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The Formation of Transient Aromatic Ions in Solutions by the Flash Illumination

Kiyoshi KAWAI, Naoto YAMAMOTO and Hiroshi TSUBOMURA

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka

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Flash illumination of an oxygen-free acetonitrile solution containing *p*-dimethoxybenzene (DMB) and *s*-trinitrobenzene or chloranil gave a transient absorption spectrum of DMB cation. The decay of the transient absorption spectra follows the second-order reaction kinetics proving that the decay is brought about by the recombination of the anion and the cation after the flash illumination. The formation of the ion-pair may be explained as follows:

$$\begin{array}{l} \mathrm{A} + h\nu \longrightarrow \mathrm{A}^* \\ \mathrm{A}^* + \mathrm{D} \longrightarrow \mathrm{A}^- \text{—} \mathrm{D}^+ \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\quad \mathrm{A}^-_{\text{solv.}} + \mathrm{D}^+_{\text{solv.}} \longrightarrow \mathrm{A} + \mathrm{D} \end{array}$$

It was found by Leonhardt and Weller that the fluorescence of perylene in non-polar solvents was quenched by addition of anilines or amines and new fluorescence bands appeared, which were ascribed to the charge transfer fluorescence (CT-fluorescence) emitted from the excited CT-complex formed by an excited perylene and an amine in the ground state.[1,2]

In polar solvents, such CT-fluorescence was not observed and by the flash illumination a transient absorption spectrum attributed to perylene anion was observed. This anion was assumed to be formed *via* the CT-complex of the excited perylene with the ground state amine or *via* a solvent-shared ion pair ($\mathrm{A}^-_{\text{solv.}}\cdots\mathrm{D}^+_{\text{solv.}}$).[3]

Though this is a very interesting result, there had been a few reports[1-4] concerning this problem. It is our opinion that further work is needed in order to prove the formation of an ion pair, $\mathrm{A}^-_{\text{solv.}}$ and $\mathrm{D}^+_{\text{solv.}}$, by the mechanism proposed by Weller.

Recently, we have found that *N,N,N'N'*-tetramethyl-*p*-phenylenediamine (TMPD) and α-methylnaphthalene, or other naphthalene derivatives, show similar fluorescence spectrum attributable to the CT-fluorescence in non-polar solvents.[5] In polar

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[1] H. Leonhardt and A. Weller, *Ber. Bunsenges. Physik. Chem.*, **67**, 791 (1963).

[2] H. Leonhardt and A. Weller, *Z. Physik. Chem. N. F.*, **29**, 277 (1961).

[3] H. Knibbe, K. Röllig, F. P. Schäfer and A. Weller, *J. Chem. Phys.*, **47**, 1184 (1967); H. Knibbe, D. Rehm and A. Weller, *Ber. Bunsenges. Physik. Chem.*, **72**, 257 (1968).

[4] M. Koizumi and H. Yamashita, *Z. Physik. Chem. N. F.*, **57**, 103 (1968).

[5] N. Yamamoto, Y. Nakato and H. Tsubomura, This Bulletin, **40**, 451 (1967).

solvents, the same system showed transient absorption spectra assigned to the TMPD cation and naphthalene in the triplet state.[6] This result indicates that excited TMPD and ground state naphthalene derivatives partly form TMPD cation (and probably α-methylnaphthalene anion, though its spectrum was not observed), and partly form the triplet state of α-methylnaphthalene by energy transfer. We have confirmed that the yield of the cation in solution is independent of the light intensity but dependent on the total light input. This finding provides evidence for the generation of the cation by a single-photon process and therefore supports Weller's mechanism.

It was thought to be interesting to find more examples of the ion-pair formation from the donor-acceptor pairs by the flash technique. In the present paper some of the results are reported.

Experimental

The instrument used for the flash illumination has been described elsewhere.[7] The electric energy of a flash was about 250 J and the flash light had the duration time of about 3μsec. A cylindrical quartz sample cell 20 cm long and 1.5cm in diameter was used. Two photolysis flash lamps were made of quartz tube, 20 cm long and 1.0 cm in diameter, with tungsten-electrodes at both ends. These tubes were filled with argon to a pressure of about 100 mmHg. Oxygen in the sample solution was removed by bubbling highly purified nitrogen gas. *p*-Dimethoxybenzene (DMB) used was recrystallized from ethanol and was sublimed. Chloranil was sublimed in vacuum. Acetonitrile was refluxed with phosphorus pentoxide and distilled. Ethanol was dried with calcium oxide and barium oxide and then distilled.

The spectra shown in Fig. 4 were recorded with Cary Spectrophotometer Model 15. All other spectra were obtained by the photographic method followed by recording with a Nalumi microphotometer NLM V11.

Results

***p*-Dimethoxybenzene-*s*-Trinitrobenzene System.** Flash illumination of *s*-trinitrobenzene (2×10^{-3} M) in an oxygen-free acetonitrile solution containing 10^{-3} M *p*-dimethoxybenzene (DMB) gave a transient absorption spectrum showing maxima at 456 mμ and 431 mμ and a shoulder at 414 mμ (Fig. 1a). The transient absorption spectrum was detectable by the photographic measurement until about 50 μsec after the flash illumination. The flash light was filtered by a highly concentrated DMB solution so that only the acceptor molecule, trinitrobenzene, was excited. The sample solution showed no absorption band ascribable to the CT-complex between DMB and trinitrobenzene. In the absence of DMB, no transient absorption spectrum was observed by the flash irradiation of trinitrobenzene in acetonitrile. No transient absorption spectrum attributable to DMB cation was observed by the flash illumination of DMB and trinitrobenzene in non-polar solvents such as benzene or methylcyclohexane.

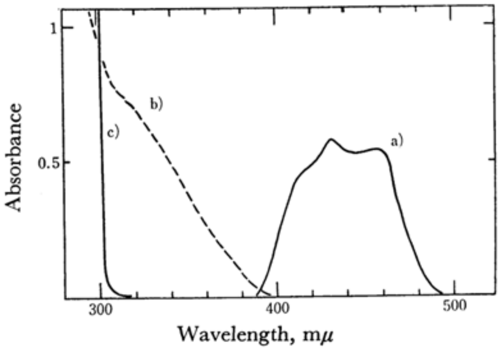

Fig. 1.
(a) Transient absorption spectrum caused by the flash illumination of *s*-trinitrobenzene (2×10^{-3} M) and *p*-dimethoxybenzene (10^{-3}M) in an acetonitrile solution at room temperature. A concentrated *p*-dimethoxybenzene solution was used as a filter.
(b) Absorption spectrum of *s*-trinitrobenze in acetonitrile solution.
(c) Absorption spectrum of *p*-dimethoxybenzene in acetonitrile solution.

***p*-Dimethoxybenzene - Chloranil System.** In the case of the flash illumination of an oxygen-

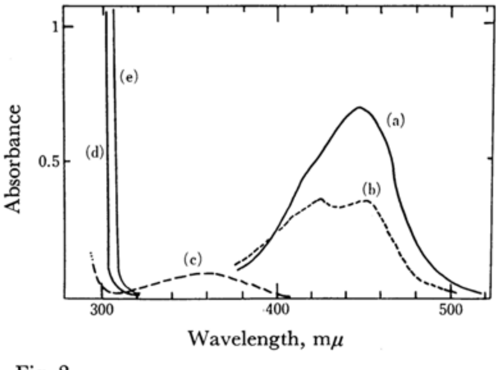

Fig. 2.
(a) Transient absorption spectrum caused by the flash illumination of chloranil (10^{-4}M) and *p*-dimethoxybenzene (10^{-3}M) in an acetonitrile solution.
(b) The same spectrum as above in an ethanol solution.
(c) Absorption spectrum of chloranil in an ethanol solution.
(d) Absorption spectrum of *p*-dimethoxybenzene in acetonitrile solution.
(e) Absorption spectrum of glass filter.

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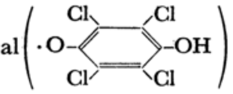
[6] Y. Nakato, N. Yamamoto and H. Tsubomura, This Bulletin, **40**, 2480 (1967).

[7] N. Yamamoto, Y. Nakato and H. Tsubomura, *ibid.*, **39**, 2603 (1966).

free acetonitrile solution containing about 10^{-3} M DMB and 10^{-4} M chloranil, a transient absorption spectrum was observed with maxima at 446 mμ and a shoulder near 420 mμ as shown in Fig. 2a. A glass filter was used so that only chloranil was excited. The sample solution showed no characteristic band of the CT-complex of DMB and chloranil. The flash illumination of a solution containing only chloranil gave a transient absorption spectrum different from that shown in Fig. 2(a), which may probably be attributable to the semiquinone radical  formed by the hydrogen abstraction from solvent on account of the resemblance of the spectrum with that of *p*-benzosemiquinone.

The change of the absorbance of the transient spectrum of Fig. 2(a) was followed by the photographic method until about 300 μsec after the flash illumination. If the transient species formed by the flash illumination is assumed to decay by the second-order reaction kinetics, the absorbance (a) may be represented as follows:

$$\frac{1}{a} = kt + c \quad (k, c\text{: constant, } t\text{: time})$$

Figure 3 shows that the above relation holds well for the absorbance at 446 mμ.

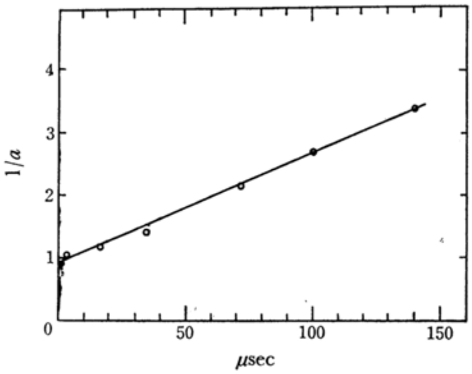


Fig. 3. Relation between the reciprocal of the absorbance (a) of the transient absorption spectrum shown in Fig. 2(a) and the time after the flash. The absorption was measured at 446 mμ.

In the case of an ethanol solution of chloranil and DMB, a flash illumination gave an absorption spectrum with maxima at 428 mμ and 452 mμ and a shoulder at 408 mμ (Fig. 2b).

Spectra of DMB$^+$ and Chloranil$^-$. In order to obtain the spectrum of DMB cation (DMB$^+$), DMB was added to an acetonitrile solution containing a small amount of antimony pentachloride at room temperature. The yellow solution thus obtainde showed a spectrum with maxima at 433 mμ and 458 mμ and a shoulder near 410 mμ as shown in Fig. 4a. The ESR spectrum obtained coincides well with that of DMB$^+$ measured by Sullivan and Forbes in a sulfuric acid solution of DMB.[8] The visible absorption spectrum (Fig. 4a) also agrees with that of DMB$^+$ formed by the photolysis of DMB in the 1 : 1 mixture of concentrated sulfuric and acetic acid at 77°K.[9]

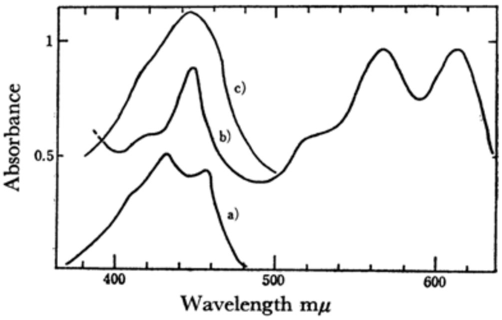


Fig. 4.
- (a) Absorption spectrum of *p*-dimethoxybenzene cation formed in the acetonitrile solution containing a small amount of antimony pentachloride.
- (b) Absorption spectrum of an acetonitrile solution of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine and chloranil.
- (c) Reproduction of curve (a) of Fig. 2.

Figure 4 (b), in the 400—500 mμ region shows the spectrum of chloranil anion prepared by the chemical reduction of chloranil with tetramethyl-*p*-phenylenediamine (TMPD) in the acetonitrile solution at room temperature. The two maxima at 448 mμ and 422 mμ agree with the absorption spectrum of chloranil anion obtained by reducing chloranil with sodium in tetrahydrofuran solution.[10] The spectrum beyond 500 mμ is obviously that for the cation of TMPD.[7]

Discussion

The spectra shown in Fig. 1(a) and Fig. 4(a) agree well in the positions of their maxima and shoulders. If we take into acount of the fact that Fig. 1(a) was obtained by the photographic method followed by recording with a microphotometer and Fig. 4(a) was obtained by the Cary spectrophotometer, we may conclude that the identity of the spectra shown in Fig. 1(a) and Fig. 4(a) are fairly good. These results indicate that DMB

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[8] W. H. Forbes and P. D. Sullivan, *Canad. J. Chem.*, **44**, 1501 (1966).

[9] H. Tsubomura, K. Kimura, H. Yamada and M. Kato, *Tetrahedron Letters*, **47**, 4217 (1965).

[10] H. Kainer and A. Überle, *Chem. Ber.*, **88**, 1147 (1955).

cation was formed by the flash illumination of *s*-trinitrobenzene in the acetonitrile solution containing DMB and *s*-trinitrobenzene. The formation of DMB cation radical (DMB^+) may be explained by the same mechanism as that proposed by Weller *et al.*[2]:

$$\begin{aligned} A + DMB \xrightarrow{h\nu} A^* + DMB &\longrightarrow (A^* \cdots DMB) \text{ or } \\ & (A^{\delta-} \cdots DMB^{\delta+}) \\ &\longrightarrow A^-_{\text{solv.}} + DMB^+_{\text{solv.}} \end{aligned}$$

A: *s*-trinitrobenzene (or chloranil)

No spectrum attributable to trinitrobenzene anion was observed. This result shows that trinitrobenzene anion is either very unstable at room temperature or has no absorption band in the visible region.

In the case of DMB-chloranil system, the absorption spectrum obtained (Fig. 2a) is considerably different from that of DMB^+. It seems obvious that this spectrum represent the sum of the absorption spectra of DMB^+ and chloranil anion from the comparison of curves (a), (b) and (c) of Fig. 4.

As stated before, the decay of the transient absorption spectra follows the second order reaction kinetics (Fig. 3). The fact proves that the decay is brought about by the recombination of the anion and the cation after the flash illumination.

In the case of the flash illumination of chloranil in the ethanol solution containing DMB and chloranil, only the transient DMB^+ spectrum appeared, indicating that the chloranil anion is very short-lived in the ethanol solution. To confirm it, the acetonitrile solution containing 10^{-4} M chloranil, 5×10^{-1} M ethanol, and 10^{-3} M DMB was flash illuminated. After the flash illumination the transient spectrum was identical with that shown in Fig. 2 (a) for a time shorter than about 20μsec, then the shape of the transient spectrum gradually changed until about 50μsec after the flash, and finally became identical with that shown in Fig. 2 (b). This experiment shows that chloranil anion formed by the flash illumination reacts very quickly with ethanol.

From the experimental results stated above, it has been unambiguously settled that the cation of *p*-dimethoxybenzene is formed by the flash illumination of it with some acceptors (*s*-trinitrobenzene or chloranil), in polar solvents such as acetonitrile or ethanol. It is well known that these molecules form the charge transfer complexes. But in our experiment the concentrations are so low that essentially all molecules are free from complex formation. In non-polar solvents, no transient ions were observed by similar flash experiments. Leonhardt and Weller showed that the excitation of a donor resulted in the formation of a transient ion of the donor. Our results have shown that the excitation of acceptors also leads to the formation of the transient donor cation.