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Laser Induced Biphotonic Dissociation of Nitrobenzene Derivatives in Solution

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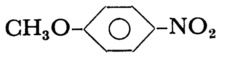
By irradiation with a focused laser beam, *p*-nitroanisole and *N*-[2-(*p*-nitrophenoxy)ethyl]aniline (**2**) in acetonitrile were found to show new reactions yielding nitroso compounds different from the case of the defocused laser beam irradiation. The laser intensity dependence of the product yield shows that the new reaction of **2** proceeds *via* a biphotonic process. The quenching effects of oxygen and *cis*-1,3-pentadiene upon the reaction rate indicate that the intermediate state is an excited singlet state.

Recently, laser induced chemical reactions have been studied by many authors, importance being attached to such multiphoton processes in the gas phase as unimolecular dissociation, ionization and sequential reactions.[1] However, reports on laser induced multiphoton reactions in the solution (at room temperature) are limited to the process with unstable products.[2]

In the present study, we have found a new phenomenon that two different kinds of stable products are obtained with the photochemical reaction of nitrobenzene derivatives in acetonitrile by changing the focusing degree of laser beam for excitation. The result seems to be a typical example of switching of laser photoreactions to yield different kinds of stable products in the solution.

Experimental

Acetonitrile (Wako, Spectroscopic grade) was used as solvent without further purification. *p*-Nitroanisole (compound **1**) (Tokyo Kasei, Extra pure) was used after recrystallization from ethanol. *N*-[2-(*p*-nitrophenoxy)ethyl]aniline (compound **2**) was offered by Prof. K. Mutai, The University of Tokyo.



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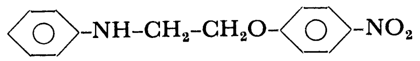

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p-Nitrosoanisole was prepared by the method of Mijs *et al.*[3]

An N_2 laser (Molectron UV-24, peak power 900 kW, pulse duration 10 ns) was used as a source of irradiation. When a laser beam is defocused, the minimum cross section of beam, S, is about 1.0×0.3 cm^2 and $S \leq 0.5 \times 0.1$ cm^2 when the laser beam is focused inside a sample cell. The incident energy per pulse was kept constant (10^{16} photons) for both cases. The repetition rate (20 Hz) and peak intensity of the exciting laser pulse were monitored with a photodiode throughout the reaction. Calibrated neutral density filters were used to attenuate the laser intensity.

Absorption spectra were measured with a Hitachi 320 spectrophotometer. Transient absorptions were measured by the apparatus reported previously.[4] Experiments were carried out at room temperature. Dielectric break down in the sample solution was not observed even for the maximum laser intensity.

Results and Discussion

The spectral change of **1** in acetonitrile by irradiation with defocused and focused beams of the N_2 laser were measured with the spectrophotometer and the results are shown in Figs. 1a) and 1b), respectively. The absorption intensity of **1** at 305 nm shows a slight decrease by the irradiation with a defocused beam, while the irradiation with a focused beam results in a large decrease of the absorption intensity and growing up of a new absorption band around 335 nm. These results show that the reactivity of **1** depends on the focusing degree of laser beam.

Similar experiments were made for **2** and the results are shown in Figs. 2a) and 2b). Mutai *et al.* concluded that a photo-Smiles rearrangement reaction occurs when **2** is irradiated with a defocused beam.[4,5] The absorption band of the photo-Smiles reaction product grows up at 390 nm (Fig. 2a)). By focusing the laser beam, however, a new band turns out to appear at 335 nm as is shown in Fig. 2b). This implies that a high density excitation induces a new reaction and produces a photoproduct other than that of the photo-Smiles rearrangement.

Both products from **1** and **2** by the irradiation with the focused laser beam have the band at 335 nm. This suggests that both products are similar to each other

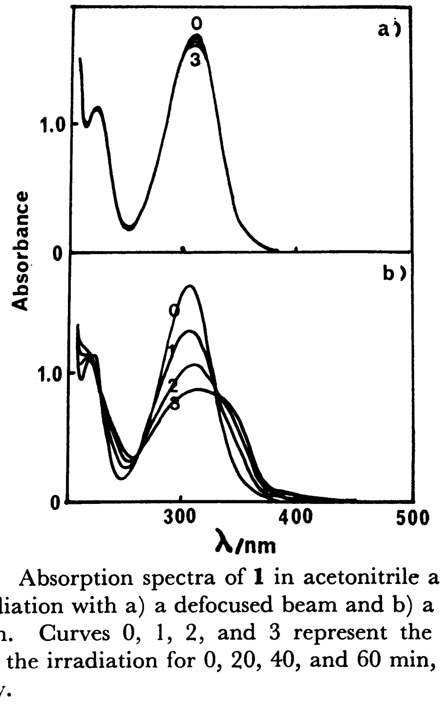


Fig. 1. Absorption spectra of **1** in acetonitrile after the irradiation with a) a defocused beam and b) a focused beam. Curves 0, 1, 2, and 3 represent the spectra after the irradiation for 0, 20, 40, and 60 min, respectively.

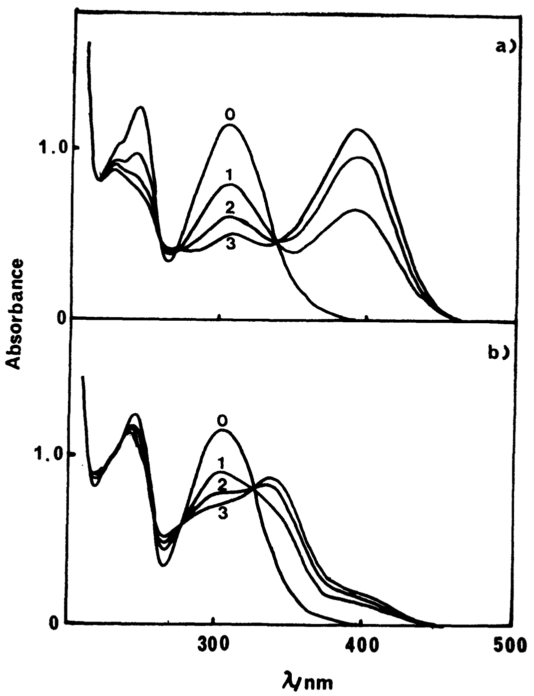


Fig. 2. Absorption spectra of **2** in acetonitrile after the irradiation with a) a defocused beam and b) a focused beam. Curves 0, 1, 2, and 3 represent the spectra after the irradiation for 0, 10, 20, and 30 min, respectively.

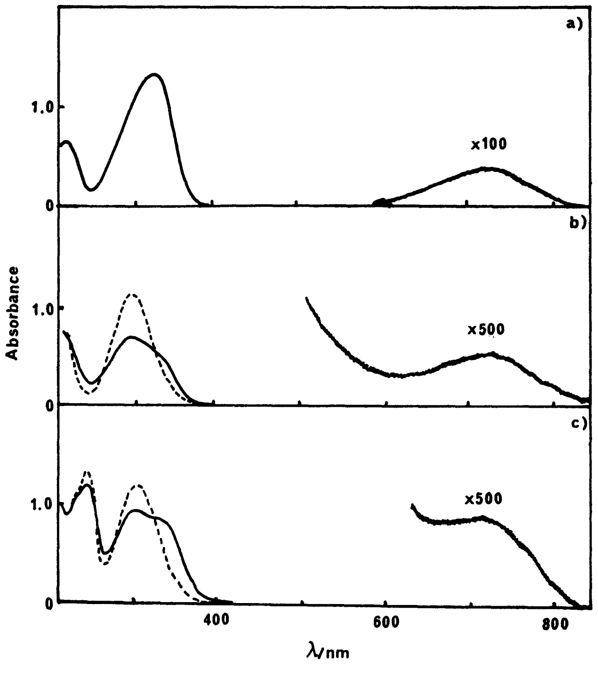
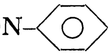
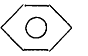


Fig. 3. Absorption spectra of *p*-nitrosoanisole and the new photoproducts from **1** and **2**. Cell thickness; 1 mm for the range of 200—500 nm and 100 mm for the range of 500—800 nm. a) The spectrum of *p*-nitrosoanisole. b) The spectrum of **1** after the irradiation. c) The spectrum of **2** after the irradiation. (Broken lines; the spectra before the irradiation.)

in their electronic structures. Since the 335 nm bands remain unchanged by addition of O_2 to the sample solutions or storing them in air for a few days, the new products responsible for the 335 nm bands are stable compounds. The process is unimolecular because the relative rate of the reaction is independent of the concentrations of the parent molecules.

In order to identify the new products which have the band at 335 nm, their spectra were measured in the wavelength region of 850—200 nm and a weak band was observed at 730 nm (Fig. 3). This finding suggests that the new products are nitroso compounds. For the purpose of comparison, the absorption spectrum of *p*-nitrosoanisole chemically prepared was measured and the result is shown in Fig. 3a). The spectrum is similar to the spectra of the products from **1** and **2** by the irradiation with the focused laser beam. This leads us to the conclusion that nitroso compounds are produced by the dissociation of an oxygen from the nitro group. Similarity of the absorption spectrum of the nitroso compound produced from **2** to that of *p*-nitrosoanisole is explained by the fact that conjugation between the ON--O-CH_2- and -HN- moieties is prohibited by the alkyl bridge.

The laser intensity dependence of the yield of the nitroso compound produced from **2** was studied. The

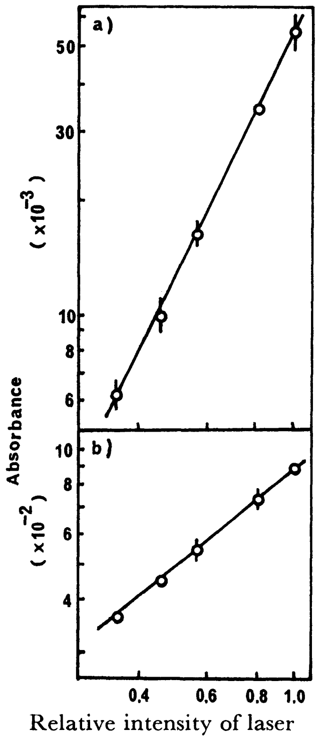


Fig. 4. The dependence of the yield of the photoproducts from **2** on the laser intensities. a) A plot of the logarithm of the absorbance of the nitroso compound at 335 nm *vs.* the laser intensity. The acetonitrile solution of **2** was irradiated with a focused beam for 5 min after bubbling with O_2 gas for 30 min. b) A plot of the logarithm of the absorbance of the final product of the photo-Smiles reaction at 390 nm *vs.* the laser intensity. The acetonitrile solution of **2** was irradiated with a defocused beam for 3 min.

logarithmic plot of the absorbance at 335 nm against the laser beam intensity shows a straight line with a slope of 2.0 (Fig. 4a)). This shows that the reaction proceeds *via* a biphotonic process. On the other hand, the laser intensity dependence of the yield of the final product in the photo-Smiles reaction shows a straight line with a slope of about 0.8, indicating that the reaction proceeds *via* a one photon process.

Considering the fact that the molar extinction coefficients of the nitroso compound at 335 nm and the final product of the photo-Smiles reaction at 390 nm are nearly equal, comparison between Figs. 2a) and 2b) induces the conclusion that the relative yield for the biphotonic process exceeds that for the one photon process when the laser beam is focused. This indicates that the new reaction proceeds *via* a consecutive two step process rather than a simultaneous two-photon process, since the transition probability of simultaneous two-photon absorption is much smaller than that of one photon absorption even in the resonance condition.[6]

The rate of reaction by the irradiation with a focused laser beam was not affected markedly by the addition of triplet quenchers (O_2 gas bubbled for 30 min or *cis*-1,3-pentadiene (0.1 mol dm^{-3})). This indicates that the intermediate state for the two step process is not the lowest triplet state with the lifetime of about 70 ns,[7] but an excited singlet state.

The biphotonic dissociation caused by the irradiation of the 337 nm laser beam indicates that an excited state existing at 6—7 eV above the ground state is responsible for the reaction. According to the calculation based on the CNDO/S-CI method[8] or the composite molecule method,[9] a state locally excited within the NO_2 group is located at 6.6 eV for nitrobenzene. This state has large transition component from a nonbonding MO to an antibonding MO on the NO bond as is shown in Fig. 5. The antibonding character of the NO bond is expected to result in the cleavage of the bond.

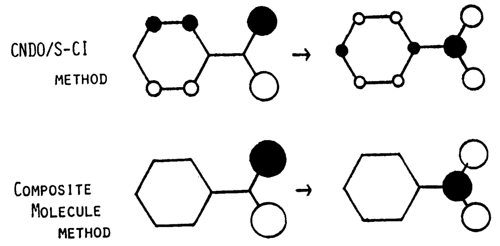


Fig. 5. The lower and upper MO corresponding to the local excitation within the nitro group.

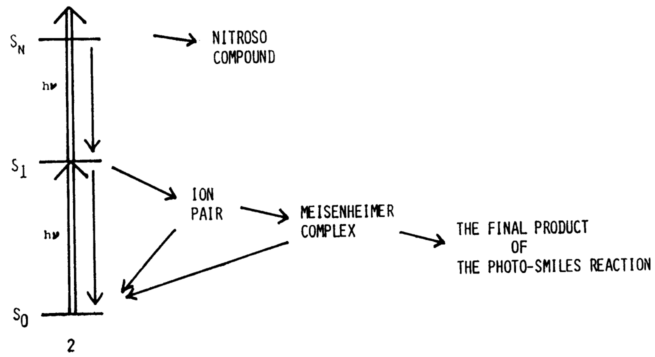


Fig. 6. The reaction scheme of **2**.

Figure 6 shows the most probable scheme of photoreaction of **2**. The photo-Smiles reaction initiated with a defocused beam starts from the S_1 state and proceeds *via* an ion pair and a Meisenheimer complex to the final product.[4] This conclusion is confirmed by the fact that the yields of the two intermediates show linear dependences on laser intensity. By the irradiation with a focused laser beam, an effective excitation from S_1 to S_n state competes with the process of the photo-Smiles reaction and results in the production of the nitroso compound.

Nitrobenzene derivatives are known to have a large decay rate of the excited singlet state resulting in a nonfluorescent character. Thus, the focusing of laser beam seems to be necessary for the occurrence of the second absorption in a very short time of picosecond order. In turn, the short lifetime of intermediate state is consistent with the fact that the observed dependence of the amount of the produced nitroso compound on the laser intensity is quadratic, because a long lifetime of intermediate state would bring an approximately linear dependence on laser intensity.

Hasting and Matsen reported that nitrobenzene was converted into nitrosobenzene in the vapor phase by the irradiation of d.c. arcs with metal electrodes.[10] The detailed experimental conditions including the wavelength distribution of the irradiating source are not shown in their paper and the reaction mechanism is not clear. The present study has confirmed that nitro compounds can be converted into relating nitroso compounds *via* a two step process by the irradiation with light at 337 nm with the photon density of about 10^{17} photon cm^{-2} pulse^{-1} and has presented a typical example of switching between different chemical reactions in solution by changing the focusing degree of a laser beam.

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6) According to a rough numerical estimation, when laser intensity is about 10^{17} photon cm^{-2} pulse^{-1}, the number of photons absorbed by a sample molecule at an ordinary simultaneous two-photon absoption band is about 10^{-10} photon pulse^{-1}, but that at a one photon absorption band is about

one photon pulse^{-1} (I. Webman and J. Jortner, *J. Chem. Phys.*, **50**, 2706 (1969)). Thus, the transition probability of two-photon process is much smaller than that of one photon process, although the former becomes about 7 orders larger when excitation energy coincides with a transition energy of one photon absorption band (J. E. Bjorkholm and P. F. Liao, *Phys. Rev. Lett.*, **33**, 128 (1974)).

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