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The Interaction of Oxygen with Organic Molecules. III.⁽¹⁾ Electron Transfer between Oxygen and Aromatic Amines Studied by Flash Technique

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Flash photolysis of aniline derivatives in various solutions has been studied in oxygenated and deoxygenated conditions. Absorption spectra of the triplet states appeared in deoxygenated liquid paraffin solutions, but no transient absorption was observed in the oxygenated liquid paraffin solutions. Transient spectra, due to the cations of the anilines, were observed in deoxygenated ethanol solutions, but none in oxygenated ethanol. In highly polar solvents — acetonitrile, water, and formamide — either deoxygenated or oxygenated, the cation was observed. In the case of oxygenated solutions, the initial yield of the cation was found to be proportional to the intensity of the flash light, indicating that the ionization is a one-photon process. These results, together with the previous findings that the photo-ionization of organic molecules in solutions are caused by the two-step, biphotonic excitation processes strongly suggest that the charge transfer states are formed between the aromatics and the oxygen molecule, either by direct excitation or *via* the interaction of excited anilines and the ground state of oxygen, and the charge transfer states then lead to the solvated cations and anions in highly polar solvents. The decay of the ions have been found to follow the second order kinetics.

Oxygen molecule is known for its various special actions on the photochemical behaviors of organic molecules, such as quenching of phosphorescence and fluorescence, photo-oxidation, and enhancement of T←G transition (transition from the ground state to the lowest triplet state). It is also known that oxygen induces absorption spectra in ultraviolet or visible regions when dissolved in various organic solvents. The absorption has been attributed to a type of contact charge transfer absorption by Evans,[3] and Tsubomura and Mulliken.[4] This theory assumes the existence of charge transfer (CT) excited states between oxygen and organic molecules, where oxygen acts as the electron acceptor. Tsubomura and Mulliken explained the mechanism of enhanced intercombination between singlet and triplet states using this concept of CT states.

Although the assumption of these CT states is consistent with all known experimental observations, more evidence to verify the CT nature of the excited states is desirable. Measurement of the dipole moments of the excited states and other experiments to show the highly polar nature of the excited states are, however, very difficult in this case, because of the non-fluorescent nature of the CT states.

Some years ago, Leonhardt and Weller[5] showed that flash excitation of a solution of perylene and *N,N*-dimethylaniline in a polar solvent leads to the transient formation of perylene anion. They proposed that the perylene anion and the aniline cation were formed from a CT excited state where perylene acts as an acceptor and aniline a donor. We have

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[1] Part II. of this series: E. Ishida, H. Takahashi and H. Tsubomura, This Bulletin, **43**, 3130 (1970).

[2] Central Research Laboratory, Fuji Electric Co., Ltd., Nagasaka, Yokosuka.

[3] D. F. Evans, *J. Chem. Soc.*, **1961**, 1987, and other papers preceding it.

[4] H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960).

[5] H. Leonhardt and A. Weller, *Z. Phys. Chem. N. F.*, **29**, 277 (1961); *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).

obtained similar results for other organic donor-acceptor systems and shown that such transient formation of ionic species after the CT interaction is a general phenomena.[6,7]

It should be pointed out here that the formation of a CT state may not be a prerequisite for the appearance of ionic species in polar solutions, because ionic species may be formed either by spontaneous ionization from a charge transfer state or by photo-ejection of electrons (which will be discussed later in this article) followed by capture of the electron by electron acceptors. We thought that it was important to study the photochemical behavior of oxygen and organic substances under flash illumination, and to find more detailed mechanism of the formation of transient ionic species.

In order to clarify the role of oxygen in photo-ionization processes involving aromatic donor molecules, it was necessary to study whether photo-ionization could occur in solutions containing only aromatic compounds and no oxygen. It has been well established that many aromatic hydrocarbons and amines are photo-ionized in solutions. In cases where the exciting radiation contains only near-ultraviolet or visible light, the photo-ionization in low temperature matrix occurs by the two-step excitation, *via* the lowest triplet states of the aromatics.[8] We have found that the two-step ionization takes place not only in non-polar matrix at low temperature but in fairly polar solutions like ethanol[7] at room temperature. The ionic species formed are no doubt stabilized to a great extent in polar solutions. However, we found the photon energy necessary for an effective production of ions to be only a few tenth electron volt smaller than the gas-phase ionization potential of the donor.

In the present work, particular emphasis was laid on the study of the difference in the photochemical behaviors of aromatics in oxygenated and deoxygenated polar solutions.

Potashnik *et al.* reported independently that a spontaneous ionization may occur from a charge transfer triplet state of an electron-donor-acceptor pair in a polar matrix.[9] They also studied the photo-ionization of *N*,*N*,*N'*,*N'*,-tetramethyl-*p*-phenylenediamine (TMPD) at various oxygen concentrations[10] using a flash technique. Their main conclusion is that the photo-ionization in polar solutions is mainly a bi-photonic process *via* an intermediate whose nature is still not thoroughly understood, and the photo-ionization in less polar solutions is mostly a mono-photonic process due to the interaction of the triplet TMPD and oxidizing impurities.

Experimental

Materials. *N*,*N*-Dimethyl-*p*-anisidine was recrystallized from 60% ethanol and sublimed in a vacuum. *n*-Hexane was purified by passing through a silica-gel column. Acetonitrile was twice refluxed with phosphorous pentoxide for several hours, followed in each case by fractional distillation. Formamide was kept overnight with anhydrous sodium sulfate and distilled under 30 Torr at *ca.* 130°C. Water was passed through activated charcoal and ion-exchange resin columns. (Specific resistance: 10^6 ohm/cm). Liquid paraffin was purified by passing through a silica-gel column. All other materials used were purified by methods similar to those described in previous papers.

Methods. The concentrations of most of the solutions of aniline derivatives studied were made 0.3—0.5 $\times 10^{-3}$ mol/*l* so as to give optical densities of *ca.* 1 cm^{-1}. The solutions saturated with either one atmosphere oxygen or nitrogen were placed in a cylindrical silica cell, 1.4 cm in diameter and 20 cm in length. The apparatus used for the flash-spectroscopic measurements is mostly the same as that described in our earlier paper.[11] The light of the exciting flash lamps was filtered by an aqueous solution of cobaltous chloride (0.5 gr/c.c.) using a double-wall sample cell, and only the light in the range from 2800 to 3800 Å was passed in order to minimize the effect of scattered light from the exciting flash lamps.

Results

Oxygen-Saturated Solutions. The transient absorption spectra obtained by flash illumination of *N*,*N*-dimethylaniline (DMA) in acetonitrile solutions saturated with oxygen is shown in Fig. 1. Similar spectra were obtained for aqueous and formamide solutions. In the case of *n*-hexane, liquid paraffin, and ethanol as solvents, no transient spectra were obtained. In a previous paper, it was reported that the photolysis of DMA in low temperature matrices yields the DMA cation and the neutral radical, and a part of the visible spectrum was assigned as the absorption spectrum of the cation.[12] The transient spectra obtained in the present results agree well with this and the species formed is therefore identified to the DMA cation. This conclusion is supported by the fact that this transient spectrum is not found in solvents having relatively low dielectric constants, because unstable

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[6] K. Kawai, N. Yamamoto and H. Tsubomura, This Bulletin, **42**, 369 (1969).

[7] Y. Nakato, N. Yamamoto and H. Tsubomura, This Bulletin, **40**, 2480 (1967), and previous papers cited there.

[8] J. Joussot-Dubien and R. Lesclaux, *Compt. Rend*, **258**, 4260 (1964); W. A. Gibbons, G. Porter and M. I. Savadatti, *Nature*, **206**, 1355 (1965); K. D. Cadogan and A. C. Albreacht, *J. Chem. Phys.*, **43**, 2550 (1965).

[9] R. Potashnik, C. R. Goldschmidt and M. Ottolenghi, *J. Phys. Chem.*, **73**, 3170 (1969).

[10] R. Potashnik, M. Ottolenghi and R. Bensasson, *J. Phys. Chem.*, **73**, 1912 (1969).

[11] N. Yamamoto, Y. Nakato and H. Tsubomura, This Bulletin, **39**, 2603 (1966).

[12] S. Arimitsu, K. Kimura and H. Tsubomura, This Bulletin, **42**, 1858 (1969).

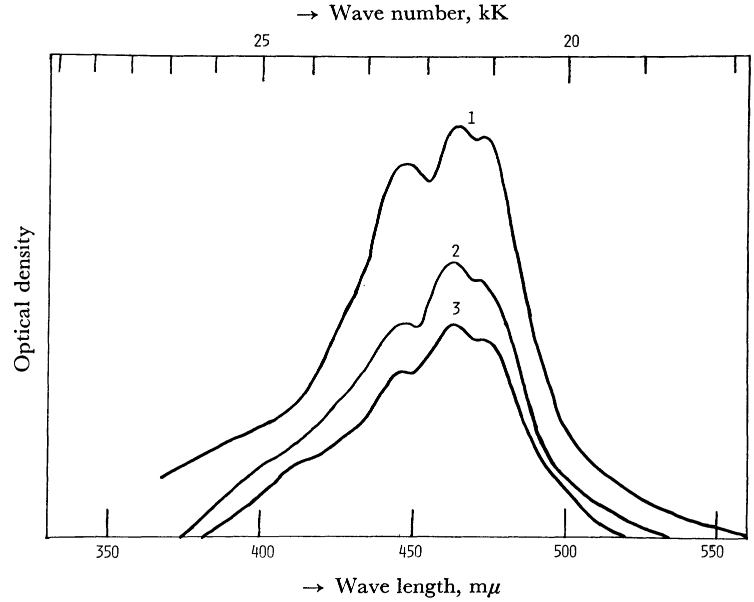

Fig. 1. Transient absorption spectra obtained by flash illumination of *N*,*N*-dimethylaniline in acetonitrile saturated with oxygen.
Delay time: 1) 8 μsec, 2) 140 μsec, 3) 300 μsec

ionic species like these are only sufficiently stabilized in very polar solvents such as acetonitrile (dielectric constant ε: 37.5), water (ε: 81), and formamide (ε: 109.5), and not in nonpolar solutions or even in ethanol (ε: 24.3). As a further evidence for the formation of DMA cation, we found that a momentary photoconductivity appeared by flash illumination of DMA in these highly polar solutions saturated with oxygen.[13] We also found a weak ESR signal by steady illumination of DMA in acetonitrile

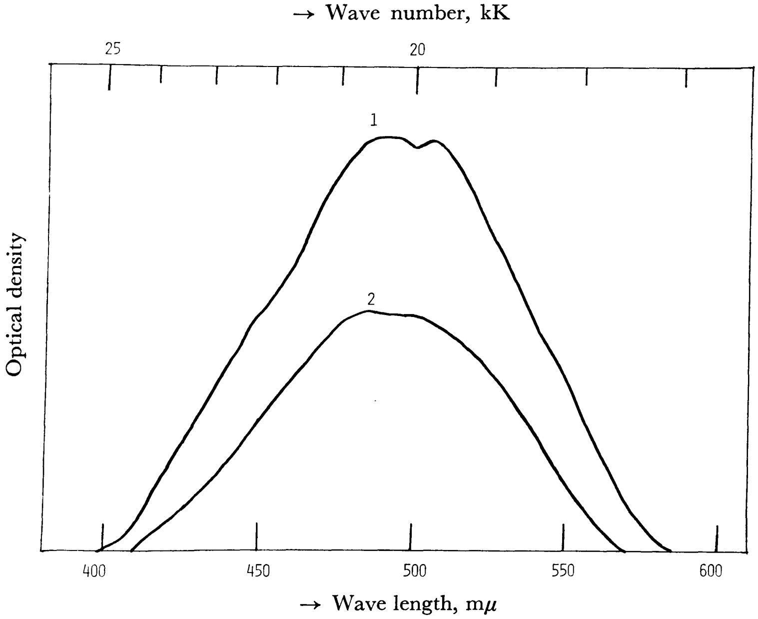

Fig. 2. Transient absorption spectra obtained by flash illumination of *N*,*N*-dimethyl-*p*-anisidine in acetonitrile saturated with oxygen.
Delay time: 1) 10 μsec, 2) 190 μsec

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[13] T. Imura, N. Yamamoto and H. Tsubomura, This Bulletin, **43**, 1670 (1970).

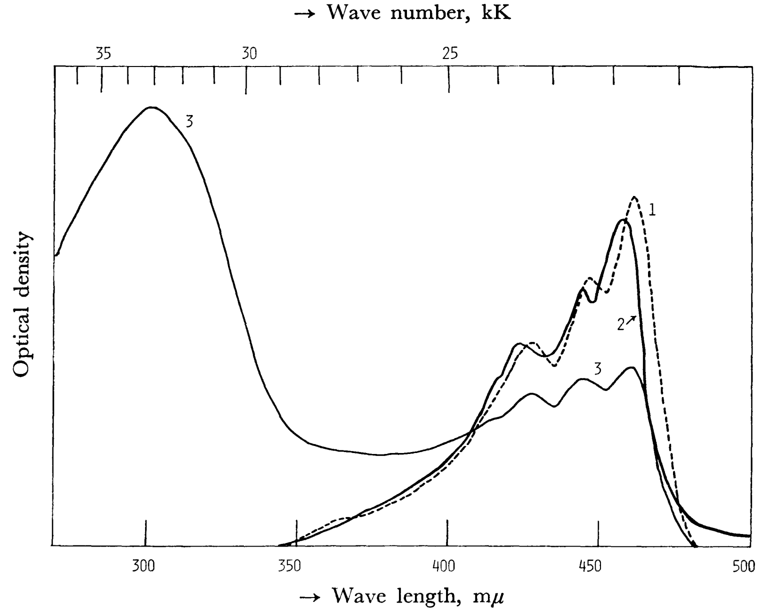

Fig. 3. Transient absorption spectra obtained by flash illumination of benzidine in solutions saturated with oxygen.
1) In ethanol. Delay time: 850 μsec, 2) In acetonitrile. Delay time: 85 μsec. 3) A spectrum obtained by ultraviolet irradiation of benzidine in a (1 : 1) ethanol - ether matrix at 77°K with a 500 W high pressure mercury lamp.

saturated with 1 atmosphere oxygen. It is very interesting that we could not find the absorption spectrum of DMA cation by flash illumination of acetonitrile solutions of DMA saturated with oxygen at 8 Torr and at 20 Torr, discussion on which will be made later in this paper.

In the case of *N*,*N*-dimethyl-*p*-anisidine (DMAN), transient spectra have been observed in acetonitrile, water, and formamide, and not in liquid paraffin or ethanol. As an example, Fig. 2 shows the transient absorption spectrum obtained for the acetonitrile solution. It agrees with that obtained in our laboratory as a result of ultraviolet irradiation of DMAN in the low temperature matrix,[14] and is attributable to that of the cation of DMAN.

In an aqueous solution of DMA or DMAN, a transient band was obtained at 3400 or 4500 Å, respectively, which decayed much faster than the cation spectra. These bands might be assigned to *N*-methylaniline cation and *N*-methyl-*p*-methoxyaniline cation, respectively.

In the case of benzidine, transient absorption spectrum was obtained by flash illumination in ethanol, acetonitrile, water and formamide, and not in liquid paraffin. Absorption spectrum obtained for the case of an ethanol solution is shown in Fig. 3 together with that obtained by the photolysis of benzidine in a low temperature matrix. That the

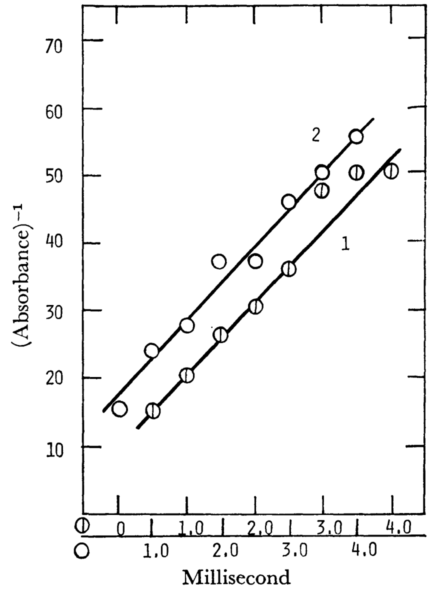

Fig. 4. Plot of reciplocal of absorbance of the cation formed by flash illumination of *N*,*N*-dimethylaniline in oxygenated acetonitrile against time.
1) At a flash with capacitors charged at 11.5 kV.
2) At a flash with capacitors charged at 11.0 kV.

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[14] K. Kimura, K. Yoshinaga and H. Tsubomura, *J. Phys. Chem.*, **71**, 4485 (1967).

spectrum appearing in the latter is due to the benzidine cation is concluded from the following: 1) The spectrum does not appear by irradiation in a non-polar matrix. 2) When biphenyl is added in the matrix to be irradiated, the spectrum of biphenyl anion was observed. 3) Thermoluminescence was observed from the irradiated matrix. Agreement between the two spectra clearly shows that benzidine cation was produced by flash illumination of oxygenated benzidine solutions. The result that the cation is formed even in ethanol, contrary to results for DMA and DMAN, is probably related with the lower ionization potential of benzidine compared with the other two.

In the cases of DMA and DMAN in acetonitrile, water and formamide, the decay of the absorption due to the cation formed by flash illumination was found to be second order with respect to the concentration of the cation. As an example, the reciprocal of the absorbance of the cation produced from DMA plotted against time is shown in Fig. 4. By taking the molecular extinction coefficient of the cation at 4600 Å to be 1200,[12] the rate constant of the second order reaction is determined to be as shown in Table 1.

Table 1. Second order decay constants of the cations in various solvents, together with relative viscosities and dielectric constants of the solvents at room temperature

Solvent	Acetonitrile	Water	Formamide
Relative viscosity, centi-poise	0.345	1.00	3.764
Dielectric constant	37.5	80.0	109.0
The second-order decay constant, $10^8 \mathrm{M}^{-1} \cdot \mathrm{sec}^{-1}$, for *N*,*N*-dimethylaniline	2.4	0.2	0.7
The same for *N*,*N*-dimethyl-*p*-anisidine	6.8	7.4	3.0

By extrapolation to zero time, we could obtain the initial cation concentration produced by the flash. Intensity of the flash light can be changed by controlling the voltage applied to the condenser. It was confirmed that the profile of the flash light is fairly constant at all firings of the flash and, therefore, not only the integrated intensity but also the intensity at any stage of a flash is almost exactly proportional to the square of the voltage. Based on these results, the initial concentration of the cation produced was plotted against the flash light intensity. The results for DMA and DMAN are given in Fig. 5. As seen from the figure, the initial concentrations of the cations are proportional to the light intensity for both compounds. For aqueous and formamide solutions, the kinetic data are a little complicated by the formation of other species.

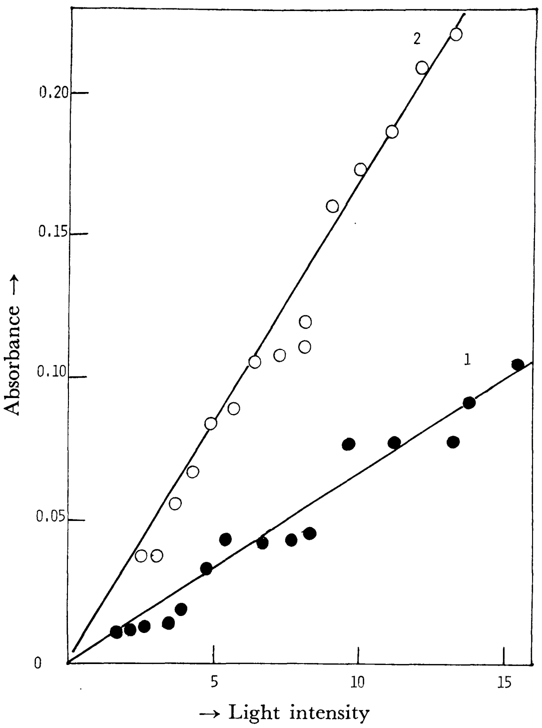

Fig. 5. Plot of initial concentration of the transient cation, in units of absorbance, formed in acetonitrile solutions saturated with oxygen against flash intensity.

1) *N*,*N*-dimethylaniline, 2) *N*,*N*-dimethyl-*p*-anisidine.

However, the results obtained show that the decay of the cation in these cases is of the second order and the initial concentration is proportional to the light intensity of the flash.

Deoxygenated Solutions. Flash photolyses of DMA and DMAN have been studied in carefully deoxygenated solutions.

The flash photolysis of DMA in deoxygenated liquid paraffin was studied by Land and Porter,[15] who assigned the spectrum with maxima at 3140 and 4000 Å tentatively to *N*,*N*-dimethylanilino radical. Kimura *et al.*[16] obtained a similar spectrum with maxima at 3400 and 4800 Å and a life time of the order of 100 μsec, and assigned it to the *T*–*T* transition. Later, the same authors found that the ultraviolet spectrum consists of two components: one probably due to *T*–*T* transition and another decaying much more slowly, We studied the flash photolysis of DMA and DMAN in carefully deoxygenated liquid paraffin again. The resulting spectra for DMA are shown in Fig. 6. The visible

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[15] E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).

[16] K. Kimura, S. Arimitsu, N. Yamamoto and H. Tsubomura, This Bulletin, **41**, 1274 (1968).

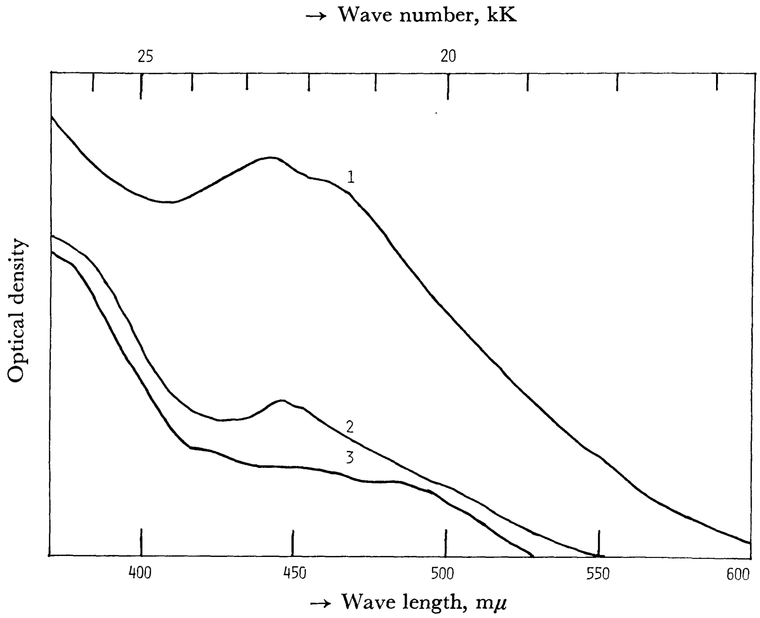

Fig. 6. Transient spectra obtained by flash illumination of *N*,*N*-dimethylaniline in deoxygenated liquid paraffin.
Delay time: 1) 8 μsec, 2) 80 μsec, 3) 270 μsec

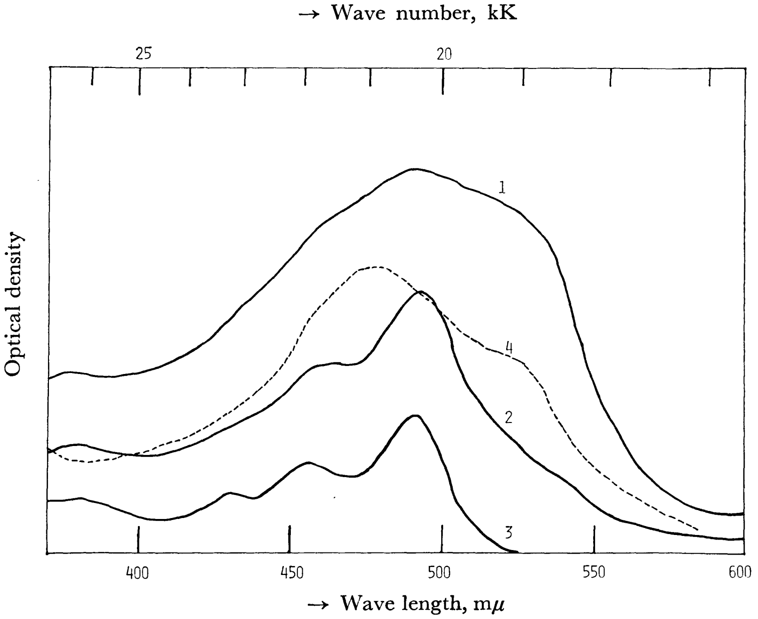

Fig. 7. Transient spectra obtained by flash illumination of *N*,*N*-dimethyl-*p*-anisidine in deoxygenated liquid paraffin.
Delay time: 1) 20 μsec, 2) 180 μsec, 3) 500 μsec, 4) *T*-*T* absorption spectrum measured in liquid paraffin at 77°K.

part of the spectrum decays exponentially with a life time of the order of 80 μsec, while most of the ultraviolet part remained after 80 μsec. These results confirm those obtained by Kimura *et al.* and show that the visible spectrum is the *T*–*T* absorption and most of the ultraviolet spectrum is probably due to *N*-methyl-anilino radical.

The spectra for DMAN also show that there are two components (Fig. 7): one, lying between 4500 and 5500 Å, decayed exponentially with a life time of 1.2 msec. and another, with peaks at 4290, 4500, and 4900 Å, remained for a long time. The yield of the short-life component was found to be proportional to the flash light intensity, while that for the long-life component, although more difficult to analyse, is roughly proportional to the square of the light intensity. All these results are consistent with the assignment of the short-life component as a *T–T* band. That of the long-life component is uncertain. It does not agree in positions of the maxima with those of the DMAN cation nor those of *N,N*-dimethylamino-phenoxyl radical. One possible assignment is to *p*-methoxy-*N*-methylanilino radical.

The *T–T* spectrum of DMAN was also measured in an ethanol matrix and in a liquid paraffin matrix at 77°K using an apparatus constructed in our laboratory.17) The result in Fig. 7 shows that the *T–T* spectrum lies in the same region as that of the fast decaying component of the transient spectrum.

The transient spectra obtained for various polar solutions of DMA and DMAN show complicated aspects. In ethanol and acetonitrile, transient spectra quite similar to those of the DMA and DMAN cations were obtained. The decay curves, however, showed in most cases that there are two components with different life times. The decay kinetics and the dependence of the yield of the transient species on the flash light intensity were difficult to determine exactly.

For aqueous solutions of DMAN, the transient spectrum obtained looks like that of the *T–T* transition. The spectrum, however, is found to have two components: the long-life component decays exponentially, with a life time of 23 min, and the short-life component also decays approximately in the first order with a life time of *ca.* 1 msec., and may be assigned to the *T–T* band. The long-life component is probably the cation band. Its initial absorbance, extrapolated to zero time, increases approximately proportional to the square of the flash light intensity. For the aqueous solution of DMA, the transient spectra can also be divided into *T–T* and cation components with life times of 80 μsec and 87 sec, respectively.

Flash photolysis of DMA and DMAN in formamide also showed transient spectra similar to those of the corresponding cations. The decay curves followed the second order kinetics, and the initial yields of the cations were found to be proportional to $I^{1.2}$—$I^{1.3}$.

Discussion

The transient species detected by the flash method are summarized in Table 2. It has been established that the anilines form their cations when flash-photolysed in highly polar solutions, irrespective of whether the solution is saturated with 1 atmosphere oxygen or deoxygenated. This is consistent with the result of our previous work that *N,N,N′N′*-tetramethyl-*p*-phenylenediamine (TMPD) forms its cation when flash-illuminated in deoxygenated ethanol.7) As has been described earlier, it has been well established that TMPD ionizes from a higher triplet state by the two-step, biphotonic excitation.7) The photolysis of aniline derivatives in organic matrices at 77°K were studied also in our laboratory.12) It was concluded that they form the cation and the anilino-radical and the former yields more in polar matrices. The present results of flash photolysis in deoxygenated solutions seem

Table 2.* Transient species formed by flash excitation of aniline derivatives in solutions at room temperature

Solvent	*N,N*-Dimethylaniline		*N,N*-Dimethyl-*p*-anisidine	
	no O_2	O_2	no O_2	O_2
Liquid Paraffin	triplet DMA, 80 μsec radical $\gg$200 μsec	no transient	triplet DMA, 1.2 msec raidcal >400 msec	no transient
Ethanol	cation	no transient	cation, 6 msec long life species	no transient
Acetonitrile	cation, 1 msec long life species (radical?)	cation, decays in 2nd order	cation, 1.5 msec long life species	cation, decays in 2nd order
Water	triplet DMA, 80 μsec cation, increases until 1—2 msec, and decays, 87 sec	short-life species cation, decays in 2nd order	triplet DMAN, 1 msec cation, 23 min	short-life species cation, decays in 2nd order
Formamide	cation K_2, $1.6\times10^8 \text{M}^{-1}\cdot\text{sec}^{-1}$	cation K_2, $0.8\times10^8 \text{M}^{-1}\cdot\text{sec}^{-1}$	cation K_2, $2.0\times10^8 \text{M}^{-1}\cdot\text{sec}^{-1}$	cation K_2, $3.0\times10^8 \text{M}^{-1}\cdot\text{sec}^{-1}$

* O_2 means that the solution is saturated with oxygen at 1 atm. The species with life times indicated after them are found to decay in the first order. K_2 indicates the second order rate constant.

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17) The details will be reported in a later paper.

to be consistent with the two-step photo-ionization mechanism, although quantitative analysis in the deoxygenated solutions is complicated by the formation of more than one species.

In previous papers,$^{7)}$ we stated that TMPD is photoionized by flash photolysis in deoxygenated ethanol, but the presence of dissolved oxygen retards it to a great extent. In accordance with these findings, it has been found in the present work that DMA and DMAN do not form cations in oxygenated ethanol. The cation of DMA has been found to form in both deoxygenated and oxygenated acetonitrile, but not in acetonitrile saturated with oxygen at 8—20 Torr, as stated previously. This shows that the photo-ionization is retarded by a small amount of oxygen; this may be explained by taking into account the fact that oxygen quenches the lowest triplet states of the donor molecules very efficiently, so that the second step of the excitation hardly takes place.

The most important results obtained in the present work are that the aniline analogues form their cations in highly polar solutions saturated with 1 atmosphere oxygen, and the yields of the cations are proportional to the flash-light intensity. These results indicate that the cations are formed by the single-photon excitation from the ground states. The most plausible interpretation for this is that these cations are formed from the CT states, $D^+\cdots O_2^-$ by the interaction of the highly polar solvents.

$$D^+\cdots O_2^- \longrightarrow D^+_{solv} + O^-_{2\,solv}$$

The CT states may be formed either by direct excitation from the ground states through the CT absorption, or by the interaction of the singlet excited states of the donor with oxygen in the ground state as follows:

$$^1D^* + O_2 \longrightarrow D^+\cdots O_2^- \longrightarrow D^+_{solv} + O^-_{2\,solv}$$

As mentioned before, the cations are not detected in the acetonitrile solution of DMA containing a very small amount of oxygen, and this indicates that the excited triplet DMA is quenched by a very small amount of oxygen, because of its long lifetime. Consequently, it is concluded that the encounter of the triplet DMA in its lowest vibrational level and the oxygen molecule in the ground state does not lead to DMA cation even in highly polar solvents. The CT absorption of $DMA\cdots O_2$ extends far beyond the (0–0) band of phosphorescence spectrum (27 kK) of DMA, indicating that the triplet state (v=0) of DMA is higher in energy than the CT (v=0) level. The above result, therefore, seems to be explained by assuming that the process

$$D^+\cdots A^- \rightsquigarrow D^+_{solv} + A^-_{solv}$$

should have an energy barrier as indicated in Fig. 8. In a highly polar solution, the charge transfer $D^+\cdots A^-$ state is thought to be stabilized by the solvation effect. The stabilization is the greater as the distance R_{DA} gets larger, possibly causing an energy maximum as indicated by the broken curve. In such a solution, the ground state $D\cdots A$ pair is excited to the charge transfer $D^+\cdots A^-$ state, not to the $D^+_{solv}\cdots A^-_{solv}$ state, in accordance with the Franck-Condon principle. It is conceivable, then, that only the excited DA pair, having energy higher than the maximum of the barrier, and accordingly larger intermolecular distance, will transfer to the $D^+_{solv}\cdots A^-_{solv}$ state.

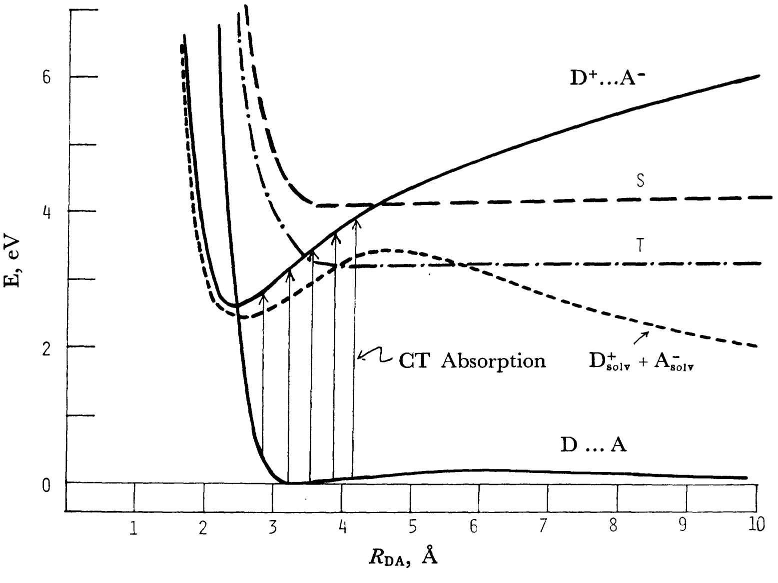

Fig. 8. Schematic diagram of the energy curves for the ground and various excited states of a donor-acceptor system.

Another mechanism, in which collison of oxygen with the donor in the singlet excited state leads to $D^{+}{}_{solv}$ and $O_2^{-}{}_{solv}$ seems rather unlikely, because the short lifetime of the singlet excited donor and relatively low concentration of oxygen in the solution ($\sim$0.01 M) suggest that such a process is of minor importance.

The above interpretation of the experimental results assumes the formation of oxygen anion. In aqueous solutions it has been proved by pulse radiolysis of H_2O–O_2 system.[18] According to this and also to spectroscopic studies of the oxygen-doped alkali-halide crystals,[19] the oxygen anion has absorption spectrum lying in the region around 2400 Å. In our experimental conditions, therefore, it was impossible to detect the spectrum of oxygen anion even if it exists for a certain length of time. It is also very likely that the O_2^- anion reacts with the solvent rapidly, forming other types of anions.

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18) G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, **68**, 1169 (1964).

19) J. Rolfe, F. R. Lipsett and W. J. King, *Phys. Rev.*, **123**, 447 (1961).