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DIRECT EVIDENCE OF PHOTODISSOCIATION OF CARBAZOLE VIA THE HIGHER EXCITED TRIPLET STATE BY A DOUBLE EXCITATION METHOD

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Photodissociation of carbazole is investigated in cyclohexane at room temperature by a double excitation method which utilizes two successive excitation light pulses; the first flash L_1 is used to populate the lowest excited triplet state T_1 of carbazole and the second flash L_2 to excite T_1 into the higher excited triplet state T_n. Selective $T_n \leftarrow T_1$ excitation of carbazole by L_2 brings about both the formation of carbazyl radical and the depletion of T_1. Therefore, it is concluded that carbazyl radical is formed via T_n.

Biphotonic dissociations of various solutes and solvents have been studied almost exclusively in rigid solvents at low temperature, and several mechanisms have been proposed.$^{1-6)}$ Biphotonic dissociation of a solute in fluid solution has recently been reported by Borovkova et al.$^{7)}$ who studied the photodissociation of carbazole in hexane by μs flash and ns laser photolysis.

Whether the process of photodissociation is monophotonic or biphotonic has usually been determined by examining the dependence of the rate of photodissociation on the intensity of incident light I; the rates of monophotonic and biphotonic dissociation are proportional to I and I^2, respectively. However, such examination does not clarify whether the second photon in biphotonic process is absorbed by the lowest excited triplet state T_1 or other transient species.

In the present letter, we propose a method which can directly determine whether the transient species absorbing the second photon is T_1 or others. This method has been termed as a double excitation method, because it utilizes two successive excitation light pulses.$^{8)}$ In order to confirm the photodissociation via the higher excited triplet state T_n, the photodissociation of carbazole is reinvestigated in cyclohexane by this method.

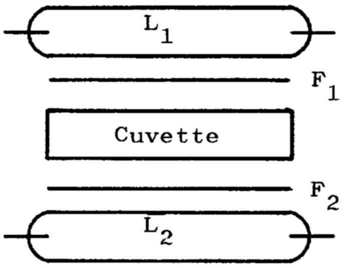

Fig.1 The flash irradiation apparatus.

The flash irradiation apparatus used for the double excitation method is shown in Fig. 1. The sample cell, 10 mm in diameter and 100 mm in length, was placed in parallel between two flash lamps. The input energy of each flash lamp was 144 J and fwhm was about 10 μs. The first flash lamp L_1 is filtered by a system F_1 consisting of Toshiba UV-D25 band path filter and a solution filter (K_2CrO_4, 0.27g and N_2CO_3, 1g in 1 dm^3 aqueous solution). The second lamp L_2 is filtered by a system F_2 consisting of a plastic plate (cut off $\lesssim$ 370 nm) and a solution filter (I_2 saturated CCl_4 solution). The transmittances of above filter systems are shown in Fig. 2. L_1 is used to populate T_1 and L_2 is used to excite T_1 into T_n. L_2 is fired after flashing of L_1 with an appropriate delay time Δt ($=t_2 - t_1$) which is controlled by an electronic delay unit. A typical oscillogram showing the profiles of two successive flashes is shown in Fig. 3c.

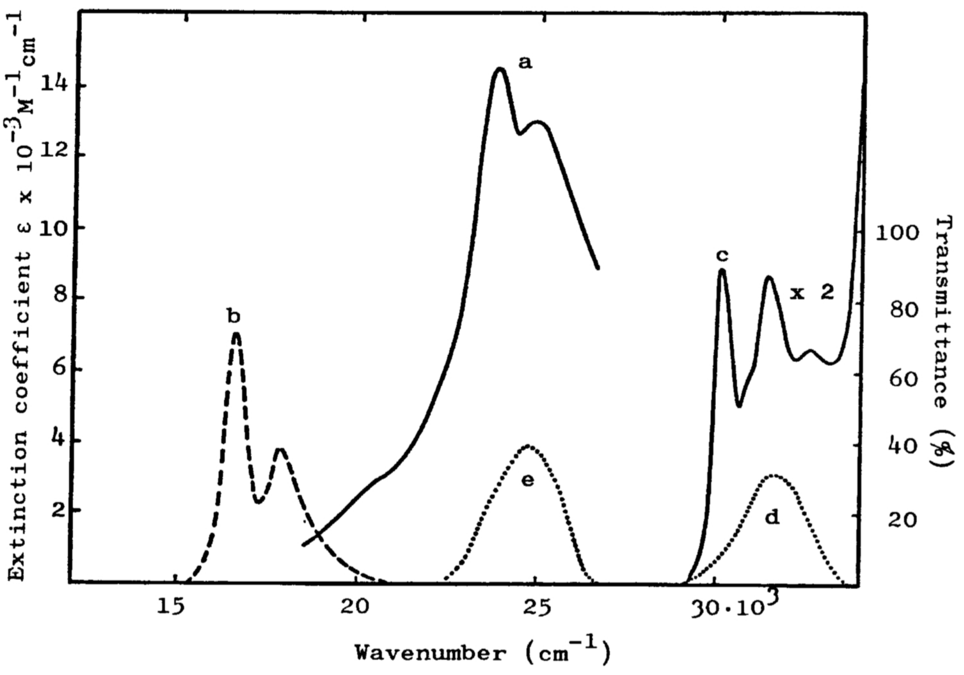

Fig.2 Absorption spectra in cyclohexane and transmittances of filters employed. a) $T_n \leftarrow T_1$ absorption spectrum, b) absorption spectrum of carbazyl radical, c) $S_1 \leftarrow S_0$ absorption spectrum, d) transmittance of filter system F_1, e) transmittance of filter system F_2.

Carbazole (Zone refined, Tokyo Kasei) was treated by thin layer chromatography and sublimed twice in vacuo. Cyclohexane solutions were degassed by freeze-pump-thaw cycles. All measurements were made at 25°C.

By a conventional flash photolysis of carbazole in cyclohexane, two transient absorption spectra shown in Fig. 2 were observed. The spectrum a) decays as a first order process with the rate constant 6 x 10^3 s^{-1} and identical with $T_n \leftarrow T_1$ absorption spectra of carbazole.[7,9,10] The spectrum b) decays as a second order process with the rate constant k/ε = 7 x 10^5 cm s^{-1} at 600 nm and is similar to the spectrum of carbazyl radical.[7,11]

Figure 3 shows typical oscillograms concering the double excitation method. Single excitation by L_1 at time t_1 gives the oscillograms shown by dashed lines. Solid lines correspond to the successive double excitations by L_1 at time t_1 and L_2 at time t_2. The oscillograms shown in Fig. 3a were measured at 420 nm and

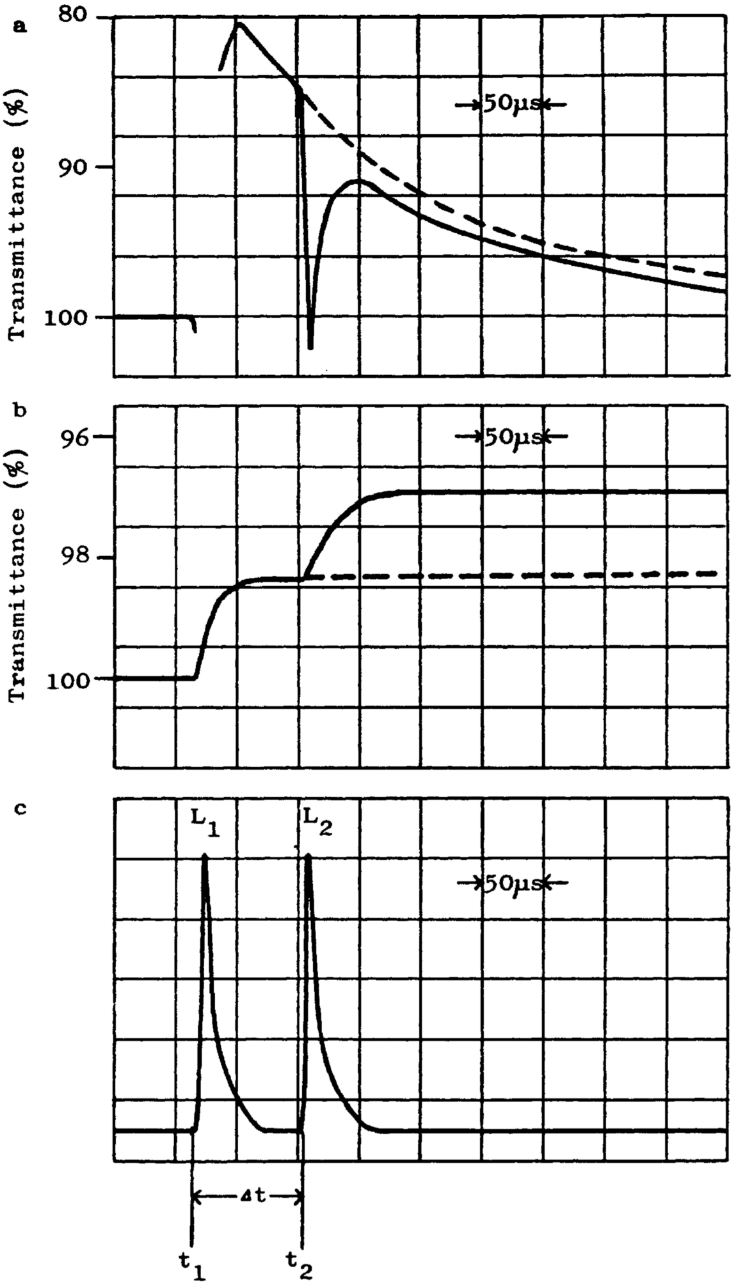

Fig.3 Typical oscillograms obtained by the double excitation method. a) the change of transmittance of $T_n \leftarrow T_1$ absorption measured at 420 nm, b) the change of transmittance of the absorption of carbazyl radical measured at 600 nm, c) an oscillogram showing the profiles and the time interval of two successive excitation pulses.

indicate the decay of T_1. The oscillograms shown in Fig. 3b were measured at 600 nm and indicate the decay of carbazyl radical. In the case of the successive double excitation, the transmittance increases at 420 nm and decreases at 600 nm after the irradiation with L_2. The spectrum of the increment of absorption in the neighborhood of 600 nm is the same as that of carbazyl radical. Single excitation by L_2 causes no absorption change. Therefore, we can conclude that carbazyl radical is formed via T_n, because L_2 with filter system F_2 excite only T_1 into T_n.

However, it is still unknown whether carbazyl radical is formed directly by the self-dissociation in T_n or indirectly through the energy trnsfer from T_n to solvent molecule.

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