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A Hot Molecule as an Intermediate in Multiphoton Reactions: First Photoinduced Reactions of Biphenylene

Tomoyuki Yatsuhashi,* Tsuyoshi Akiho, and
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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Biphenylene (BP) has been deemed to be a photoinert molecule because it fluoresces very weakly, has little triplet transition, and does not react photochemically.[1] However, here we assumed that such a photoinert molecule was a worthwhile target for reinvestigation based on the fact that a high internal conversion yield demonstrates an efficient yield of a vibrationally hot molecule (S_0*). Such a hot molecule is in a microcanonical state with a small width of energy distribution, which means the reaction will give a specific rate constant and can be explained in terms of the statistical reaction theory.[2] To increase the reaction rate constant of a hot molecule, the accumulation of internal energy by a successive second photon absorption is necessary.[3,4] We have found some examples of multiphoton hot molecule reactions.[5] Other examples have also appeared.[6] The multiphoton reaction via a vibrationally hot molecule, which is strongly expected for BP, is a method that will incite fresh interest in molecules that are currently regarded as photoinert.

Gaseous BP was prepared at 373 or 403 K and photolyzed with an ArF laser (193.3 nm, 14 ns/fwhm). The sample and cell were renewed with every laser shot to prevent any effects due to the accumulation of photoproducts on transient absorption measurements. The transient time profiles and transient absorption spectra of BP are shown in Figure 1. Figure 1a clearly shows the collisional deactivation of a hot species by a foreign gas followed by stable absorption. Fluorescence, $S_n \leftarrow S_1$ absorption,[7] the triplet state,[8] and the cation radical[9] of BP were not observed. These results are in good agreement with the reported high internal conversion yield of BP.[1] The depletion of the ground state of BP and the appearance of positive absorption observed in the transient absorption spectra clearly indicated the existence of a chemical reaction resulting in stable product formation. Product formation by laser irradiation is an important focus of this investigation, and indeed, product from the first photoinduced unimolecular reaction of BP was found. To determine the origin of the products, the transient spectrum was corrected with the ground-state absorption of BP. Transient species obtained at the peak of the sharp hump (defined as 0 s) in the transient time profile I in Figure 1a is certainly the initial intermediate. The corrected spectrum (Figure 1c) has a broad and extended shape compared with the absorption spectrum of BP at 373 K. The spectral shape, by analogy to the high-temperature spectrum of BP measured by the shock wave method,[10] is understood to be that of the vibrationally hot BP. It is concluded that the initially prepared intermediate is hot BP.

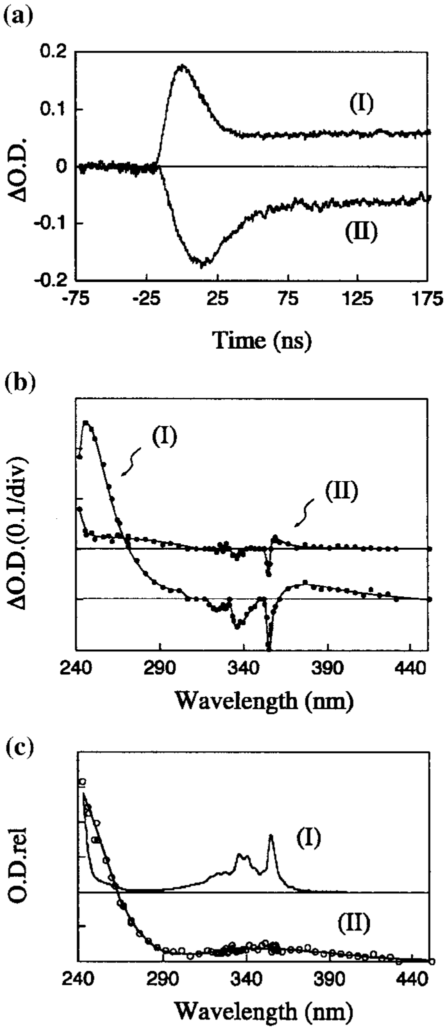

Figure 1. (a) Transient time profiles of BP at 270 nm (I), where the ground-state absorption of BP is minimal, and at 355 nm (II), where it is the peak wavelength of the ground-state absorption of BP. The 0 s was defined as the peak of the sharp hump as observed at 270 nm. (b) Transient absorption spectra of BP at 0 s (I) and 100 ns (II) after the laser pulse. The spectrum has been shifted in optical density to provide a clearer presentation. (c) Absorption spectrum of BP at 373 K (I) and the corrected transient spectrum of BP at 0 s (II). Data were taken in the presence of 504 Torr of nitrogen at 373 K. Laser fluence was 10.0 ± 0.5 mJ cm^{-2}.

To understand the nature of the reaction, the correlation between the transient absorbance and laser fluence was examined. Figure 2 clearly shows that hot BP is formed by a single-photon process and that the product is formed by a two-photon process. This result is consistent with the absence of a photoreaction under steady-state photoirradiation by a lamp.[1a] The missing cation radical strongly indicates that the intermediate in the two-photon process is not an electronic excited state but an electronic ground

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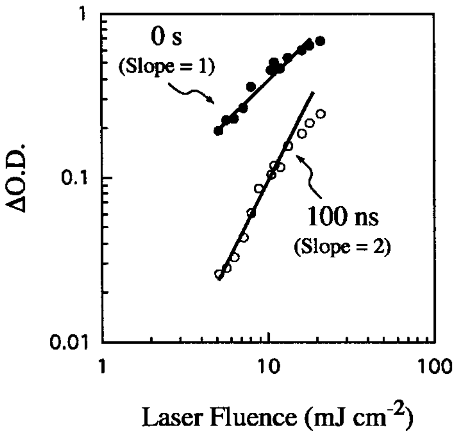


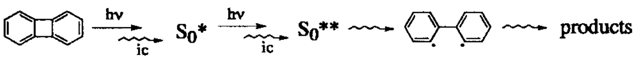
Figure 2. The correlation between the transient absorbance of BP and laser fluence (270 nm, 403 K, 410 Torr nitrogen).

state (vibrationally hot state). The photon energy is redistributed to the whole modes of vibrations, and the absorption of the second photon is insufficient to ionize the molecule in the case of a hot molecule. On the other hand, the second photon, which can increase the internal energy of hot BP by photoexcitation−internal conversion sequences, is necessary for inducing the chemical reaction. From the results described above, the reactions of BP are rationalized in terms of the multiphoton hot molecule mechanism.

The most likely hot molecule reaction of BP is that a C−C bond cleavage between two benzene rings forms a biphenyl-2,2′-diradical. Large geometrical changes upon photoexcitation[11] would be effective for internal conversion and also for the cleavage of the C−C bond. The rate constant of the C−C bond cleavage was estimated on the basis of RRKM theory. Assuming a bond dissociation energy of 374 kJ mol^{-1},[12] the rate constants were calculated to be 1.8×10^3 s^{-1} ($1h\nu$) and 2.0×10^9 s^{-1} ($2h\nu$), respectively. In the case of a single-photon absorption condition, hot BP is formed and presents a relevant case for studying the collisional deactivation of a vibrationally hot molecule, as was clearly shown by Fay and Luther.[13] Croce et al. did shock wave experiments on BP at the temperature range of 1470−1860 K[10] and mentioned the possibility of a chemical reaction of hot BP produced by a photoexcitation. As we described above, the chemical reaction would not be expected because the rate constant of the C−C bond cleavage cannot compete with the collisional deactivation at an internal energy equivalent to a single photon energy of 193 nm under our experimental conditions. The second photon absorption is necessary to induce a chemical reaction of hot BP (Scheme 1).

To analyze the final products, the vapor of BP irradiated in a thin optical cell by laser pulses, was trapped in a cold trap at 77 K. The photolysates were analyzed using GC−MS, UV absorption, and NMR. The identified products were phenyl acetylene, naphthalene, biphenyl, and acenaphthylene. In GC analysis, an unknown product with *m*/*z* 152 appeared between biphenyl and acenaphthylene,[14] and two unknown products with *m*/*z* 126 appeared between phenyl acetylene and naphthalene. On the basis of the results of products analysis, we considered that the primary reaction of BP should be a cleavage of the C−C bond between two benzene rings. Although the primary reaction is similar by all pyrolysis methods applied, the final products differed and were dependent on the pyrolytic method. Tetraphenylene was formed in the case of ordinary pyrolysis at 670 K.[15] The dimerization is dominant in a molten phase. A variety of products were found by a reflected shock wave method.[10] Cyclopent[*a*]indene is obtained by a flash vacuum pyrolysis.[16] On the basis of well-established findings in the literature,[16] we surmised that acenaphthylene may be a secondary rearrangement product of cyclopent[*a*]indene. In our apparatus under the photolysis conditions at high temperature, cyclopent[*a*]indene would finally be converted to acenaphthylene or recovered to BP. The presence of biphenyl as a final product indicated that the BP diradical has a sufficiently long lifetime to abstract hydrogen. However, the transient time profiles and spectra were not affected by the addition of 30 Torr of NO and 410 Torr of nitrogen. The bimolecular reaction rate constant between phenyl radical[17] and NO was reported to be 1.26×10^{10} M^{-1} s^{-1} at 295 K.[18] Applying this rate constant to the reaction of BP diradical and NO, the reaction rate constant was estimated to be faster than 1.4×10^7 s^{-1}. It leads to the conclusion that either the NO-trapped diradical has a molar extinction coefficient smaller than that of other species or that unimolecular reactions of BP diradical are much faster than the intermolecular reaction with NO. The similarity of the final products between photolysis (hot molecule reaction) and the shock wave experiment accounts for complex subsequent processes such as dissociation, hydrogen abstraction, and ring closure after the initial ring opening of BP. Identification of the products and a detailed study of the subsequent reaction of the BP diradical is in progress with the use of other reactants such as benzo[*c*]cinnoline and 2,2′-biphenyldicarboxylic anhydride.

Scheme 1



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[12] The dissociation energy was taken from ref 10. The vibrational energies and the 54 eigenvalues of vibration which were required for RRKM calculation were taken from Kautz, I.; Koch, T.; Malsch, K.; Hohlneicher, G. *J. Mol. Struct (THEOCHEM)* **1997**, *417*, 223. The vibrational frequencies of the activated complex were assumed to be reduced to 90% of those in the ground state. The collisional deactivation of a hot molecule before the second photon absorption was not considered in the calculation. The obtained values are then the maximum values.

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[14] This unknown product would be similar to that obtained in the flash vacuum pyrolysis of 3,4-biphenyldicarboxylic anhydride reported in ref 16b. The product may be ethynylnaphthalene judged from the fragmentation pattern of mass spectrum and absorption spectrum.

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