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Photo-Ionization of Molecules in Solutions. VI. Studies on the Photocurrent Arising from the Flash-Excitation of Aromatics in Solutions

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A technique is described for the study of the photocurrent due to the transient ionic species produced by the flash photolysis of aromatics in solutions at room temperature. The technique has proved to give valuable information in a way complementary to conventional flash spectrometry. The photo-ionization of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine was studied by this method in polar and non-polar solvents. The photocurrents of the solutions of some electron donor-acceptor systems were also measured, and the results were compared with that obtained from flash spectrometry. The recombination rate constants of the ionic species were estimated from the decay of transient photocurrents.

Flash spectroscopy is a powerful tool for studies of chemical reaction intermediates, including unstable ionic species.

The photo-ionization of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) has been studied extensively by steady state illumination in low-temperature matrices and by flash spectroscopy at room temperature. The photo-ionization was shown to

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take place by the two-step process, with the triplet state as the intermediate.[1-5]

By flash spectrometry for the intermolecular electron-transfer processes between an electron donor (D) and acceptor (A), Leonhardt and Weller found that the cation (D^+) from a donor molecule and the anion (A^-) from an acceptor molecule were formed momentarily by photo-excitation in a polar solvent, and disappeared immediately by the recombination process.[6,7] This process is closely related with the mechanisms of fluorescence quenching in polar solutions. More evidence on the formation of ionic intermediates has been obtained recently by photo-excitation of donor-acceptor systems in polar solutions.[8]

However, the flash-spectroscopic technique has limitations: 1) Measurement of the spectra of the intermediates is difficult when they lie in the same region as that of the solvent or the original solute molecules. 2) It is often difficult to make the assignment of the transient spectrum. 3) The spectroscopic data cannot give information on whether there are loose associations between cations and anions (or solvated electrons).

We have attempted to extend information on the ionic intermediates formed by flash-illumination of aromatics in solutions at room temperature by measuring the transient photocurrent arising from these intermediates. In the present paper, some of the results are reported.

As an earlier photoconductivity work of the same kind, Jarnagin *et al.*,[9-11] studied photocurrents caused by the flash illumination of aromatic hydrocarbons in solutions which they attributed to a result of bimolecular triplet-triplet interaction of the aromatics. Recently, Pilloff and Albrecht have measured the photocurrent appearing in a non-polar solvent containing TMPD,[4] and found the photocurrent signal to be proportional to the square of the total intensity of flash light.

Experimental

Commercially-available TMPD dihydrochloride was neutralized in an aqueous solution with a little excess of ammonia. The precipitate of TMPD was washed slightly with water, dried, and sublimed twice in a vacuum. Anthracene and maleic anhydride were recrystallized from a benzene and a chloroform solution. *p*-Dimethoxybenzene and 1,3,5-trinitrobenzene were recrystallized from ethanol solutions and sublimed twice in a vacuum. Acetonitrile and ethanol were purified by methods described in an earlier paper.[1] G. P. grade formamide and spectro-grade dimethylformamide were used without further purification.

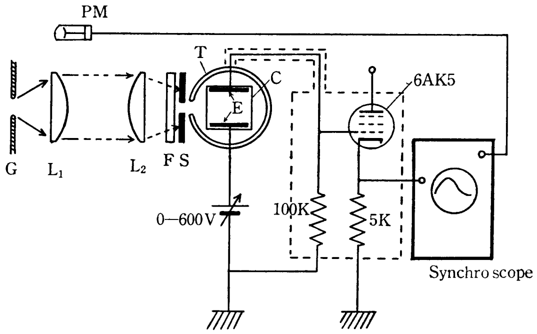

Fig. 1. Schematic diagram of the apparatus. G: tungsten gap. L_1 and L_2: quartz lenses ($\phi = 100$ mm). F: filter. S: slit. T: copper shield tube. C: quartz sample cell. E: electrodes. PM: photomultiplier.

In Fig. 1, a schematic diagram of the apparatus is shown. Flash light was generated from the condenser discharge through a tungsten gap (G), initiated with a high voltage trigger pulse. In order to decrease the electrical noises due to the flash discharge, a distance of about 5 m was taken between quartz lenses L_1 and L_2. The quartz sample cell was put into a copper shield tube (T). The light comes into the cell through a slit 2 mm in width, so that direct irradiation on the two electrodes (spaced by approximately 9 mm) was avoided. The electrode was a plate having the dimensions 1 cm × 4 cm. Aluminum, nickel and platinum electrodes were tested and no substantial difference in the photocurrent response was found by use of any electrode, although the first two electrodes were somewhat stained gradually in the course of experiments. The photocurrents for the acetonitrile solutions containing TMPD were measured by the above mentioned procedure. As photocurrents were very weak in all other cases, the light source (G) was placed directly before the filter so as to increase the light intensity. The tungsten gap (G) used as the light source was fired at 250J (5 μF, 10 kV) in the case of the acetonitrile solution of TMPD and at 125J (2.5 μF, 10 kV) in other cases. The duration of the flash was less than 3 μsec.

The upper part of the sample cell (C) can be sealed with a ground glass stopper. Before each of the experiments a fine Teflon tube was inserted into the cell and commercial high-purity nitrogen was bubbled

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[9] A. Kawada and R. C. Jarnagin, *J. Chem. Phys.*, **44**, 1919 (1966).

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through the solution.

The circuit rise time was less than 0.4 μsec. The d.c. dark current in the case of polar solvents was of the order of 10^{-4} A. An Iwasaki SS-5302 type synchroscope was used for measurements of the currents. A part of the flash light was received by a photomultiplier(PM) and the signal was used to trigger the synchroscope. Electrical noise resulting from flash-firing on the photocurrent signal disappeared within 20 μsec after the flash.

Results

Flash-excitation of TMPD. In Fig. 2 are shown the synchroscope tracings of the photocurrents produced by the flash irradiation of deoxygenated solutions containing TMPD. The lower straight lines indicate the dark current. Two maxima of the photocurrent were found for the acetonitrile solution. The first one appeared at about 0.2 msec, more accurately 170 μsec as found by magnifying the sweep velocity of the synchroscope. The second maximum was at about 50 msec under this applied electric field.

Flash light intensity was so weak in this experiment that the characteristic color of TMPD cation (Würster's blue) did not appear. But under the condition of very strong flash intensity the irradiated TMPD solution was colored and exhibited a large photocurrent signal having a prolonged tail measurable even at 60—90 sec after the flash.

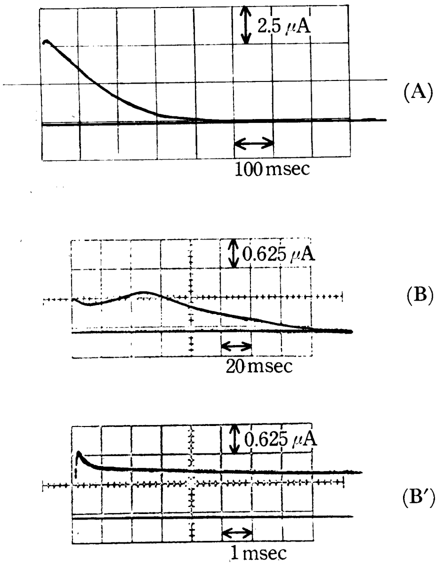

Fig. 2. The photocurrent of TMPD solution.
(A) In dimethylformamide, 1.5×10^{-4}M. Applied field: *ca.* 100 V cm^{-1}. 2.5×10^{-6} A/div, 100 msec/div.
(B), (B′) In acetonitrile, 3.7×10^{-3}M. Applied field: *ca.* 700 V cm^{-1}. 6.25×10^{-7} A/div., (B) 20 msec/div, (B′) 1 msec/div.

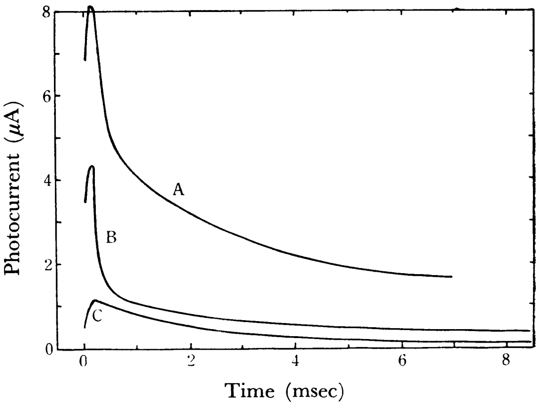

Fig. 3. The photocurrent of solution of DMB and TNB in acetonitrile. Applied field: *ca.* 100 V cm^{-1}. Concentration of DMB and TNB: both 1.5×10^{-3}M.
A: Deoxygenated. B: Not deoxygenated. C: Deoxygenated, and a 0.1M DMB solution was used as a filter.

Flash-excitation of Donor-Acceptor System. Figure 3 shows the photocurrent signals in an acetonitrile solution of *p*-dimethoxybenzene (DMB) and 1,3,5-trinitrobenzene (TNB). Curve A is the transient photocurrent signal for a deoxygenated solution, and curve B for an aerated solution. The difference between curve A and B indicates the effect of dissolved oxygen which seems to reduce the formation of charge carriers. Curve C indicates the photocurrent for the case where only 1,3,5-trinitrobenzene (acceptor) was selectively excited by the flash light through a filter solution of *p*-dimethoxybenzene (0.1M, 10 mm) in front of the sample cell. The photocurrents observed for these samples indicate only one maximum at 140 μsec. There is no such a maximum for the absorbance of the ionic species in the flash spectroscopic measurement of the same solution.[8] Assuming that the decay is second order, the rate constant is derived from curve C of Fig. 3 to be $9.2\times10^{8}M^{-1}sec^{-1}$. The value is about the same as that of the decay rate constant of *p*-dimethoxybenzene cation reported in a previous paper,[8] by taking the molar extinction coefficient of the cation to be about 3×10^{3}. The initial concentration of the ions interpolated to zero time becomes $\sim10^{-5}$M.

The photocurrent of a dimethylformamide solution containing *p*-dimethoxybenzene and 1,3,5-trinitrobenzene (both 1.4×10^{-3}M) was also measured. Its shape was essentially the same as that of the acetonitrile solution, but the photocurrent at the maximum was only one half. The maximum comes later and the decay is slower than for the acetonitrile solution.

In Fig. 4, curve A shows the photocurrent of an acetonitrile solution containing 1.1×10^{-3}M anthracence and 1.4×10^{-3}M maleic anhydride. Curve

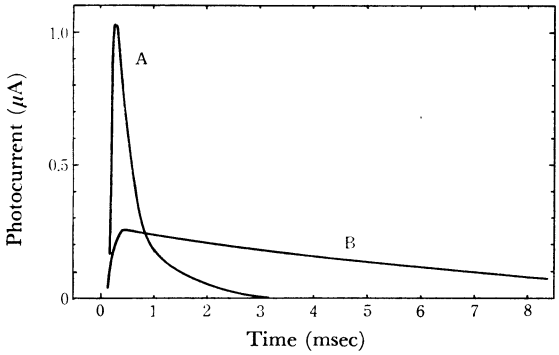

Fig. 4. The photocurrent of solution of anthracene and maleic anhydride in acetonitrile. Filter: UV-35.
A: anthracene (1.1×10^{-3}M), maleic anhydride (1.4×10^{-3}M). Applied field: *ca.* 100 V cm^{-1}.
B: anthracene alone (1.1×10^{-3}M). Applied field: *ca.* 600 V cm^{-1}.

B shows the photocurrent of anthracene alone (1.1×10^{-3}M) in the same solvent. A filter (Toshiba UV-35) was used to excite selectively the first bands (^1L_a) of anthracene. The recombination rate constants were calculated from the decay of the photocurrents to be $\sim10^{10}$M^{-1} sec^{-1} from both curves A and B, if the effective volume where the ions were generated was taken to be 0.1 cm^3. The schematic aspect of curve B resembles that obtained by Kawada and Jarnagin.[9] When dissolved oxygen was not removed by bubbling with pure nitrogen gas, the photocurrent for curve B was so weak that the measurements were almost impossible.

After more than ten flashes, it was found that the ^1L_a absorption bands of anthracene in the sample solution decreased, indicating that the concentration of anthrancene was reduced. This seems to be most probably due to the Diels-Alder type addition reaction between anthracene and maleic anhydride. Attempts to detect the absorption spectra of intermediates from this donor-acceptor system by means of the flash spectrometry[12] were made. But no spectrum of ionic species was obtained in the wavelength range from 300 to 650 mμ, though transient T–T′ absorption bands of anthracene were found near 420 mμ.

Discussion

The photocurrent density is given by

$$i(t) = \sum_j Z_j e n_j(t) \mu_j E,$$

in which e represents the charge of the electron, E the applied electric field and μ_j the carrier mobility. $n_j(t)$ represents the number of positive and negative charge carriers in unit volume which changes with time by reactions between the carrier and solvent (or impurities), by the recombination reaction, or by the electrical discharge at the electrodes when E or μ is very large.

The lower limit C_l (mol/l) of the concentration of ions produced by a flash irradiation in the sample solution, is expressed by

$$C_l \sim (1/VF)\int_0^\infty i(t)\mathrm{d}t,$$

where V is the volume of the sample solution in liter and F Faraday constant. C_l is calculated to be less than 10^{-9}M for the acetonitrile solution of TMPD. Lower values, 10^{-10}M, are obtained for the donor-acceptor systems.

The behavior of the photocurrents may be classified into three types as shown below, where τ is the lifetime of charge carriers or ionic species, and t_t the time required for the charge carriers produced near the center of two electrodes to arrive at the electrode, *i. e.* the 'transit time' which depends upon E and μ:

(1) $t_t \gg \tau$: In this case, the velocity of the charge carriers in the electric field is negligibly small, and the behavior of the photocurrent may be explained only by taking account of the reactions of the ionic species, *i. e.*, the charge neutralization or the electron transfer reactions;

(2) $t_t \ll \tau$: In this case, the ionic species remain stable enough until they arrive at the electrodes. This case is suitable for the study of the electrical transfer phenomena in solutions;

(3) $t_t \simeq \tau$: This is an intermediate case of the former two.

It is generally stated that the mobilities of inorganic ions in aqueous solutions are of the order of 10^{-4} cm^2 V^{-1} sec^{-1}, and those of organic ions in organic solutions may also be roughly estimated at the same order.[6,7] Taking the mobility to be this order of magnitude, the distance between the electrodes to be 1 cm, and the applied electric field to be 10^2 V cm^{-1}, the drift velocity of ions and the transit time become the order of 10^{-2} cm sec^{-1} and 50 sec, respectively. As all samples, except TMPD solution, examined in the present work have decay times of the order of 1 msec to 10 msec, they fall into the above-mentioned case (1). As the lifetime of TMPD cation is exceptionally long, estimated at 10^2—10^3 sec from the decay of its absorption spectrum in flash photolysis,[1] the photocurrent for this case falls into case (3).

Without exception, the photocurrent measured showed an initial rise to a maximum, which is attained at about 100 μsec. This behavior is contrary to the results of transient absorption spectra obtained from the flash spectrometry of donor-acceptor systems.[8] This delayed photocurrent was also found for the flash illumination of anthracene *etc.* in tetrahydrofuran by Jarnagin *et al.*[9–11] who regarded it as evidence for the 'delayed

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12) The apparatus used here was the same as described in Ref. 3.

ionization' through the triplet-triplet interaction of the aromatics. Our results in an acetonitrile solution of anthracene closely resembled theirs. This interpretation does not apply, however, to the donor-acceptor systems or to the photo-ionization of TMPD in solutions. The fact that the rise time of the photocurrent gets longer for the more viscous solvent favors the interpretation that the photochemically produced ions initially exist in the form of loose ion-pairs,[13,14] which do not contribute to the electric current, and then seperate into free ions by the thermal motion of surrounding solvent molecules. The fact that the photocurrents reach maxima at about 100 μsec, however, seems too long for such diffusional processes.[15] Therefore, the explanation for the appearance of the maxima of the photocurrents is difficult at present.

TMPD Solutions. In previous papers,[1-3] it was found by means of flash spectrometry that TMPD in polar solvents is photo-ionized by biphotonic process *via* the triplet state as the intermediate. The fact that photocurrent has been detected for the irradiated solution certainly indicates that ions are generated and are present rather as separate positive and negative ions (or solvated electrons) than in the form of ion-pairs.

It has already been stated in the early part of this paper that the photocurrent in an acetonitrile solution of TMPD has two maxima (at 170 μsec and at about 50 msec). This behavior of the photocurrent was not found in formamide, dimethylformamide and *n*-hexane and for all other solutes examined in this work. Kawada and Jarnagin had found two maxima in a tetrahydrofuran solution of anthracene or phenanthrene and considered the second maximum to be due to impurities.[9] The second maximum of the photocurrent in this work suggests the existence of a different kind of charge carrier (Q_2). If the recombination rate of the charge carrier corresponding to the first maximum (Q_1) is larger than that of Q_2 and the mobility of Q_2 is larger than that of Q_1, it is possible that the photocurrent has double maxima. The dark reaction of Q_1 with the surrounding solvent molecules or impurities might form Q_2. The carrier, Q_2 might be cyanide anion (CN^-), methylene cyanide anion (CH_2CN^-) or $CH_3\underset{\substack{|\\ CH_2CN}}{C}=N^-$, as conjectured from the reaction of acetonitrile with sodium metal. Cationic intermediates will not be concerned with the second maximum, since TMPD cation is rather stable.

The position of the second maximum was found to be proportional to the reciprocal of the applied voltage. This fact suggests that the time of the appearance of the maximum, t_m is of the same order of magnitude as t_t, because if t_m is much smaller than t_t, t_m should be determined mainly by the charge annihilation processes in the solution and not by the change with applied voltage.

The influence of some macroscopic properties of solvents on the photocurrent for TMPD is listed in Table 1. In ethanol the photocurrent was hardly detectable though the transient electronic spectrum of the TMPD cation appeared after flash illumination. This seems to imply that the ionic species produced by the photo-ionization in ethanol is in the form of ion-pairs.[16] In *n*-hexane a weak photocurrent (less than 6×10^{-8} A) having the decay time of a few milli-seconds was observed. Further, it appears from Table 1 that the photocurrent depends both on the dielectric constant and on the viscosity, and not on the refractive index. This is a reasonable result, because (1) the ion-pair may be

TABLE 1. PHOTOCURRENT OF TMPD SOLUTION

($\sim10^{-4}$M. Applided field: *ca.* 100 V cm^{-1}. A glass plate (5 mm thick) was used as a filter.)

Solvent	Dielectric constant (25°)	Square of refractive index	Viscosity (centipoise)	Peak of photocurrent (10^{-7}A)	Appearance of TMPD cation spectrum
n-Hexane	1.9	1.890	0.324 (15°C)	<0.6	—
Ethanol	24.3	1.856	1.08 (20°C)	very weak	+
Dimethylformamide	36.7	2.015	0.908 (25°C)	3.75	+
Acetonitrile	37.5	1.812	0.375 (15°C)	43.8*	+
Formamide	109.5	2.089	3.76 (20°C)	10.0	+

* At the first peak. The light source was placed directly before the filter, as was done in all other solutions.

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[13] G. S. Hooper and C. A. Kraus, *J. Amer. Chem. Soc.*, **56**, 2265 (1934). R. M. Fuoss and C. A. Kraus, *ibid.*, **57**, 1 (1935).

[14] T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 307, 318 (1966).

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dissociated into free ions the more easily, the higher the dielectric constant, and (2) the mobility of the charge carrier becomes the smaller, the more viscous the solvent.

Donor-Acceptor Systems. It has been fairly well established by means of the flash spectrometry that the flash excitation of a donor-acceptor system in polar solvents produces transient cations and anions through excited charge transfer states, as described below,[6-8)]

$$\mathrm{A}+\mathrm{D}+h\nu \longrightarrow \mathrm{A}^*+\mathrm{D}\ (\text{or } \mathrm{A}+\mathrm{D}^*) \rightleftarrows (\mathrm{A}\text{---}\mathrm{D})^*$$

$$(\mathrm{A}\text{---}\mathrm{D})^* \longrightarrow (\mathrm{A}^-\text{---}\mathrm{D}^+)_{\mathrm{solv}} \longrightarrow \mathrm{A}^-_{\mathrm{solv}}+\mathrm{D}^+_{\mathrm{solv}} \longrightarrow \mathrm{A}+\mathrm{D},$$

where (A---D)* means the charge transfer state and $(\mathrm{A}^-\text{---}\mathrm{D}^+)_{\mathrm{solv}}$ the ion-pair. The existence of the photocurrent for the system of *p*-dimethoxybenzene-1,3,5-trinitrobenzene in acetonitrile as revealed in the present research confirmed the formation of free ions in the solution. This may be taken as a supplementary evidence for the electron transfer process of the same system observed by flash spectroscopy.[8)]

For the system of anthracene-maleic anhydride-acetonitrile, no flash-spectrum of the ionic species was found. The reason for this may probably be the insensitivity of the photographic film used here at the near infrared region where the anthracene cation is expected to have the absorption spectrum. The weak absorption bands of this cation to be present in the visible and ultraviolet region should also overlap with those of the orginal solutes. The observation of photocurrent in this system, therefore, shows the superiority in the sensitivity of detection of ionic species by the present photocurrent method over the spectroscopic method.

As described in the Results, the flash irradiation of an acetonitrile solution of anthracene alone showed a photocurrent. But the intensity of the photocurrent was much weaker than that for the solution containing both anthracene and maleic anhydride. It seems reasonable, therefore, to attribute the photocurrent for anthracene (An)-maleic anhydride (Ma) system to the formation of An^+ and Ma^- through the charge transfer excited state, similar to the *p*-dimethoxybenzene-1,3,5-trinitrobenzene system. The photocurrent observed for the former is much weaker compared with that for the latter, although the experimental conditions for both cases are about the same. The main reason for this may be attributed to the difference in the strengths of the acceptors. Thus, 1,3,5-trinitrobenzene, with larger electron affinity than maleic anhydride may produce more free ionic species in the course of the reaction

$$(\mathrm{D}^+\text{---}\mathrm{A}^-)_{\mathrm{solv}} \longrightarrow \mathrm{D}^+_{\mathrm{solv}}+\mathrm{A}^-_{\mathrm{solv}}.$$

As is well known, anthracene and maleic anhydride form Diels-Alder type adducts by the effect of ultra-violet light. The quantum yield of this reaction in dioxane was determined to be 0.02.[17)] This low value of the quantum yield seems to show that most of the 'encounter complex' of excited anthracene and maleic anhydride (An*---Ma) will transfer to the charge transfer state (An---Ma)* which should be lower in energy than the former, and then to free ions and a small part of the encounter complex will undergo addition reaction.

$$\begin{tikzcd}
{}^1\mathrm{An}^* + \mathrm{Ma} \arrow[r] & (\mathrm{An}^*\text{---}\mathrm{Ma}) \arrow[r, dashed] \arrow[d] & \text{adduct} \\
 & (\mathrm{An}\text{---}\mathrm{Ma})^*_{\mathrm{solv}} \arrow[d] & \\
\mathrm{An} + \mathrm{Ma} \arrow[uu, "h\nu"] & \mathrm{An}^+_{\mathrm{solv}} + \mathrm{Ma}^-_{\mathrm{solv}} &
\end{tikzcd}$$

[17)] J. P. Simons, *Trans. Faraday Soc.*, **56**, 391 (1960).