

FLUORESCENCE QUENCHING PROCESSES OF CARBAZOLE-AMINE
SYSTEMS AS REVEALED BY LASER PHOTOLYSIS METHOD

Hiroshi MASUHARA, Yuichi TOHGO, and Noboru MATAGA
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

The fluorescence quenching mechanisms of carbazole in acetonitrile were studied in detail by the laser photolysis method. Proton transfer and hydrogen atom transfer in the excited state were observed in the case of the triethylamine quencher, while ionic photodissociation due to electron transfer was confirmed in the case of the *N,N*-dimethylaniline quencher. However, no transient was detected in the case of the quenching by pyridine.

The dynamics of the excited proton donor-acceptor system has been investigated in detail by fluorescence measurements.^{1,2)} A new fluorescence band due to the ion formed by the intermolecular proton transfer reaction between the excited proton donor and an alkyl amine was observed while, in the case of the proton donor-pyridine systems, the fluorescence of the proton donor was quenched but any new emission was not detected. A conventional flash photolysis study³⁾ and some energetic considerations⁴⁾ indicate that the hydrogen atom transfer in the excited state plays an important role in the fluorescence quenching process of the latter systems. However, it was not possible by the conventional flash photolysis method to confirm directly the formation of radicals due to the hydrogen atom transfer in the above systems. Accordingly, laser photolysis studies on these systems in nsec or psec time regions seem to be necessary. In this paper, the results obtained for carbazole by the nsec laser photolysis method will be reported.

The laser photolysis apparatus for the nsec transient absorption and photocurrent measurements is the same as used before.⁵⁾ Carbazole was chromatographed on activated alumina using petroleum benzine for elution. Purified *N*-ethylcarbazole was kindly supplied by Dr. S. Tazuke of Tokyo Institute of Technology. Acetonitrile (Merck, Uvasol) was distilled before use. 2-Methyltetrahydrofuran (MTHF), triethylamine (TEA), *N,N*-dimethylaniline (DMA) and pyridine were purified by the ordinary procedures and stored under deaerated condition. All solutions for measurements were deaerated by freeze-pump-thaw cycles.

The transient absorption spectra of the carbazole-TEA-acetonitrile system are shown in Fig.1. The spectra at 70 nsec after the Q-switching show absorption bands at 630 nm and 720 nm, whose decay times are different from each other. Since the 630 nm band could not be observed in the *N*-ethylcarbazole systems and is similar to the absorption band of carbazyl radical,⁶⁾ the *N*-H bond of carbazole is concluded to be broken. This radical was confirmed to be produced through one photon process from

the intensity effect of the exciting pulse. Moreover, we have confirmed that the 630 nm band is not observed in the transient spectra of the carbazole-acetonitrile system, where only the absorption band of carbazole cation radical produced by the biphotonic process was detectable. Therefore, the carbazyl radical seems to be formed by the hydrogen atom transfer from the excited carbazole to TEA. The assignment of the 720 nm band is not very clear at the present stage of investigation.

As previously reported,¹⁾ the carbazole-TEA-acetonitrile system shows a new red-shifted fluorescence band due to the carbazole anion formed by the proton transfer from the excited carbazole to TEA. The rise time of the red-shifted fluorescence was very short, i.e. the rise curve was the same as the time integrated function of the laser pulse, and its decay time was ca. 20 nsec. We have confirmed also that the rise curve of the 630 nm band of carbazyl is identical with the time integrated function of the exciting pulse, not corresponding to the decay curve of the red-shifted fluorescence. Hence the carbazyl radical is not formed through the excited carbazole anion but the proton transfer and the hydrogen atom transfer to TEA seem to be competing with each other in the excited carbazole-TEA pair.

In contrast to the above results, the fluorescence of N-ethylcarbazole is hardly quenched by TEA and its $S_n + S_1$ spectra similar to those observed in n-hexane,⁷⁾ were obtained. No other transient was detected.

The fluorescence of carbazole is completely quenched by pyridine while that of N-ethylcarbazole is not. In order to examine whether the carbazyl radical is formed in the quenching process by pyridine, we have made a laser photolysis study on the carbazole-pyridine-acetonitrile system. However, no transient absorption spectra were observed with the same experimental method and under the same conditions as the above case of TEA, which suggests a quenching mechanism different from the above one. Namely, the fluorescence quenching in this case cannot be ascribed simply to the formation of radicals due to the hydrogen atom transfer from the excited carbazole to pyridine. A rapid deactivation process where the N-H hydrogen atom might play some role but no effective dissociation to radicals occurs, must be assumed for the interpretation of this result.

In addition to the above studies we have examined the carbazole-DMA-acetonitrile system since the fluorescence quenching occurs in this case, too. The transient absorption spectra obtained by the laser photolysis are shown in Fig.2. We have examined also the N-ethylcarbazole-DMA-acetonitrile system and obtained spectra quite similar to those of the carbazole-DMA-acetonitrile system. The band at 450-470 nm is similar to that of the DMA cation. For the assignment of the band at 700 nm, N-ethylcarbazole in MTHF glass at 77°K was irradiated with γ -ray. Since the irradiation of MTHF matrix gives usually solute anion,⁸⁾ the obtained spectra can be assigned to the N-ethylcarbazole anion. Since the absorption band at 700 nm in the transient spectra is similar to that of the N-ethylcarbazole anion, ionic photodissociation due to the electron transfer from DMA to the excited carbazole is concluded to occur in these systems. This result is quite similar to the case of the quenching of the aromatic hydrocarbon fluorescence by DMA in polar solvents, where the electron transfer from DMA to the excited aromatic hydrocarbon occurs.

Thus, the proton transfer as well as the hydrogen atom transfer is important

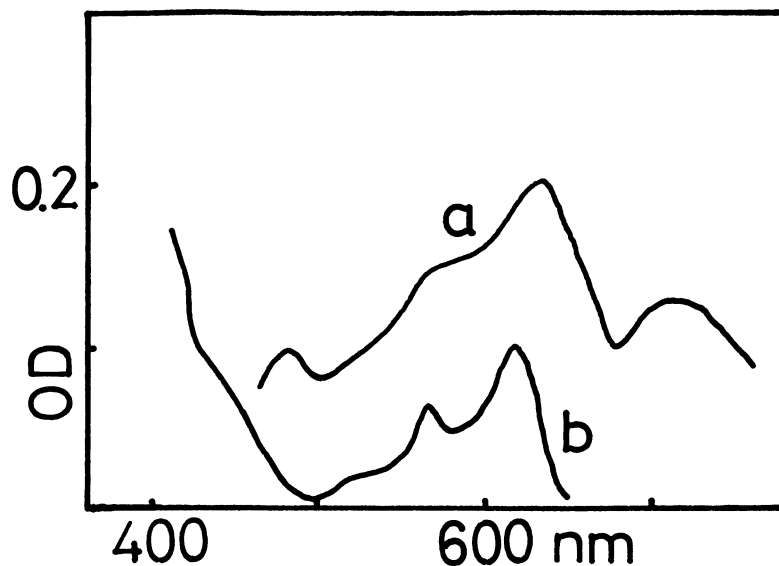


Fig.1. Transient absorption spectra of the carbazole-TEA-acetonitrile system.
 [carbazole]= 3.8×10^{-3} M, [TEA]=0.65 M.

(a) The delay time after the Q-switching is 70 ± 15 nsec. (b) The electronic spectra of carbazyl radical obtained by radiation-chemical method. See ref. 6.

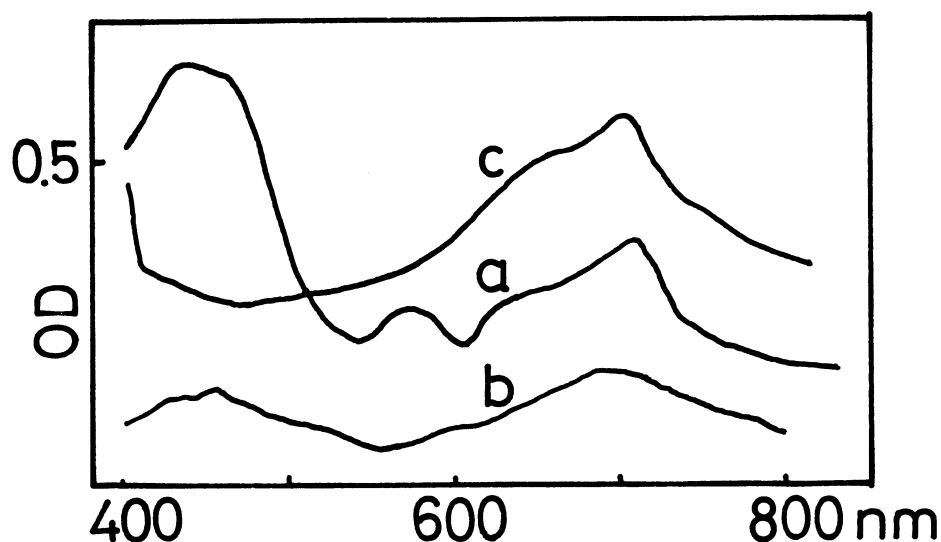


Fig.2. Transient absorption spectra of carbazole as well as N-ethylcarbazole quenched by DMA in acetonitrile. (a) [carbazole]= 3.7×10^{-3} M, [DMA]=2.1 M, at 180 nsec after the Q-switching. (b) [N-ethylcarbazole]= 4.4×10^{-3} M, [DMA]=1.1 M, at 150 nsec after the Q-switching. (c) The electronic spectra of the intermediate obtained at 77°K by irradiating N-ethylcarbazole in MTHF with ^{60}Co γ -ray. Total dose was 1×10^5 rad.

in the case of the quenching by TEA, while electron transfer is the main process in the case of the DMA quencher. However, the rapid radiationless conversion to the ground state is the predominant process in the case of the quenching by pyridine.

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