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Fluorescence Quenching and the Charge Transfer in the Excited State. III. Flash Photolytic Studies*[1]

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It has been established by the flash photolysis that the *N,N*-dimethyl β-naphthylamine (DMN) cation is produced by the interaction of excited DMN with dimethyl isophthalate (DMP). The assignment has been made by comparing the transient spectrum with that obtained by the γ-radiolysis of DMN in *s*-butyl chloride. The decay of the DMN cation is first order in acetone (DK, 20.7), ethanol (24.3) DMF (36.7), second order in formamide (109.5) and it is the superposition of first and second order in acetonitrile. This strongly suggests that the radical cation exists as the solvent-shared ion pair in medium polar solvents while as free species in highly polar solvents. The decay of the former has been found to be not essentially affected by oxygen. The finding that the transient spectrum is observed even in the aerated solution supports the view that it is produced at the singlet excited state. From the effect of [DMP] on the yield of triplet DMN, it has been inferred that the radiationless process occurring in the ex-CT complex is mainly internal conversion. The reactivity of the triplet DMN against DMP has been found very small as compared with that of the signlet excited state; the rate constant for $(\mathrm{DMN})^{\mathrm{T}}+\mathrm{DMP}\rightarrow\mathrm{DMN}+\mathrm{DMP}$ was $k_{10}\simeq10^5\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$. The erroneous discussion given in the previous paper has been corrected; the decrease both in the quenching constant (for normal fluorescence) and in the emissivity of the ex-CT emission with the solvent polarity (in slightly polar solvents) is most likely to be attributed to the solvent-solute interaction, the increase of which (with the increase in solvent polarity) is unfavorable both to the formation of the ex-CT complex and to the emissivity of the ex-CT emission.

In 1961 Weller *et al.*[1] discovered anomalous fluorescence in the system of perylene and aromatic amines dissolved in non polar solvents, the emission due to the charge transfer complex which is formed only in the excited state. At the same time, they also established by means of a flash technique, the formation of radical anions for the similar systems dissolved in polar solvents. These discoveries are the first confirmative evidence for charge transfer (CT) and electron transfer (ET) mechanisms for the quenching of fluorescence. Since then, extensive studies on the similar systems have been made by Mataga *et al.*[2-6] as well as Weller's group[7-9] and much information has been obtained in particular, on the behavior of excited CT (ex-CT) complexes.

In our previous papers,[10,11] one of the present authors (M. K.) with collaborators, has shown that the quenching action of methylbenzoate and dimethyl isophthalate (DMP) on the fluorescence of *N,N*-dimethyl β-naphthylamine (DMNA) can be interpreted satisfactorily by CT and ET mechanisms. Thus in support of CT mechanism, a new emission with a longer wavelength peak and with a large solvent effect, was observed in non polar or slightly polar solvents. (DK$<$10), the emission which is most likely to be ascribed to ex-CT complex. In highly and medium polar solvents (DK$\gtrsim$20) on the other hand, such an emission was absent and yet the quenching constant was very large and increased with the polarity of the solvent, in consistence with

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*[1] A short communication was published in *Z. physik. Chem. N. F.*, **57**, 103 (1968).

[1] H. Leonhard and A. Weller, *ibid.*, **29**, 277 (1961); *B. Bunsenges. physik. Chem.*, **67**, 791 (1963); "Luminescence of Organic and Inorganic Materials," ed. by H. P. Kellmann and G. M. Spruch, John Wiley & Sons, New York (1962), p. 74.

[2] N. Mataga, T. Okada and N. Yamamoto, This Bulletin, **39**, 2562, 2563 (1966).

[3] N. Mataga, T. Okada and K. Ezumi, *Mol. Phys.*, **10**, 201 (1966).

[4] N. Mataga, K. Ezumi and T. Okada, *ibid.*, **10**, 203 (1966).

[5] N. Mataga, T. Okada and N. Yamamoto, *Chem. Phys. Letters*, **1**, 119 (1967).

[6] N. Mataga and K. Ezumi, This Bulletin, **40**, 1355 (1967).

[7] H. Beens, H. Knibbe and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967).

[8] H. Knibbe, K. Röllig, F. P. Schäffer and A. Weller, *ibid.*, **47**, 1184 (1967).

[9] H. Knibbe, D. Rehm and A. Weller, *Z. physik. Chem. N. F.*, **56**, 95, 99 (1967).

[10] T. Miwa and M. Koizumi, This Bulletin, **39**, 2603 (1966).

[11] K. Kaneta and M. Koizumi, *ibid.*, **40**, 2254 (1967).

ET mechanism. A difference between our system and Weller-Mataga's systems (W-M systems) are that the donor-acceptor relation is inversed, namely the fluorescer is a donor in our system while it is an acceptor in W-M systems.

The present paper is concerned with the flash photolytic studies on the system consisting of DMP and DMNA or β-napthyl ethyl ether (NEE) in various solvents. The principal purpose is of course, to detect the radical cation of fluorescer in highly or medium polar solvents in order to confirm definitely ET mechanism in our system. This has been verified in the case of DMNA; the transient spectrum observed, agreed satisfactorily with that of the radical cation obtained by the γ-radiolysis of DMNA in *s*-butyl chloride. In the case of NEE, the similar transient spectrum was observed but it did not agree with the one obtained by the γ-ray radiolysis. The conclusive assignment, therefore, must await further studies.

The second purpose of the present work, *i. e.*, the investigation of the behavior of the radical cation in various solvents, has been carried out, in view of the above results, mainly on the DMNA radical. It has been established that the free radical cation or the solvent-shared ion pair is formed depending on the polarity of the solvent.

The third purpose is to elucidate, in relation to the solvent effect, the radiationless processes occurring in the ex-CT complex. This has been done by examining the influence of quencher concentration on the yield of triplet DMNA. It has been found that the non radiative process in question is mainly the internal conversion to the ground state molecule. In connection with this investigation, the reactivity of triplet DMNA toward the quencher in various solvents has also been investigated. This has been found to be far less than that of the singlet excited state.

Finally comprehensive discussion has been given in which an erroneous discussion made in the previous paper[11] has been corrected.

Experimental

Materials. *N,N*-Dimethyl β-naphthylamine, *m*-dimethyl isophthalate, cyclohexane, benzene, isopropyl ether, ethyl ether, ethyl acetate, methyl acetate, ethyl benzoate and dimethyl formamide were purified in the same way as in a previous paper.[10]

β-Naphthyl ethyl ether was prepared according to reference.[12] The crude product was recrystallized four times from ethanol and finally sublimed *in vacuo*.

Phthalic anhydride of Kanto-Kagaku G. R. grade was recrystallized twice from benzene and was dried *in vacuo*.

Phthalonitrile of Wakojunyaku was recrystallized from the water-ethanol mixture (1 : 1 in volume) three times.

Liquid paraffin of Kanto-Kagaku G. R. grade was used without purification.

Bromobenzene of Wakojunyaku E. P. grade was fractionally distilled. Bp 155.0—155.5°C.

Ethanol of Wakojunyaku G. R. grade was distilled with a column of precision type. Bp 78.3°C.

Methanol of Wakojunyaku G. R. grade was treated with metallic magnesium and iodine, and then distilled. Bp 64.5°C.

Formamide of Wakojunyaku G. R. grade was purified by fractional solidification three times.

Apparatus and Procedure. The flash apparatus and the procedures were the usual ones.

Results and Discussion

Transient Spectra in the Presence and in the Absence of a Quencher. Figure 1 gives a transient spectrum obtained upon flashing the solution of DMNA in cyclohexane. This spectrum can safely be ascribed to T–T absorption on the ground of its short life time of about 60 μsec (first order decay, see below) and of the non-appearance in the aerated solution. A similar spectrum was obtained in liquid paraffin and in isopropyl ether*[2] but was not in bromobenzene, ethyl acetate and ethyl benzoate, all of which belong to slightly polar solvent. This seems very curious and should be reinvestigated.

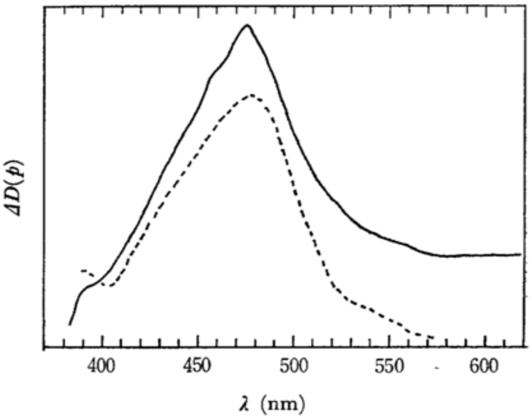

Fig. 1. T-T absorption spectra of DMNA in cyclohexane in the absence and in the presence of quencher.
30 μsec after flash
——: [DMNA]$=5\times10^{-4}$ M, [DMP]$=0$ M
- - -: [DMNA]$=5\times10^{-4}$ M, [DMP]$=5\times10^{-2}$ M

Upon addition of DMP as much as 5×10^{-2} M to the DMNA solution in cyclohexane, a similar T–T absorption was still observed although the intensity was somewhat weakened, and no new transient absorption was detected. This is just the result expected, since the ex-CT complex formed in nonpolar solvents, being very short-lived, cannot be observed by the usual flash technique.

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[12] W. A. Davis, *J. Chem. Soc.*, **77**, 33 (1900).

*[2] The statement that no T-T absorption appeared in isopropylether, in the previous paper, should be corrected.

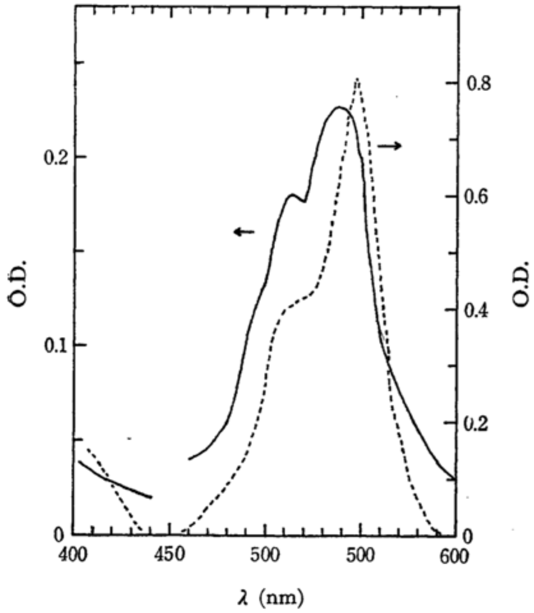

Fig. 2. Transient absorption of DMNA radical cation.
[DMNA]$=10^{-3}$ M, [DMP] 5×10^{-2} M
——: in DMF at room temp. by flash photolysis
- - -: in *s*-butylchloride at 77°K by γ-radiolysis

In highly or medium polar solvents (DK$\gtrsim$20) such as acetone, ethanol, acrylonitrile, dimethylformamide (DMF) and formamide, DMNA gave somewhat broadened T–T absorption.

Upon addition of $\lesssim 10^{-2}$ M DMP, a new absorption with a peak around 540 nm appeared in all the above solvents. Figure 2 shows as an example, a transient spectrum in the DMF solution. This is compared with the absorption spectrum of the DMNA cation obtained by the γ-ray radiolysis of the solution in *s*-butyl chloride at 77°K.[*3] Fairly good agreement of the two spectra supports the assignment of our transient species as a radical cation.[*4]

Figure 3 gives the transient spectra in the acetone solutions. One can see the similar spectrum in the aerated solution. This indicates that the formation of radical cation occurs at the singlet excited state and that it is insensitive to oxygen, in agreement with the general behavior of radical cation.[13)]

Furthermore, the usage of phthalic anhydride and phthalonitrile as quencher, gave the similar transient spectra.

According to the unpublished results of our group, the fluorescent behavior of NEE-DMP system is similar to that of DMNA-DMP system in the points that it gives ex-CT emission in a slightly polar solvent but not in highly or medium polar solvents where high quenching is significant.

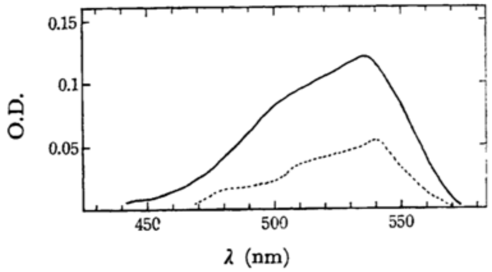

Fig. 3. Transient absorption spectra of DMNA radical cation in acetone in the absence and in the presence of oxygen, 30 μsec after flash.
[DMNA]$=5\times10^{-4}$ M, [DMP]$=5\times10^{-2}$ M
——: in degassed acetone
- - -: in aerated acetone

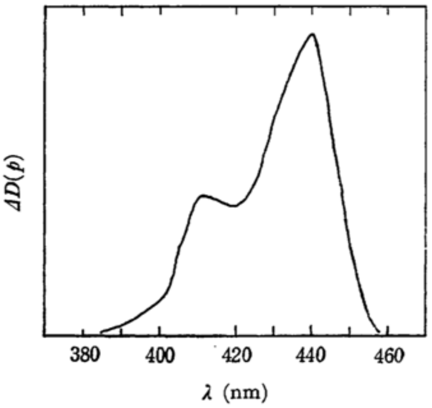

Fig. 4. T–T absorption spectra of NEE in cyclohexane, 30 μsec after flash.
[NEE]$=1.2\times10^{-3}$ M

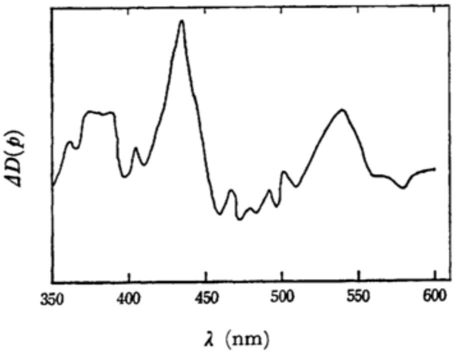

Fig. 5. Transient absorption spectra of NEE in DMF in the presence of quencher, 30 μsec after flash.
[NEE]$=10^{-3}$ M, [Q]$=10^{-1}$ M

[*3] The authors are gratefull to Dr. T. Shida (*Inst. Phys. Chem. Research, Tokyo)* for having performed this experiment.

[*4] Possibility that the absorption of radical cation and anion overlaps in the same region cannot altogether be denied (although not likely), since the latter could not be detected in the present work.

13) T. Ohno, S. Kato and M. Koizumi, This Bulletin, **39**, 232 (1966).

Table 1. The decay constants and the yields of the DMNA radical cation in various conditions

Concentrations of		k (sec^{-1})		D_{540}	
DMNA, M	m-DMP, M	degassed	aerated	degassed	aerated
5×10^{-4}	10^{-2}	1.7×10^{4}	2.7×10^{4}	0.106	0.05
5×10^{-4}	5×10^{-2}	2.6×10^{4}	1.9×10^{4}	0.15	0.08
5×10^{-4}	10^{-1}	2.0×10^{4}	2.7×10^{4}	0.30	0.08
10^{-3}	5×10^{-2}	2.0×10^{4}	2.0×10^{4}	0.10	0.06
10^{-3}	10^{-1}	1.8×10^{4}	2.6×10^{4}	0.18	0.06

Table 2. The half-life periods and the yields of the DMNA radical cation in acetonitrile

Concentration of		τ sec		D_{540}	
DMNA, M	m-DMP, M	degassed	aerated	degassed	aerated
5×10^{-4}	10^{-2}	3.4×10^{-4}	4.8×10^{-4}	0.097	0.064
5×10^{-4}	5×10^{-2}	4.1×10^{-4}	4.1×10^{-4}	0.098	0.086
5×10^{-4}	10^{-1}	4.4×10^{-4}	5.0×10^{-4}	0.11	0.084
10^{-3}	5×10^{-2}	3.3×10^{-4}	3.2×10^{-4}	0.084	0.074
10^{-3}	10^{-1}	4.7×10^{-4}	6.0×10^{-4}	0.093	0.075

Hence the similar flash experiments were performed on this compound.

Figure 4 gives a T–T absorption spectrum of NEE in cyclohexane, which agrees with the one reported by Porter and Windsor.[14] In the case of slightly polar solvents, the addition of $\sim10^{-2}$ M DMP gives essentially the similar transient spectrum.

In highly polar solvents such as DMF and acetonitrile, quite a different spectrum is observed as shown in Fig. 5. The spectra in these solvents are very similar to each other with two peaks around ~540 and 500 nm and furthermore they resemble that of DMNA to some extent. It seems most likely to ascribe this spectrum to a radical cation of NEE, but the spectrum of the radical cation obtained by the γ-radiolysis in s-butyl chloride was quite different and the conclusive assignment should await further sutdies.

The Behavior of DMNA Radical Cation in Various Polar Solvents. In DMF, the decay rate and the yield of the radical cation immediately after flashing (measured by the optical density at 540 nm) were investigated in various conditions. The results are listed in Table 1. The decay was first order.

One can say that the first order rate constant is essentially the same for both aerated and deaerated solutions. The yield in the degassed solution increases evidently with the increase in the concentration of DMP. The yield in the aerated solution is less than half that in the degassed solution. This may be due to the competitive deactivation reaction of the singlet excited DMNA by oxygen. All the above results support the view that the radical cation is produced at the singlet excited state.

In the case of acetone and ethanol used as solvents, the decay obeys first order in the degassed solution. The rate constants is 4.1×10^{3} sec^{-1} for ethanol, and 7.5×10^{3} sec^{-1} for acetone. In the aerated solution, the yield is negligible in the case of ethanol and very small for acetone.

In acetonitrile, the decay is always the superposition of the first and the second order processes. Table 2 gives the yield as measured at the maximum of the optical density at 540 nm and the half life period (τ) (not very accurate) as evaluated from the decay curves.

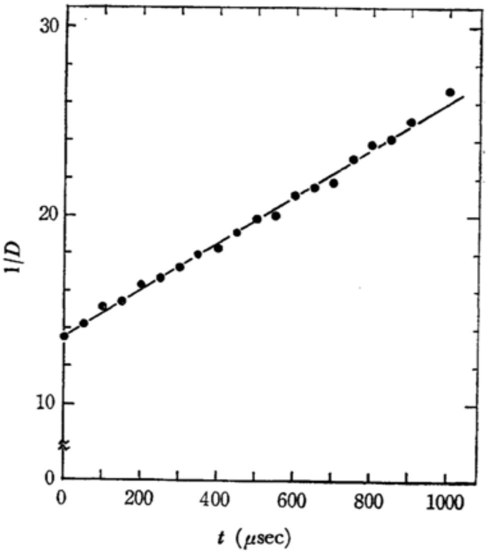

Fig. 6. Second order decay of DMNA radical cation in formamide.
[DMNA]$=1\times10^{-3}$ M, [DMP]$=5\times10^{-2}$ M

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[14] G. Porter and M. W. Windsor, *Proc. Roy. Soc.*, **A245**, 238 (1958).

TABLE 3. THE RATE CONSTANTS AND THE YIELD OF THE DMNA RADICAL CATION IN FORMAMIDE (PA, phthalic anhydride)

Concentration of			k ($\text{M}^{-1}\,\text{sec}^{-1}$)		D_{540}
DMNA, M	DMP, M	PA, M	(degassed)	(aerated)	(degassed)
1.5×10^{-3}	5×10^{-2}	—	1.35×10^{5}	1.0×10^{5}	0.264
1.5×10^{-3}	—	5×10^{-2}	4.3×10^{4}	7×10^{4}	0.305

TABLE 4. HALF-LIFE VALUES AND THE YIELDS OF THE DMNA RADICAL ION

Solvent		[DMNA], M	Acceptor, M	τ sec	D_{540}
Acetone		5×10^{-4}	5×10^{-2} (DMP)	1.3×10^{-4}	0.116
	Aerated	5×10^{-4}	5×10^{-2}	3.3×10^{-4}	0.056
Ethanol		5×10^{-4}	5×10^{-2}	2.5×10^{-4}	0.115
DMF		5×10^{-4}	5×10^{-2}	3.8×10^{-5}	0.047
	Aerated	5×10^{-4}	5×10^{-2}	5.3×10^{-5}	0.036
		5×10^{-4}	5×10^{-2} (PA)	2.6×10^{-5}	0.056
Acetonitrile		5×10^{-4}	5×10^{-2} (DMP)	4.1×10^{-4}	0.098
	Aerated	5×10^{-5}	5×10^{-2}	4.1×10^{-4}	0.086
Formamide		1.5×10^{-3}	5×10^{-2}	5.4×10^{-4}	0.264
		1.5×10^{-3}	5×10^{-2} (PA)	7.7×10^{-4}	0.305
		1.0×10^{-3}	5×10^{-2} (DMP)	1×10^{-3}	0.074

In this case the yield in the aerated solution is not so different from that for the degassed solution.

In the case of formamide, the decay of the DMNA radical cation is second order as is shown in Fig. 6. The similar result was obtained when phthalic anhydride was used instead of DMP. The results are listed in Table 3.

Summarizing the behavior of the radical cation of DMNA in various solvents, the notable finding is that the radical cation decays according to first order in the solvents of medium polarity (acetone (DK=20.7), ethanol (24.3) and DMF (36.7)) while in a solvent of high polarity (formamide (DK=109.5)), it is second order and in acetonitrile (intermediate in the above two groups), the decay is a superposition of the first and second order. In view of the quite similar absorption spectra observed in all the cases, there seems to be no other interpretation than the following. In the medium polar solvents, the radical cations and anions exist as solvent-shared ion pairs which reconvert to the stable species by a unimolecular process, while in the highly polar solvents the free radical ions exist as two separate species and recombined bimolecularly. In acetonitrile, the separated radical species and the ion pairs may coexist.

In Table 4, half-life values and the yields of the DMNA radical ion in various solvents are summarized.

The result that the half-life in DMF is one order smaller than in formamide despite the several ten times smaller yield in the former, reconfirms that the radical cation exists as ion pair in the former and further it indicates that the ion pair in DMF is rather unstable. The order in the τ-values (DMF$<$ethanol, acetone$<$acetonitrile) suggests that the ion pair becomes more stable in this order.

Interaction between Triplet DMNA and DMP in Nonpolar Solvents. It is interesting to examine the influence of the addition of DMP on the yield of triplet DMNA and on its decay. The former is expected to afford the information as to the radiationless processes for the ex-CT complex while the latter will enable us to compare the reactivity of singlet and triplet excited states against the acceptor-type quencher. Cyclohexane is the most suitable solvent because the yield of ex-CT complex is very high and accordingly the quenching constant is also very high (K=65) in this solvent.

Before describing the results, it is convenient to list up the usuful relations which can be derived on the basis of the following plausible scheme.

$$\begin{array}{lll}
\text{F} + h\nu \rightarrow {}^1\text{F}^* & I_{\text{ab}} & \\
\left.\begin{array}{ll} {}^1\text{F}^* \rightarrow \text{F} + h\nu & k_1 \\ {}^1\text{F}^* \rightarrow \text{F} & k_2 \\ {}^1\text{F}^* \rightarrow {}^3\text{F} & k_3 \end{array}\right\} & & \begin{array}{l}\text{free}\\ \text{fluorescer}\\ \text{molecule}\end{array} \\
\left.\begin{array}{ll} {}^1\text{F}^* + \text{Q} \rightarrow {}^1\text{F}^* \cdots \text{Q} & k_4 \\ {}^1\text{F}^* \cdots \text{Q} \rightarrow {}^1\text{F}^* + \text{Q} & k_{-4} \\ {}^1\text{F}^* \cdots \text{Q} \rightarrow (\text{F}^+ \cdots \text{Q}^-)^* & k_5 \end{array}\right\} & & \begin{array}{l}\text{encounter}\\ \text{complex}\end{array} \\
\left.\begin{array}{ll} (\text{F}^+ \cdots \text{Q}^-)^* \rightarrow \text{F} + \text{Q} + h\nu_{\text{CT}} & k_6 \\ (\text{F}^+ \cdots \text{Q}^-)^* \rightarrow \text{F} + \text{Q} & k_7 \\ (\text{F}^+ \cdots \text{Q}^-)^* \rightarrow {}^3\text{F} + \text{Q} & k_8 \end{array}\right\} & & \begin{array}{l}\text{ex-CT}\\ \text{complex}\end{array}
\end{array}$$

The above scheme is essentially the same as the one proposed in the previous paper;[11] small differences are 1) discrimination of the internal conversion and intersystem crossing processes (k_2, k_3 and k_7, k_8) and 2) neglect of any kinds of deactivation process, such as $({}^1F^*\cdots Q)\rightarrow F+Q$ or $({}^1F^*\cdots Q)\rightarrow {}^3F+Q$, for the encounter-complex. The former is necessary to treat the triplet yield. The latter neglect may be permitted since in the present system, the formation of ex-CT complex is considered to be a principal process for quenching. It is to be added that the ex-CT complex is assumed to behave irreversibly.

On the basis of the above scheme, the application of the steady method leads to the following formulas straighforwardly.

$$D_T/D_{T_0} = \frac{1+\dfrac{k_4k_8}{k_3}\gamma\tau_2[Q]}{1+\gamma k_4\tau_1[Q]} \tag{1}$$

$$I_F/I_{F_0} = \frac{1}{1+k_4\tau_1\gamma[Q]} \tag{2}$$

$$I_{F,CT} = \frac{k_4k_6\gamma\tau_1\tau_2[Q]I_{ab}}{1+k_4\tau_1\gamma[Q]} \tag{3}$$

where

$$\gamma = k_5/(k_{-4}+k_5),\quad \tau_1 = 1/(k_1+k_2+k_3)$$

$$\tau_2 = 1/(k_6+k_7+k_8)$$

From the above equations and by using the relations

$$K = k_4\gamma\tau_1 \tag{4}$$

$$\Phi_{CT} = k_6\tau_2 \tag{5}$$

$$\Phi_0 = k_1\tau_1 \tag{6}$$

where K is a quenching constant and Φ_{CT} is a probability of CT emission, the follwoing relations can easily be obtained.

$$I_{F,CT} = \frac{K\phi_{CT}[Q]}{1+K[Q]} \tag{7}$$

$$\begin{aligned} I_{F,CT}/I_F &= \frac{I_F}{I_{F_0}}k_4k_6\gamma\tau_1\tau_2[Q]I_{ab} \\ &= \frac{k_4k_6\gamma\tau_2[Q]}{k_1} = \frac{K\Phi_{CT}[Q]}{\Phi_0} \end{aligned} \tag{8}$$

$$\begin{aligned} \frac{D_T}{D_{T_0}} &= \frac{I_F}{I_{F_0}}\left(1+\frac{k_4k_8}{k_3}\gamma\tau_2[Q]\right) \\ &= \frac{I_F}{I_{F_0}}\left(1+\frac{k_8\tau_2}{k_3\tau_1}K[Q]\right) \end{aligned} \tag{9}$$

Turning to the experimental results, examples of the decay for triplet DMNA are shown in Fig. 7. From such decay curves the triplet yields and the apparent first order rate constants were evaluated for several concentrations of DMP. From the latter values, the following values were obtained as the genuine rate constants for the processes,

$$F^T \xrightarrow{k_9} F$$

$$F^T + Q \xrightarrow{k_{10}} F + Q$$

$$k_9 = 1.68\times10^4\ \text{sec}^{-1}\quad k_{10} \simeq 10^5\ \text{M}^{-1}\,\text{sec}^{-1}$$

It can be concluded from the above k_{10}-value that the reactivity of the triplet DMNA toward DMP is very small as compared with that of the singlet excited state.

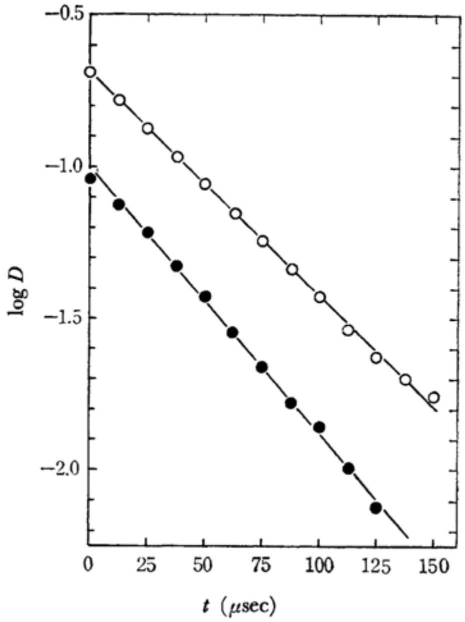

Fig. 7. First order decay of DMNA triplet in cyclohexane in the absence and in the presence of quencher.
○ [DMP]=0 M
● [DMP]=5×10⁻² M
[DMNA]=5×10⁻⁴ M

Table 5 gives the relative yields of the triplet state $[F^T]/[F^T]_0$ (suffix 0 denotes the absence of Q) as evaluated from the optical densities at 480 nm, and the relative fluorescence intensities obtained from the data given in previous paper.[11]

Although the data are rather scanty, the ratio $[F^T]/[F^T]_0$ is larger than I_F/I_{F_0} only by less than 10% or so. From Eq. (9) it may be concluded that $k_8\tau_2$ is several times smaller than $k_3\tau_1$.

TABLE 5. RELATIVE YIELDS OF TRIPLET AND RELATIVE FLUORESCENCE INTENSITIES

[Q], M	$[F^T]/[F^T]_0$	I_F/I_{F_0}	K[Q]
0	1	1	0
5×10^{-3}	0.80	0.75	0.33
10^{-2}	0.65	0.6	0.65
5×10^{-2}	(0.59)	0.23	3.3

Summary and Comprehensive Discussion

The present investigation has demonstrated clearly that the electron transfer occurs from the excited DMNA molecule to DMP in polar solvents.

The evidence for the view that the radical ions do not always exist as free ions but exist as solvent-shared ion pair, is afforded by the finding that the transient species in medium polar and in highly polar solvents, give essentially the similar spectrum and yet the decay feature in the former is first order whereas the latter is second order.

In nonpolar or slightly polar solvents, the ex-CT complexing has already been amply demonstrated in the previous paper, and some additional information has been obtained by the present flash studies. Since some papers dealing with the ex-CT complex appeared last year at about the same time as Part II of the present series, and since a part of the discussion given in the previous paper,11) has been found to be improper, the authors would like to take up some of the previous results as well as the present ones and generally discuss them, referring also the results of other workers.

In the previous paper it was shown that the relative quenching efficiencies $(a\gamma)_i/(a\gamma)_2$ (2; cyclohexane) and the relative emissivity of ex-CT complex $(\phi_{0,\mathrm{CT}})_i/(\phi_{0,\mathrm{CT}})_2$ in slightly polar solvents, ($\phi_{0,\mathrm{CT}}$; a ratio of the acts of an emitting process to those of the effective quenching process for normal fluorescence) decrease with the polarity of the solvent in somewhat similar manner. The result itself is correct, but the interpretation was erroneous. Thus the statement[*5] "… one common process for CT emission and the quenching process, *i. e.*, the process of formation of the ex-CT complex essentially affects both CT emission and the quenching process … and that this perhaps the main reason why ϕ_{CT} and $a\gamma$ decreases with the solvent polarity." is not correct. As is clear from the definition, ϕ_{CT} should reflect the emissivity of ex-CT complex itself. As long as the CT mechanism prevails, the decrease in $a\gamma$ naturally causes the decrease in the quantum yield of ex-CT emission, but the parallel decrease in ϕ_{CT} and $a\gamma$ should be interpreted to indicate that the more difficult the formation of ex-CT complex becomes, the less emitting the ex-CT complex becomes. This is very plausible on the basis of solvent-solute interaction, because as the solvent becomes more polar, the reorientation of solvent molecules becomes more and more difficult and at the same time, the interaction between the pdrouced ex-CT complex and solvent molecules becomes also larger, and this will cause the decrease in emissivity of ex-CT complex.

The previous results reinterpreted in this way is quite consistent with other workers' results. Thus Mataga *et al.*5) showed that in the ex-CT complex of pyrene and dimethylaniline, the rate constant for emission, k_f', decreases while that for radiationless process, k_i' increases and that the quantum yield, Q_F', largely decreases with the polarity of the solvent. Weller *et al.*8) also found that in the anthracen-diethylaniline system, the relative intensity of the ex-CT complex decreases with the solvent polarity and decreases far more than the lifetime of ex-CT emission. This is because, they interpreted, the former depends on the tendency with which the ex-CT complex is formed and also on the emissivity of the ex-CT complex, while the latter is concerned with the ex-CT complex itself.

As to the molecular processes which cause the decrease in the emissivity of the ex-CT complex with the solvent polarity, Mataga stressed the interaction between fluoresent species and solvent molecules which affect not only the molecular configurations (the configuration of the ex-CT complex and that of the surrounding solvent molecules) but also the electronic state of the ex-CT complex. Weller on the other hand considered that the increase in the solvent polarity enhances the process

$$(\mathrm{A}^-\cdots\mathrm{D}^+) \xrightarrow{k_{\mathrm{IP}}} \mathrm{A_S}^-\cdots\mathrm{D_S}^+ \qquad \text{(a)}$$

where $\mathrm{A_S}^-\cdots\mathrm{D_S}^+$ is nonfluorescent. Furthermore he attributed the decrease in the probability of ex-CT complexing with the increase of solvent polarity, to the competition of the following two processes,

$$\mathrm{A}^* + \mathrm{D} \rightarrow (\mathrm{A}^-\cdots\mathrm{D}^+) \qquad \text{(b)}$$

$$\mathrm{A}^* + \mathrm{D} \rightarrow (\mathrm{A_S}^-\cdots\mathrm{D_S}^+) \rightarrow \mathrm{A} + \mathrm{D} \qquad \text{(c)}$$

of which the latter prevails over the former as the solvent becomes more polar.

Although there is no doubt that such processes must generally be taken into consideration, the authors are inclined that Mataga's picture fits better to our system at least in slightly polar solvents. Because in slightly polar solvents ($\mathrm{DK} \lesssim 10$) the formation of the ion pair was not observed. More strong evidence is, as reported in the previous paper, that the addition of a small quantity of the highly polar solvent to the DMNA solution in nonpolar solvents causes a decrease of $a\gamma$ itself. This result can never be interpreted if only the competition between Process (b) and (c) is essential for quenching phenomena. That reorientation of solvent molecules is necessary for the ex-CT complexing was also clearly demonstrated by Mataga *et al.*6) by comparing the fluorescent spectra of aromatic hydrocarbons dissolved in aromatic dimethyl amines at low and high temperatures.

As to the radiationless processes occurring in the ex-CT complex, the authors, in the present paper, have demonstrated fairly clearly that in our system it is the internal conversion to the ground state molecule and not the intersystem crossing. This is somewhat similar to Mataga's result,5) that pyrene in acetonitrile involving dimethylamine gives no T-T absorption, but is contrary to Weller's result for the perylene-aromatic amine system.1)

[*5] p. 2262 in Part II, Ref. 11.

The finding that the reactivity of triplet DMNA toward DMP is much smaller than that of singlet state agrees with the current view that the triplet state generally resembles the ground state rather than the singlet excited state and it is of radical nature rather than ionic. Similar results have been reported also by Mataga *et al.*;⁶⁾ they found that the phosphorescent spectra of some hydrocarbons in dimethylaniline are practically the same as those in *n*-hexane and that the phosphorescent decay times are also the same in the both solvents.