2}. Each profile was normalized at 0 s. (b) Laser fluence dependency of the transient absorption at 400 ns after the laser irradiation in the presence of 570 Torr of nitrogen observed at 260 nm (○) and at 355 nm (●). The solid lines have a slope of 1.0 (○) and 2.0 (●), respectively.

Benzyne Formation by Single-Photon Process. The laser fluence dependencies of the transient absorption were examined. A definite difference was observed in the transient profile depending on the laser fluences. Figure 5a shows the normalized transient profiles at 260 nm. Trace (I) was measured at a relatively high laser fluence (35 mJ cm^{-2}), and trace (II) was observed at 15 mJ cm^{-2}. In the low-laser fluence region, transient time profiles consisted of a sharp hump, which was assigned to be the formation and collisional deactivation of the

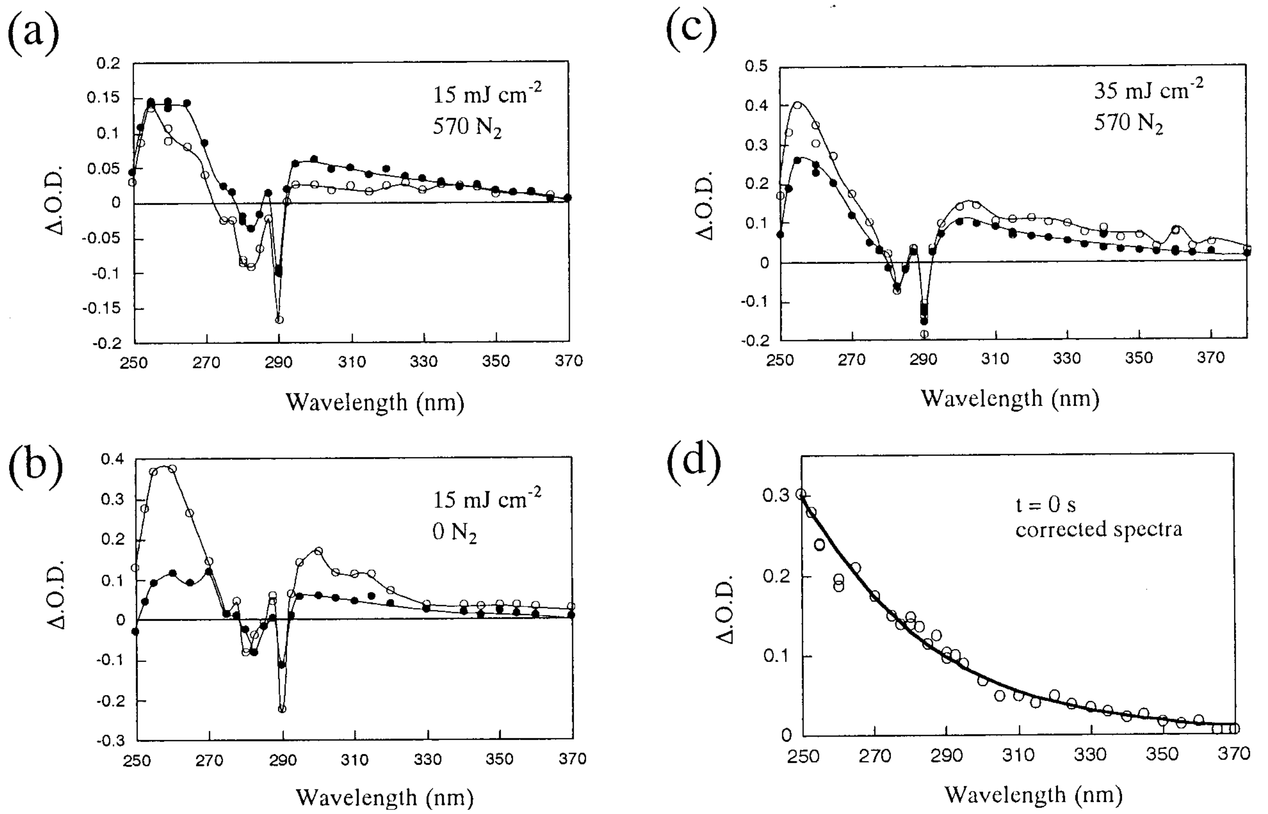

Figure 6. Transient absorption spectra of PA at 0 s (●) and 400 ns (○) after the laser excitation. (a) Low-laser fluence condition in the presence of 570 Torr of nitrogen (15.1 ± 0.9 mJ cm^{-2}). (b) Low-laser fluence condition in the absence of nitrogen (15.0 ± 0.6 mJ cm^{-2}). (c) High-laser fluence condition in the presence of 570 Torr of nitrogen (36.1 ± 1.5 mJ cm^{-2}). (d) Corrected transient absorption spectra of Figure 6a. The solid line on the corrected spectrum is the simulated spectrum of hot molecule by modified Sulzer–Wieland model calculation (see the text).

vibrationally excited molecule, and a long-lived absorption. In the high-laser fluence region, the rise component after the small hump was clearly observed even in the presence of nitrogen. This behavior should not originate in the hot species. The laser fluence dependency on the optical density was then examined (Figure 5b). The slope of the plot (open circle, 260 nm) was greater than 1 in the high-fluence region (>10 mJ cm^{-2}). These results indicated that the observed transient at the high-laser fluence condition was formed by an intermolecular reaction. The most likely species that appears at the high-laser fluence condition would be triphenylene, which has a strong absorption at 260 nm (2 × 10^{4} M^{-1} cm^{-1}), as shown in Figure 2. After a single-shot laser irradiation at 35 mJ cm^{-2}, the formation of triphenylene was clearly observed. The formation of triphenylene contributes to the transient absorption at 260 nm in the high-laser fluence region.

Figure 5b also shows the laser fluence dependencies observed at 355 nm. The slope (2.0) indicated that the transient was formed by a bimolecular reaction or a two-photon reaction. The latter possibility will be neglected because the transient has a rise profile at 355 nm. In the region of 355 nm at 400 ns after laser irradiation, neither hot PA nor benzyne will have a significant absorption. At 400 ns after the laser pulse, biphenylene would be a dominant product. Biphenylene is formed by the dimerization of benzyne, and benzyne should be formed by a single-photon reaction. Porter et al. reported the photodecomposition of PA and the formation of benzyne and its dimerization by a microsecond flash lamp excitation.[19b] The PA could be decomposed by a single-photon process with ArF laser excitation.

Benzyne Formation from Hot Phthalic Anhydride. The transient absorption spectra of PA are shown in Figure 6. The spectra were recorded under different conditions. The spectra exhibited strong bleaching between 270 and 300 nm under all conditions, which corresponded to the depletion of the ground-state PA. The absorbance at 0 s monotonically decreased with increasing wavelength, and no vibrational structure was observed in the region of 300–370 nm under all conditions, where the ground-state PA did not have significant absorption. The monotonic spectra were understood to be those of a hot molecule by analogy to the other hot molecules.[31] The highly vibrationally excited PA, hot PA, has broader and structureless spectra. The absorption spectrum of the hot molecule was successfully simulated for many molecules such as benzene[32] and naphthalene,[33] which have high vibrational temperatures of 3390 and 2320 K, respectively. The transient spectra of PA were then adjusted until there was no spectral structure of the ground-state PA. The corrected transient absorption spectrum of PA is shown in Figure 6d. The other spectra taken under different conditions were also corrected, and they were essentially identical at 0 s. The solid line on the corrected spectrum in Figure 6d was the theoretical simulation curve of the hot molecule spectrum by modified Sulzer–Wieland model.[34] PA hardly emits fluorescence above room temperature.[35] The triplet yield of PA was not definitively determined,[36] but the internal conversion may be a dominant process by analogy, with many aromatic molecules whose internal conversion yield is nearly unity when they are excited by a VUV laser in the gas phase.[23] Based on these facts, it is reasonable that the hot PA, which was instantaneously formed with a laser pulse, is a dominant absorber at 0 s.

Benzyne, however, also has a broadened spectrum between 250 and 400 nm in a matrix isolated condition.[20] It is difficult to distinguish the vibrationally hot PA from benzyne because the absorption spectra may overlap in the entire region. The clue to distinguishing a hot spectrum from that of a vibrationally ground state was the rapid collisional decay (sharp hump) induced by a foreign gas, as seen in Figure 3a. The rapid decay was observed up to 350 nm, depending on the experimental conditions. At longer wavelengths, the identification of the sharp hump induced by a foreign gas was difficult because of the low signal-to-noise value. After 400 ns, the structured spectrum of biphenylene (340−370 nm) clearly appeared under the high laser fluence conditions as shown in Figure 6c.

The estimation of the vibrational temperature of the hot molecule is important when considering the chemical reaction of the hot molecule. The vibrational temperature of the hot PA, q, was then calculated using the equation below:[33]

$$E_0\,(\mathrm{ini}) = h\upsilon\,(193.3\ \mathrm{nm}) + E_{kT}\,(423\ \mathrm{K}) = h\upsilon\,(193.3\ \mathrm{nm}) + \sum_{i=1}^{39} \frac{h\upsilon_i}{\exp\left(\dfrac{h\upsilon_i}{k_\mathrm{B}T}\right) - 1}$$

$$E_0\,(\mathrm{vib}) = \sum_{i=1}^{39} \frac{h\upsilon_i}{\exp\left(\dfrac{h\upsilon_i}{k_\mathrm{B}\theta}\right) - 1}$$

where E_0 is the internal energy of the molecule, E_{kT} is the vibrational energy at the experimental temperature, h is Planck's constant, T is the experimental temperature (423 K), n_i is the normal vibrational mode of PA, and k_B is the Boltzmann constant. If the initial energy, E_0 (ini), is distributed to the vibrational modes of PA (υ_i, $i = 1 \sim 39$), E_0 (ini) should equal the vibrational energy, E_0 (vib). PA has 39 normal vibrational modes, including 33 IR active modes and 6 IR inactive modes. All the vibrational modes were not experimentally obtained. An ab initio calculation (Gaussian 94, HF/6-31G(dp))[37] was then carried out to theoretically obtain all the modes. The scaling factor (0.91) was used for adjusting the calculated vibrational frequencies to the experimental results, and used for equivalent vibrational temperature calculation.[38] Thus the vibrational temperatures were 2694 K (PA-h_4, single-photon absorption) and 2596 K (PA-d_4, single-photon absorption). These high-temperature conditions may be enough to induce the decomposition reaction of PA, which releases carbon dioxide and carbon monoxide.

The influence of deuteration on the benzenoid ring was examined. It was assumed that the degree of deuteration in the PA-d_4 was the same as in the deuterated phthalic acid (98%) from which the PA-d_4 was synthesized. The transient absorption profiles were compared at 260 nm. The laser flash photolysis experiments were performed using the saturated PA concentration. No significant difference between the deuterated and nondeuterated PA was observed in either the initial optical density or rise profiles at different temperatures of 393 and 403 K. The former result (initial optical density) meant that the internal conversion yields of PA-h_4 and PA-d_4 were identical. When the molecules were excited to the higher energy state, the internal conversion rate became so fast[23] that it diminished the effect of the deuteration, because the density of states was very high whether molecules were deuterated or not. The latter result (rise profile) indicated that the collisional deactivation of the hot PA with the ground-state PA was not affected by the deuteration on the benzenoid ring. The yields of biphenylene were then compared after the laser experiments. Again, no significant difference was observed. The deuterium isotope effect was, however, seen in the dissociation process of the alkyl benzene derivatives.[39] The difference between the alkyl benzene derivatives and PA could be attributed to the position of the deuteration. The hydrogen was directly attached to the C−C bond, which will be cleaved in the case of alkyl benzene derivatives, whereas hydrogen was not attached to the quaternary benzenoid carbon and the carbonyl carbon, which will be cleaved.

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(29) We have not succeeded in measuring the rise time of benzyne. Benzyne, which showed absorption in the UV region shorter than 400 nm, was decreased by adding foreign gases; therefore, hot PA does not produce immediately hot benzyne. Benzyne was still observable even in the presence of 570 Torr of nitrogen (Figure 3a). The collision time is estimated to be 35 ps, and every collision does not always quench the formation of benzyne. The rise time can be estimated to be an order of 100 ps on the basis of the foreign gas effects and is beyond our time resolution. The calculated enthalpy change of PA to benzyne was 313 kJ mol^{-1}. The enthalpies of formation are: phthalic anhydride (−371 kJ/mol), carbon dioxide (−393 kJ/mol), carbon monoxide (−110 kJ/mol), benzyne (443 kJ/mol). These values were taken from ref 8 and Wenthold, P. G.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 7414.

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