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Hot Molecule as an Intermediate in Multiphoton Reaction: Two-Photon Decarbonylation of Coumarin

Tomoyuki Yatsuhashi* 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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The photodecarbonylation of gaseous coumarin was studied using an ArF excimer laser. The triplet state, fluorescence, and cation radical of coumarin were not observed in the transient spectra. The addition of nitrogen effectively quenched the formation of 2,3-benzofuran, indicating that 2,3-benzofuran was derived from the highly vibrationally excited state of coumarin. Transient absorption was proportional to the square of the laser fluence. All of the results showed that the hot coumarin was an intermediate in the two-photon decarbonylation reaction. The decarbonylation reaction of coumarin is the first example of the multiphoton reaction of hot molecules other than hydrocarbons. This new photochemical reaction pathway of coumarin was opened by the hot molecular mechanism.

Introduction

Coumarin derivatives are known to be important laser dyes,[1] whereas unsubstituted coumarin will hardly emit fluorescence.[2] The photochemical reaction of coumarin, such as the dimerization, has been well studied because the regioselectivity of the dimerization is dependent on the excited-state multiplicity.[3] However, the unimolecular reaction of coumarin has not been well studied. On the other hand, the thermal reaction such as the decarbonylation of coumarin was observed by the flash vacuum pyrolysis.[4]

High-temperature conditions can be created by photoirradiation. The highly vibrationally excited state, namely a hot molecule, which has an equivalent vibrational temperature of 2000−4000 K, would be produced after a rapid internal conversion from an electronically excited state. The hot molecules are known to be formed by the VUV−UV laser irradiation of gaseous molecules.[5] However, studies of the hot molecule reactions using lasers were limited to a small variety of molecules. The molecules other than aromatic hydrocarbons[6] and olefins[7] have not been well studied. The large molecules such as aromatic hydrocarbons larger than naphthalene have also not been well studied because they did not have a sufficient vapor pressure at ambient temperature.

We have reported the hot molecule chemistry of large molecules such as naphthalene[8] and 2, 2-paracyclophane.[9] The large molecules, which have a low vapor pressure at room temperature, could be used for the experiments by elevating the experimental temperature for efficient vaporization and for adequate absorbance at the laser wavelength. In the case of 2,2-paracyclophane, the experiments were carried out at 453 K.[9] In these cases, the formation of products by the two-photon process was observed. A single-photon absorption would not be sufficient to induce a chemical reaction of such large molecules, which have many vibrational modes. It would be necessary to accumulate energy by a successive second photon absorption to overcome the activation energy of the chemical reactions as well as to achieve reaction rates higher than the collisional relaxation rates. The equivalent vibrational temperature of hot naphthalene and hot 2,2-paracyclophane formed by a single-photon absorption of an ArF excimer laser light are 2320 K[8] and 1655 K,[9] respectively. In these cases, it would be reasonable to conclude that the hot molecules, which were created by the first photon, effectively absorbed the second photon because the hot molecules have a strong absorption at the laser wavelength similar to that of the parent molecules. Multiphoton reactions of a hot molecule were first found for toluene[10] and azulene[11] in 1988. The new reaction pathway would be expected for many molecules even though they hardly react by photolysis (single-photon absorption), if hot molecules absorbed the second photon. The equivalent vibrational temperature with an internal energy of two photons is high enough to induce the reactions in the electronic ground state. The most important difference from the thermal reactions at the same temperature is that the products can be cooled by collisional relaxation for the case of the hot molecule. Therefore, different products would be expected.[5] We have found several examples of new reaction pathways in photoinert molecules. For example, we have found the two-photon reaction of biphenylene, whose internal conversion yield is nearly unity.[12]

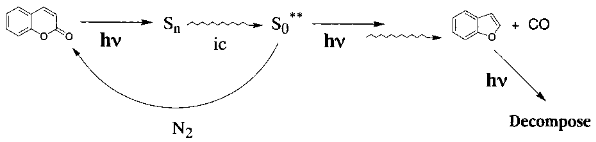

Figure 1. Reaction scheme of the photodecomposition of gaseous coumarin via hot state (S_0**). Further photodecomposition of 2,3-benzofuran was shown.

In this study, coumarin was chosen as the target molecule in order to develop a new area of photochemical reactions under the concept of “thermal reaction induced by multiphoton absorption by hot molecules”. The decarbonylation reaction of coumarin by the two-photon process was investigated. The hot coumarin was found to be an intermediate in a multiphoton reaction (Figure 1). This is the first example of a multiphoton hot molecule reaction other than those with hydrocarbons. The

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* To whom correspondence should be addressed. E-mail: tomo@sci.osaka-cu.ac.jp.

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further decomposition of 2,3-benzofuran by a third photon was also investigated.

Experimental Section

Coumarin (Nakarai, 98%) was purified by recrystallization followed by sublimation. 2,3-Benzofuran (Nakarai, 99%) was purified by trap-to-trap distillation. Nitrogen gas was purchased from Osaka Sanso, and the stated purity was 99.99%.

Coumarin to be photolyzed was dissolved in benzene, which could easily be removed. About 100 μL of coumarin solution 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 transient time profiles were recorded at temperatures of 423 (coumarin) and 296 K (2,3-benzofuran). A typical supracil gas cell was placed in a homemade 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 (coumarin) and complete mixing with nitrogen (2,3-benzofuran). The decomposition of coumarin was not observed at 423 K. The concentration of coumarin was 7.8×10^{-5} M (2.1 Torr), but the ground-state absorption of coumarin is too strong to observe the transient absorption in the regions of 220−227.5 and 240−280 nm; therefore, the spectra of this region were measured at a half-concentration of coumarin (3.9×10^{-5} M, 1 Torr) to obtain sufficient transmittance of light. The higher concentration of coumarin (1.6×10^{-4} M, 4.2 Torr) was used for the transient absorption measurements against the laser fluence. The accuracy of the concentration was ±5% due to the uncertainty of the cell volume, which was sealed off by hand. In the case of 2,3-benzofuran, the transient absorption spectra were measured at the pressure of 0.9 Torr, whereas pressure was reduced to 0.4 Torr in the region of 232.5−247.5 nm to obtain sufficient transmittance of light.

Absorption spectra were measured by a spectrophotometer (Shimadzu UV-2400). Gaseous coumarin was irradiated by an ArF excimer laser (Lambda Physik LPF 205, 193.3 nm, fwhm 20 ns, 150 mJ/ pulse) in an area of 0.5×3.0 cm^2. Laser fluence was controlled by a NaCl aqueous solution filter and by adjustment of the applied voltage of the laser. Laser fluence 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) that 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.

Results and Discussions

Absorption Spectra. The absorption spectra of gaseous coumarin and 2,3-benzofuran are shown in Figure 2. An ArF excimer laser excites coumarin to its S_3 state. After the photolysis of coumarin, the absorption spectra of the reaction mixture were measured at room temperature. The vibrational structure of the 2,3-benzofuran absorption was clearly observed around 240 and 280 nm. No other products were observed in the absorption spectra. The results show that ArF excimer laser irradiation of the gaseous coumarin results in the formation of 2,3-benzofuran.

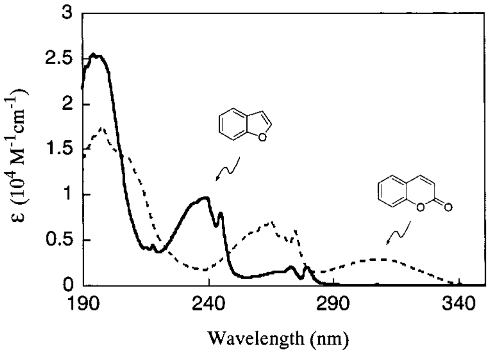

Figure 2. Absorption spectra of gaseous coumarin (dotted line, 423 K) and 2,3-benzofuran (solid line, 423 K).

Depletion of Coumarin, Formation of Benzofuran in Transient Absorption Spectra, and "0" s Spectra Assignable to Hot Coumarin. The transient absorption spectra of coumarin are shown in Figure 3. No transient was observed between 420 and 700 nm. No emission,[2] triplet state,[13] cation radical,[14] or anion radical[15] of coumarin was observed. In the presence of 570 Torr of nitrogen, the transient time profile consisted of a sharp hump and a long-lived stable absorption as shown in Figure 4a. The transient absorption spectra were then obtained at the two different times such as 0 s and 300 ns after the laser pulse. The 0 s was defined as the peak of the sharp hump as observed in Figure 4a. In the absence of nitrogen, the transient spectra were also obtained at the same time as that in the presence of 570 Torr of nitrogen. The spectra exhibited strong bleaching below 340 nm in the presence or absence of nitrogen, which corresponded to the depletion of the ground state of coumarin. In the absence of nitrogen, hot molecules are probably involved in the transient spectra over the entire region even at 300 ns after the laser pulse. On the contrary, the hot molecules should be diminished in the presence of 570 Torr of nitrogen at the same time. The characteristic product spectrum was clearly observed at around 240 nm in the presence of 570 Torr of nitrogen. The stable species can be assigned to 2,3-benzofuran on the basis of the reference spectrum, as shown in Figure 2.

The absorbance at 0 s was monotonically decreased with increasing wavelength in the region longer than 340 nm, where the ground state of coumarin did not have a significant absorption. The monotonic spectra were usually observed in the cases of hot molecules.[16] In the transient spectra, there is no cation radical, triplet state, or emission; therefore, the internal conversion should be the dominant deactivation pathway. Then, the monotonic spectrum at 0 s was understood to be that of hot coumarin. The transient spectrum of coumarin was then adjusted to minimize the spectral structure for the ground-state coumarin in the long-wavelength region. The best corrected transient absorption spectrum of coumarin is shown in Figure 3a. The solid line on the corrected spectrum in Figure 3a was the theoretical simulation curve of the hot molecule spectrum. The modified Sulzer−Wieland model[16] was applied for this case. The best-fit spectrum was obtained by minimizing the residuals in the long-wavelength region where both the ground-state coumarin and benzofuran have no significant absorption. A discrepancy between the best simulated spectrum and the corrected spectrum was observed at around 240 nm. The residuals of spectrum simulation is shown in Figure 3a. The

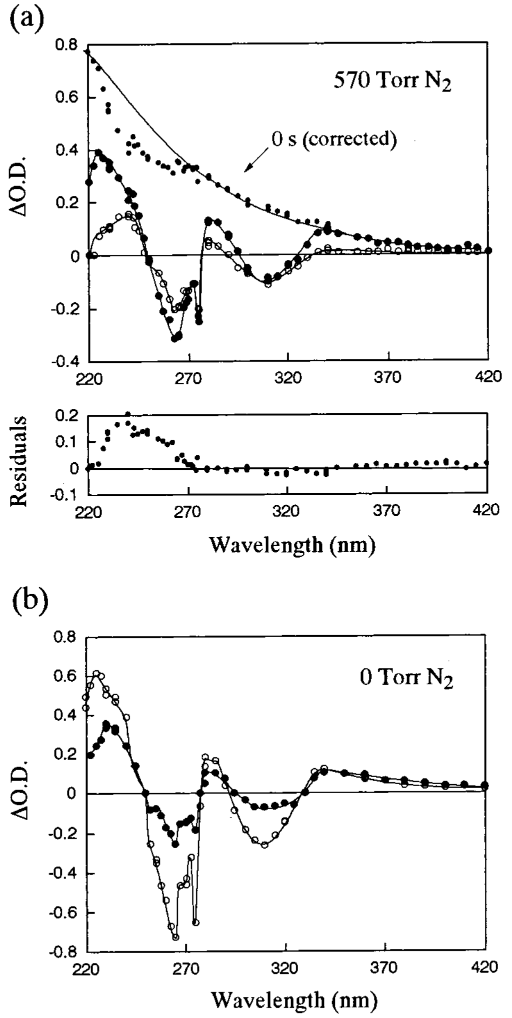

Figure 3. (a) Absorption spectra of coumarin. The upper panel shows time-resolved transient absorption spectra of coumarin in the presence of 570 Torr of nitrogen observed at 0 s (●) and 300 ns (○) after the laser pulse. The transient spectrum at 0 s was corrected with the absorption of ground-state coumarin (•). The solid line on the corrected spectrum is the simulated spectrum of hot molecule by modified Sulzer−Wieland model calculation. The details are described in the text. Laser fluence was 26.0 ± 1.8 mJ cm^{-2}. The lower panel shows the residuals of the simulated spectrum. (b) Time-resolved absorption spectra of coumarin in the absence of nitrogen observed at 0 s (●) and 300 ns (○) after the laser pulse. Laser fluence was 26.1 ± 1.3 mJ cm^{-2}.

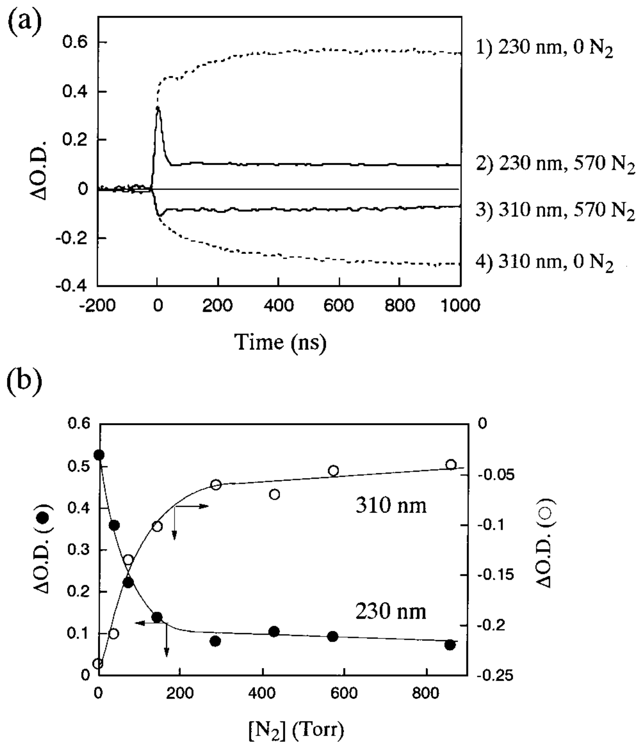

Figure 4. (a) Transient time profiles of coumarin (1, 230 nm, 0 Torr of nitrogen; 2, 230 nm, 570 Torr of nitrogen; 3, 310 nm, 0 Torr of nitrogen; and 4, 310 nm, 570 Torr of nitrogen). (b) Correlations between the transient absorbance observed at 300 ns after the laser pulse and the nitrogen gas pressure: (●) 230 and (○) 310 nm. Laser fluence was 23.3 ± 0.5 mJ cm^{-2}.

difference can be attributed to the influence of 2,3-benzofuran even at 0 s due to the large molar extinction coefficient and fast formation of 2,3-benzofuran.

Collisional Deactivation by a Foreign Gas. The transient absorption time profiles of coumarin in the absence and presence of 570 Torr of nitrogen are shown in Figure 4a. In the absence of nitrogen, a sharp rise and slow growth were observed at 230 nm, and a sharp depletion was followed by a slow decrease at 310 nm. The slow components were understood to be the collisional deactivation of the hot product (2,3-benzofuran) with the ground state of coumarin. The collisional frequency was calculated to be 1×10^8 s^{-1}.[17] On the contrary, dramatic changes in the transient absorption were observed in the presence of nitrogen.

As observed in Figure 4a, the initial intermediate, which was formed with the laser pulse, was immediately deactivated in the presence of 570 Torr of nitrogen. The addition of nitrogen effectively suppressed both the formation of 2,3-benzofuran (230 nm) and the depletion of coumarin (310 nm). Figure 4b shows the correlation between the optical density and the nitrogen gas pressure at 300 ns after the laser pulse. These facts lead us to conclude that the 2,3-benzofuran was derived from the vibrationally excited coumarin. Furthermore, the conversion of coumarin can be estimated by comparing the absorbance change at 230 and 310 nm in the presence of an excess amount of nitrogen. The decomposition amount of coumarin can be estimated from the absorbance change at 310 nm, while both absorbances of the decomposition of coumarin and the formation of 2,3-benzofuran were contained at 230 nm. The molar extinction coefficient of coumarin at 310 nm is 2900 M^{-1} cm^{-1}. The difference in the molar extinction coefficient between 2,3-benzofuran and coumarin at 230 nm is 4900 M^{-1} cm^{-1}. If the equivalent amount of 2,3-benzofuran was formed from coumarin, the ratio of the transient absorption at 230 nm to 310 nm should be equal to 1.7 (=4900/2900). From Figure 4b, the ratio was found to be 1.8−2.0 at nitrogen pressures greater than 570 Torr. These values are reasonably in agreement. It can be concluded that an equivalent amount of 2,3-benzofuran was formed from coumarin.

Two-Photon Processes. Figure 5a shows the transient absorbance of coumarin versus laser fluence. 2,3-Benzofuran was the dominant species at this wavelength at 300 ns after the laser pulse. The plot in the laser fluence region less than 20 mJ cm^{-2} was on a line with a slope of 2.0, indicating that the formation of 2,3-benzofuran was a two-photon process. Saturation of the absorbance in the high-laser-fluence region (>20 mJ cm^{-2}) was also observed. This saturation behavior would be originated from the decomposition of 2,3-benzofuran by the third photon absorption because the molar extinction coefficient of 2,3-benzofuran is greater than that of coumarin at the laser wavelength (Figure 2). The photodecomposition of 2,3-benzofuran would be expected if 2,3-benzofuran was sufficiently

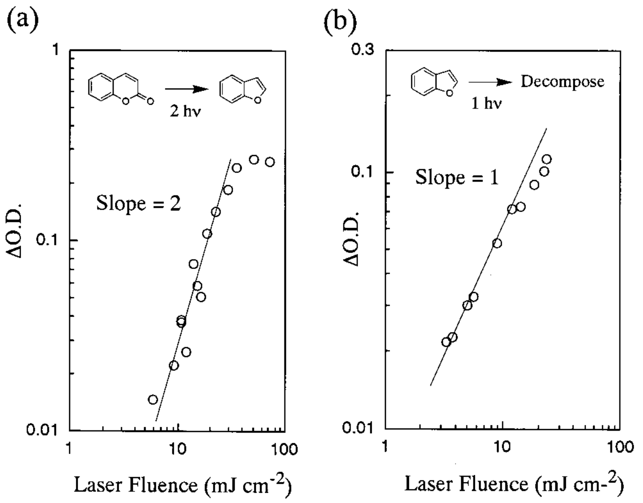

Figure 5. (a) Laser fluence dependence of the transient absorption of coumarin at 230 nm in the presence of 570 Torr of nitrogen observed at 300 ns after the laser pulse. The solid line has a slope of 2.0. (b) Laser fluence dependence of the transient absorption of 2,3-benzofuran at 300 nm observed at 300 ns after the laser pulse. The solid line has a slope of 1.0.

formed, and the apparent yield of 2,3-benzofuran would be decreased in the high-laser-fluence region.

Photolysis of 2,3-Benzofuran. The steady-state absorption spectra were used for tracing the photodecomposition reaction of the 2,3-benzofuran. The clear isosbestic points appeared in the absorption spectra after the laser irradiation (Figure 6a). The absorbance at 230 nm was decreased with laser irradiation. The unreacted coumarin was then pumped away from the reaction cell and the absorption spectrum of the residue was measured. The residue, which was deposited on the cell surface, has a broad and structureless absorption below 340 nm; however, the identification of this product was not successful. The product may be complicated mixtures of the fragmented 2,3-benzofuran.[18]

The transient absorption spectra of 2,3-benzofuran (Figure 6b,c) and the correlation between the transient and laser fluence (Figure 5b) were measured. The bleaching of 2,3-benzofuran at 230 nm was clearly observed. No absorption corresponding to the cation radical, anion radical,[19] and triplet state[20] of 2,3-benzofuran were observed, whereas a very weak emission was observed. In addition, the foreign gas efficiently suppressed the formation of the transient species (Figure 6b,c). All of the results indicated that the hot 2,3-benzofuran would mainly be formed by the ArF excimer laser irradiation.[21] The transient species at 300 ns after the laser pulse in the presence of 400 Torr of nitrogen can be a stable product (Figure 6b). The slope of the laser fluence dependencies at 300 nm (Figure 5b) was 1.0, indicating that 2,3-benzofuran was decomposed by the single-photon process via a highly vibrationally excited state. All of the results show that the saturation behavior observed in the transient absorption of coumarin (Figure 5a) is due to the further decomposition of 2,3-benzofuran by the third photon.

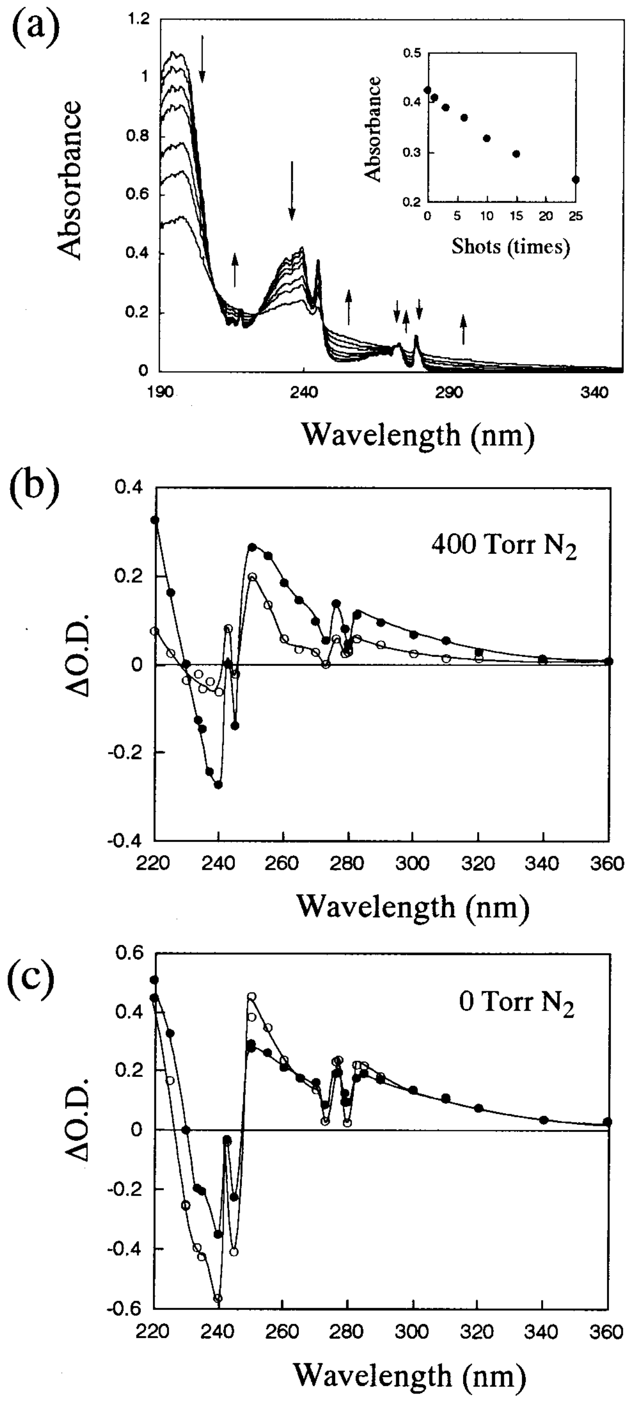

Figure 6. (a) Absorption spectral changes of 2,3-benzofuran with ArF laser irradiation. The arrow shows the increase or decrease of absorbance with laser irradiation. The inset shows the correlation between the absorbance at 239 nm and the laser shots. The experiments were performed at 296 K. (b) Time-resolved absorption spectra of 2,3-benzofuran in the presence of 400 Torr of nitrogen. The spectra were observed at 0 s (●) and 300 ns (○) after the laser pulse. Laser fluence was 25.1± 1.8 mJ cm^{-2}. (c) Time-resolved absorption spectra of 2,3-benzofuran in the absence of nitrogen. The spectra were observed at 0 s (●) and 300 ns (○) after the laser pulse. Laser fluence was 24.3 ±1.2 mJ cm^{-2}.

Conclusion

The ArF excimer laser irradiation of gaseous coumarin was examined under various conditions. The foreign gas pressure effects, laser fluence dependencies, and product identification revealed that the hot coumarin acts as an intermediate in the two-photon decarbonylation reaction. The equivalent vibrational temperature of coumarin was calculated to be 2457 K (single-photon absorption) and 4210 K (two-photon absorption).[22] The ArF excimer laser irradiation also induced a reaction similar to that observed in the flash vacuum pyrolysis at 1100 K.[4] The decarbonylation reaction of coumarin is the first example of the multiphoton reaction of a hot molecule other than hydrocarbons. The new photochemical reaction pathway of coumarin was opened by the multiphoton reaction of the hot molecules.

Acknowledgment. The present research was partially supported by a Grant-in-Aid (No. 11750720) from the Ministry of Education, Science, Sports and Culture, Japan.

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(17) Assuming that the collisional frequency is 5×10^7 Torr^{-1} s^{-1}. The concentration of coumarin is 7.8×10^{-5} M (2.1 Torr).

(18) The pyrolysis of 2,3-benzofuran was examined in a tube flow reactor. Carbon monoxide and three compounds were detected but not identified. Bruinsma, O. S. L.; Tromp, P. J. J.; de Sauvage, H. J. J.; Moullijn, J. A. *Fuel* **1988**, *67*, 334.

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(21) The equivalent vibrational temperature of 2,3-benzofuran by single-photon absorption of an ArF excimer laser light was calculated to be 2693 K. The normal mode of 2,3-benzofuran was calculated by Gaussian 94 as described in ref 22.

(22) The collisional deactivation of hot molecule before the second photon absorption was not considered in the equivalent vibrational temperature calculation. The normal modes of vibration were calculated by Gaussian 94 (HF, 6-31G(d, p)). The scaling factor of 0.91 was used for adjusting the calculated data to the experimental data. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, SGI-G94 rev. E.1; Gaussian, Inc.: Pittsburgh, PA, 1995.