BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1169—1175 (1972)

Photochemical Reactions of Aromatic Compounds. IX.[1] Photochemical Reactions of Dimethylaniline with Halobenzenes[2]

Chyongjin PAC, Takafumi TOSA, and Hiroshi SAKURAI
The Institute of Scientific and Industrial Research, Osaka University, Suita-shi, Osaka

(Received September 23, 1971)

Irradiation of methanolic solutions of DMA containing halobenzenes (chlorobenzene, bromobenzene and iodobenzene) and triethylamine (TEA) gave TEA hydrohalides in quantitative yields along with benzene (II), diphenyl, *N*-methylaniline, *o*- and *p*-dimethylaminodiphenyls (IV and V). From the properties of the products and spectroscopic and kinetic data, it was suggested that the reactions took place by way of electron transfer from DMA to halobenzenes. The electron transfer reactions were classified into a short range type (chlorobenzene and bromobenzene) and a long range type (iodobenzene) on the basis of the product ratio (IV+V)/II and the proportion of benzene-d_1 in the benzene fraction obtained from the photoreactions of DMA-d_6 with halobenzenes. From the kinetic and fluorescence data, an exciplex mechanism was suggested for the photoreactions with chlorobenzene and bromobenzene, and a direct electron transfer mechanism in the case of iodobenzene.

Photochemical bimolecular electron transfer reactions (ETR) are of physicochemical interest and have been investigated in connection with decay of exciplexes.[3-5] Except for ETR of triplet aromatic ketones with amines,[1,6] however, mechanistic details have not been fully investigated, although various photoinduced ETR have been published.[7-10]

In a series of works on photochemical ETR,[1,2,11]

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[1] Part VIII, C. Pac, H. Sakurai, and T. Tosa, *Chem. Commun.*, **1970**, 1311.

[2] A preliminary report, T. Tosa, C. Pac, and H. Sakurai, *Tetrahedron Lett.*, **1969**, 3635.

[3] A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968); H. Knibbe, D. Rehm, and A. Weller, *Z. Bunsenges. Physik. Chem.*, **72**, 257 (1968).

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

[5] H. Yamashita and M. Koizumi, This Bulletin, **41**, 2313 (1968).

[6] S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968); R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, **1969**, 1098.

[7] T. Latowski, *Z. Naturforsch.*, **23a**, 1127 (1968).

[8] M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *J. Amer. Chem. Soc.*, **92**, 6991 (1970).

[9] J. A. Barltrop and R. J. Owers, *Chem. Commun.*, **1970**, 1462.

[10] R. S. Davidson, *ibid.*, **1969**, 1450.

[11] C. Pac and H. Sakurai, *ibid.*, **1969**, 20; *Tetrahedron Lett.*, **1969**, 3829.

we published ETR from excited singlet dimethylaniline (DMA) to ground state anilinium salts.[12] The suggested mechanism was speculative, since spectroscopic investigation was limited on account of insolubility of anilinium salts in non-polar and less polar solvents. In an attempt to obtain more information on photochemical ETR mechanism, halobenzenes (chlorobenzene, bromobenzene and iodobenzene) were used as electron acceptors instead of anilinium salts, since they are soluble in most organic solvents.

In the present paper, we report the product distribution, spectroscopic and kinetic results. Qualitative discussion is given on the ETR distance depending on halobenzenes.

Results

Product Distribution. Irradiation of a methanolic solution of DMA containing a halobenzene in the presence of triethylamine (TEA),[13] by means of a Pyrex filter with a high pressure mercury arc, gave TEA hydrohalide in a quantitative yield along with benzene, diphenyl, *N*-methylaniline, *o*- and *p*-dimethylaminodiphenyls (Table 1).

$$\mathrm{DMA} + \mathrm{PhX} \xrightarrow[\mathrm{TEA}]{h\nu} \underset{\mathrm{I}}{\mathrm{TEA{\cdot}HX}} + \underset{\mathrm{II}}{\mathrm{PhH}} + \underset{\mathrm{III}}{\mathrm{Ph\text{-}Ph}}$$

$$+ \underset{\mathrm{IV}}{o\text{-}\mathrm{Ph\text{-}C_6H_4N(CH_3)_2}}$$

$$+ \underset{\mathbf{V}}{p\text{-}\mathrm{Ph\text{-}C_6H_4N(CH_3)_2}} + \mathrm{PhNHCH_3}$$

The structures of the products were confirmed by direct comparison of the physical and spectroscopic (NMR, UV, and IR) data with those of the corresponding authentic samples.

TABLE 1. PRODUCT DISTRIBUTION IN PHOTOCHEMICAL REACTIONS OF DMA WITH HALOBENZENES IN THE PRESENCE OF TEA[a)]

PhX	Yields (mmol)					Conversion[b)] (%)
	I	II	III	IV	V	
X=Cl	12.6	4.4	trace	5.3	0.7	35
X=Br	12.8	5.8	trace	4.0	0.5	50
X=I	12.0	11.3	trace	1.1	0.4	85

a) Irradiation of methanolic solutions (30 m*l*) containing 4 g DMA, 4 g halobenzenes and 5 m*l* TEA in a Pyrex tube with a high pressure mercury arc at room temperature.

b) Consumption of halobenzenes determined by vpc analyses.

Chlorobenzene and bromobenzene were stable in the absence of DMA and gave only a trace of benzene by irradiation for a long time. Iodobenzene was photolyzed to some extent, decomposition being considerably enhanced in the presence of DMA.

Control experiments showed that I, II, IV, and V increased linearly with irradiation time. Diphenyl could not be detected. However, all the products were stable under the reaction conditions and are considered to be primary products. The products ratios (IV+V)/II and IV/V were determined at 10—15% conversion and found to be dependent on halobenzenes used (Table 2).

TABLE 2. PRODUCT RATIOS (IV+V)/II AND IV/V[a)]

	PhX		
	X=Cl	X=Br	X=I
(IV+V)/II	1.8±0.17	1.1±0.1	0.24±0.07
IV/V	3.8±0.7	3.5±0.5	2.2 ±0.2

a) Irradiation of methanolic solutions (5 m*l*) containing 1.0 M DMA, 0.1 M TEA and 0.1 M halobenzenes at 313 nm. Mean values for every three runs.

It should be noted that the products except TEA hydrohalides were the same as those obtained from the photochemical reactions of DMA with trimethylphenylammonium halides.

Sensitized Decomposition of Halobenzenes by Carbonyl Compounds. Enhanced decomposition of halobenzenes by DMA could be interpreted as being caused by electronic energy transfer from an excited DMA to halobenzenes leading to decomposition of halobenzenes into phenyl radical and halogen atoms. If so, selected sensitizers would result in sensitized decomposition of halobenzenes. Sensitization with carbonyl compounds was thus carried out in order to confirm the possibility of triplet excitation transfer.

The 0–0 transition of DMA phosphorescence at 77°K was reported to lie at 26650 cm^{-1} (76.2 kcal/mol).[14] If triplet excitation transfer from DMA to halobenzenes take place, acetone (E_T 80 kcal/mol),[15] acetophenone (E_T 74 kcal/mol in non-polar solvents and 76.3 kcal/mol in polar solvents)[16] and propiophenone (E_T 75 kcal/mol in non-polar solvents)[16] can sensitize the decomposition of halobenzenes.

However, propiophenone- and acetophenone-sensitized decomposition did not occur for chlorobenzene and bromobenzene, and was not clear in the case of iodobenzene. Acetone was effective for decomposition of bromobenzene and iodobenzene, but entirely ineffective for chlorobenzene (Table 3). The results for chlorobenzene are understandable, since the lowest triplet state lies at 82 kcal/mol above the ground state.[17] Thus, the triplet energies of

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[12] C. Pac and H. Sakurai, *Tetrahedron Lett.*, **1968**, 1865; *Kogyo Kagaku Zasshi*, **72**, 230 (1969).

[13] In the absence of TEA, the photoreactions were complicated on account of the formation of DMA hydrohalides, since DMA was photochemically reactive with DMA hydrohalides.[12] For example, the photolysis of a methanolic solution containing DMA and bromobenzene gave crystal violet and bis(*p*-dimethylaminophenyl)methane along with II—V, while the photolysis in the presence of TEA gave a clean solution without the formation of the above two products.

[14] Y. Gondo and Y. Kanda, *Mem. Fac. Kyushu Univ.*, **C5**, 133 (1964).

[15] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966); *J. Amer. Chem. Soc.*, **88**, 3467 (1967).

[16] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

[17] S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

Table 3. Sensitized decomposition of halobenzenes with carbonyl compounds[a]

PhX	Ketones	E_T (kcal/mol)	Yields of benzene (mg)
X=Cl	—		0
	Acetophenone	76.3[b]	0
	Propiophenone	75.0[b]	0
	Acetone	−80[c]	>2
X=Br	—		>2
	Acetophenone		>2
	Propiophenone		>2
	Acetone		50
X=I	—		7.5
	Propiophenone		7.5
	Acetone		17.5

a) Irradiation of *t*-butanol solutions containing 0.1 M ketones and 0.1 M halobenzenes in a Pyrex tube for 10 hr with a high pressure percury arc.
b) See Ref. 16.
c) See Ref. 15.

bromobenzene and iodobenzene can be estimated to be in the range 77—80 kcal/mol.

The triplet excitation transfer mechanism can be eliminated for DMA-induced decomposition of chlorobenzene and bromobenzene, and is considered to be also unfavorable in the case of iodobenzene.

Fluorescence Spectra of DMA in the Presence of Halobenzenes. A cyclohexane solution of DMA showed a structureless fluorescence spectrum with a maximum at 334 nm. On addition of chlorobenzene and bromobenzene into a cyclohexane solution of DMA, however, the fluorescence was quenched with bathochromic shift of the spectra. When chlorobenzene and bromobenzene were used as solvents, very weak and red-shifted new emissions appeared with respective maxima at 373 and 412 nm along with total quenching of DMA fluorescence (Fig. 1).[26] Appearance of new emissions was general for chlorobenzene and bromobenzene solutions of aromatic amines. New very weak emission maxima for aniline, *N,N*-dimethyl-*p*-anisidine, *N,N*-dimethyl-*p*- and -*m*-toluidines are given in Table 4.

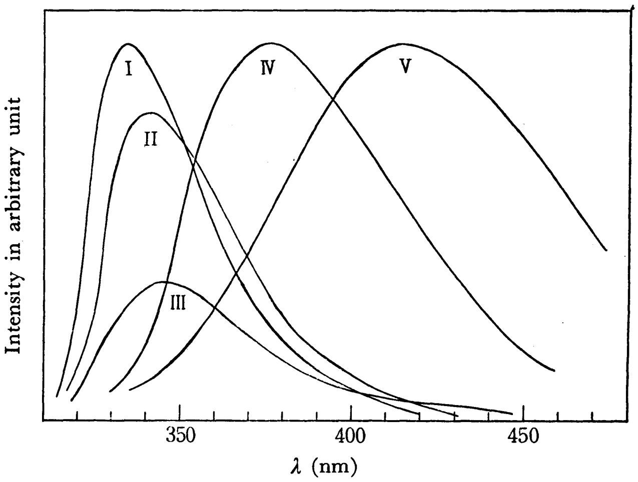

Fig. 1. The fluorescence spectra of DMA solutions in cyclohexane (curve I), in cyclohexane in the presence of 1 M PhCl (II), in cyclohexane in the presence of 0.1 M PhBr (III), in chlorobenzene (IV) and in bromobenzene (V). The spectra I—III were recorded with the same sensitivity, but the spectra IV and V with much higher sensitivities.

Table 4. Fluorescence maxima of aromatic amines in chlorobenzene and bromobenzene[a]

Amines	Benzene	Solvent PhCl (nm)	PhBr	IP[b] (eV)	Excitn[e] light (nm)
Aniline	328	370	388	7.76	298
DMA	346	373	412	7.44	305
m-DMT[c]	343	397	407	7.35	304
p-DMT	352	412	414	7.33	310
p-DMAN[d]	369	428	429		319

a) Uncorrected maxima for air saturated solutions 10^{-3} — 10^{-2} M amines.
b) Ionization potentials reported by P. G. Farrel and J. Newton.[28b]
c) *N,N*-dimethyltoluidine.
d) *N,N*-dimethylanisidine.
e) Excitation spectra were about the same.

In contrast, fluorescence quenching with iodobenzene was not accompanied with any bathochromic shift of the spectrum or new emissions even in non-polar solvents. Moreover, solvent-dependency of quenching constant $k_r\tau$ also differed in the two groups of halobenzenes. In the case of iodobenzene, $k_r\tau$ was dependent on solvent viscosity rather than solvent polarity (Table 5). On the other hand, fluorescence quenching with chlorobenzene was more effective in a polar solvent than in a non-polar solvent; the half-value concentration was 0.2 M in methanol, about 10 times lower than that in benzene (*ca.* 2 M).[18]

Table 5. Solvent dependency of fluorescence quenching with iodobenzene[a]

Solvents	η at 20°C (cpoise)	Rel. $1/\eta$	Rel. k_r
n-Hexane	0.32	2.0	1.5
Acetonitrile	0.59	1.1	1.2
Benzene	0.65	1.0	1.0
Methanol	0.611	1.06	0.98

a) Fluorescence quenching for the solutions containing 0.1 M DMA and 10^{-3}—5×10^{-2} M iodobenzene.

For methanolic solutions, however, fluorescence quenching with any halobenzene was accompanied with no change of shape of the spectra, bathochromic shift or appearance of new emissions.

Kinetic Results. Quantum yields for the formation of halide anions at 313 nm at room temperature were determined by potassium ferrioxalate actinometry.[19] Quantitative analyses for chloride and bromide anions were titrimetrically carried out by a

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[18] Since the shape of the fluorescence spectra in the presence of chlorobenzene were changed, the half-value concentration could not be explicitly determined.

[19] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

modified Vorhard's method[20] and for iodide anion by Jamieson's method.[21] The conversion was maintained below 10% for all the kinetic runs. Reciprocals of the quantum yields changed linearly with reciprocals of concentrations of halobenzenes (Fig. 2).

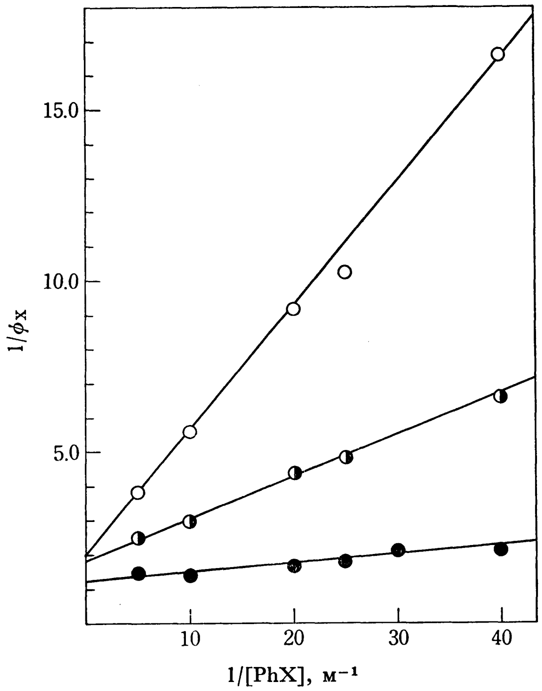

Fig. 2. The plots of reciprocals of quantum yields *vs.* reciprocals of concentrations of PhCl (-○-), PhBr (-◑-) and PhI (-●-).

Since fluorescence quenching for methanolic solutions was accompanied with no change of shape of the spectra, relative intensities of the fluorescence maximum at 352 nm in the absence and presence of halobenzenes (F_0/F) were plotted with concentrations of halobenzenes. Linear Stern-Volmer plots were obtained (Fig. 3). Table 6 lists the fluorescence quenching constants ($k_r\tau$, the slopes of the plots in Fig. 3), the rate ratios k_r/k_d ($=k_r\tau$, the intercept-to-slope ratios of the straight lines in Fig. 2) and k_n/k_e (the intercepts).

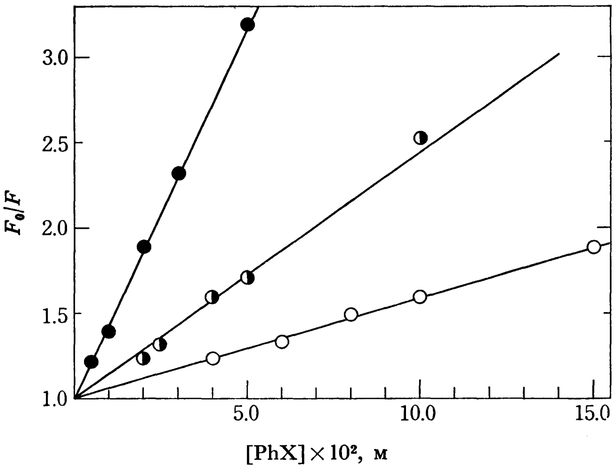

Fig. 3. The Stern-Volmer plots for the quenching of DMA fluorescence with chlorobenzene (-○-), bromobenzene (-◑-) and iodobenzene (-●-).

TABLE 6. FLUORESCENCE QUENCHING CONSTANTS AND THE RATE RATIOS OBTAINED FROM QUANTUM YIELD MEASUREMENTS

Rate ratios	PhX X=Cl	X=Br	X=I[a]
k_r/k_d (M^{-1})[b]	5.7	15.8	62.5
k_n/k_e[b]	1.0	0.8	0.25
$k_r\tau$ (M^{-1})[c]	5.2	13.6	42.0

a) The rate ratio k_n/k_e is replaced by k_q/k_r' and $k_r=(k_r'+k_q)$.
b) Mean values for every three runs within ±10% error.
c) The slopes of Stern-Volmer plots for the solutions containing 0.1 M DMA and 10^{-3}–0.15 M halobenzenes which were not affected appreciably by the presence of 0.1 M TEA.

Discussion

The products obtained from the photochemical reactions can be interpreted by ETR mechanism; electron transfer from excited DMA to ground state halobenzenes led to DMA radical cation and halobenzene radical anions. Since halobenzenes are dis-

$$\mathrm{DMA} \xrightarrow{h\nu} {}^1\mathrm{DMA} \tag{1}$$

$$^1\mathrm{DMA} \xrightarrow{k_d} \mathrm{DMA} \tag{2}$$

$$^1\mathrm{DMA} + \mathrm{PhX} \xrightarrow{k_r} \text{“exciplex”} \tag{3}$$

$$\text{“exciplex”} \xrightarrow{k_n} \mathrm{DMA} + \mathrm{PhX} \tag{4}$$

$$\text{“exciplex”} \xrightarrow{k_e} (\mathrm{DMA}^+ + \mathrm{Ph}\cdot + \mathrm{X}^-) \tag{5}$$

Cage Reaction

$$(\mathrm{DMA}^+ + \cdot\mathrm{Ph}) \begin{cases} \longrightarrow \mathrm{PhH} + \mathrm{PhN(Me)CH_2}^+ & (6) \\ \longrightarrow \text{IV and V} + \mathrm{H}^+ & (7) \\ \longrightarrow \mathrm{DMA}^+ + \mathrm{Ph}\cdot & (8) \end{cases}$$

Free Radical Reaction

$$\mathrm{Ph}\cdot + \text{Hydrogen Donors} \longrightarrow \mathrm{PhH} \tag{9}$$

$$\mathrm{Ph}\cdot + \mathrm{DMA} \longrightarrow \text{IV and V} + \mathrm{H} \tag{10}$$

Further Reactions

$$\mathrm{PhN(Me)CH_2}^+ + \mathrm{H_2O} \longrightarrow \mathrm{PhNHMe} + \mathrm{CH_2O} + \mathrm{H}^+ \tag{11}$$

$$\mathrm{NEt_3} + \mathrm{HX} \longrightarrow \mathrm{NEt_3\cdot HX} \tag{12}$$

$$\mathrm{DMA}^+ \longrightarrow \text{Polymeric products and others} \tag{13}$$

$$1/\phi_X = \left(1+\frac{k_d}{k_r[\mathrm{PhX}]}\right)\left(1+\frac{k_n}{k_e}\right) \tag{14}$$

$$F_0/F = 1 + k_r\tau[\mathrm{PhX}] \tag{15}$$

Scheme 1.

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[20] M. A. Rosanoff and A. E. Hill, *J. Amer. Chem. Soc.*, **29**, 269 (1907).

[21] G. S. Jamieson, L. H. Lavy, and H. L. Wells, *ibid.*, **30**, 760 (1908)

sociative in electron capture in vapor phase,[22a] it can be expected that the radical anions, if formed, are simultaneously decomposed into phenyl radical and halide anions in liquid phase. Phenyl radical abstracts hydrogen atom from solvent molecules, TEA, DMA radical cation and neutral DMA to give benzene, while the dimethylaminodiphenyls (IV and V) are formed by addition of phenyl radical to DMA and DMA radical cation. Thus the mechanism in Scheme 1 is suggested, from which rate equation (14) and the Stern-Volmer expression (15) for fluorescence quenching are derived.

Let F_0, F, and ϕ_X denote the fluorescence intensities in the absence and in the presence of halobenzenes and the quantum yields for the formation of halide anions, respectively in the rate equations. As is shown in Table 6, the rate ratios k_r/k_d are in good agreement with the quenching constants $k_r\tau$ within experimental errors for respective halobenzenes. Since k_d equals $1/\tau$, the agreement strongly supports the view that the photochemical reactions occur in the lowest excited singlet state of DMA (^{1}DMA).

It is noteworthy that the product ratios (IV+V)/II and IV/V change with halobenzenes. The photochemical reaction with iodobenzene leads to a remarkably low ratio of (IV+V)/II, *i.e.* dominant formation of benzene. In contrast, the dimethylaminodiphenyls are formed 1.8 times greater than benzene in the reaction with chlorobenzene. In the case of bromobenzene, the formation of the dimethylaminodiphenyls competes with that of benzene and the ratio (IV+V)/II is similar to the case of chlorobenzene rather than to the case of iodobenzene.

The results cannot be interpreted by means of a single mechanism, and suggest a competitive reaction mechanism. By assuming that ETR distance is dependent on halobenzenes, it can be predicted that the fraction of the radical pair (DMA radical cation and phenyl radical) in solvent cage increases with the decrease of distance and thus cage reaction plays a more important role in competition with free radical reaction. The product distribution is therefore expected to change with halobenzenes.

Since free phenyl radical is well known to abstract hydrogen from molecules having labile hydrogen atoms, free radical reaction affords benzene as an exclusive product. The photochemical reaction with iodobenzene is considered to fit the case. On the other hand, cage reaction may occur essentially between phenyl radical and DMA radical cation; bond formation of the radical pair giving IV and V may be competitive with hydrogen transfer from DMA radical cation to phenyl radical giving benzene. In the case of chlorobenzene and bromobenzene, therefore, the results suggest that the cage reaction plays important or dominant roles.

In order to clarify the above assumption and obtain information on ETR distances, the photochemical reactions were carried out with *N*,*N*-di(trideuteriomethyl)aniline (DMA-d_6) instead of DMA-h_{11}, and the contents of benzene-d_1 in benzene fraction of the products were estimated by vpc-mass spectrometry. Deuterium purity of DMA-d_6 was confirmed to be over 98% by NMR.

When the ETR distance is short, the cage reaction is dominant. When ETR takes place in a sufficiently long distance, the fraction of free phenyl radical will increase. The cage reaction might afford largely benzene-d_1 by deuterium transfer from DMA-d_6 radical cation to phenyl radical while free phenyl radical might abstract hydrogen atom from solvent molecules for the most part. Thus, it is reasonable to predict that the proportion of benzene-d_1 reflects a measure for the ETR distance.[22b]

$$(\mathrm{Ph}\overset{+\cdot}{\mathrm{N}}(\mathrm{CD_3})\mathrm{CD_3} + \cdot\mathrm{Ph})_{\mathrm{cage}} \rightarrow \mathrm{PhN(CD_3)CD_2}^+ + \mathrm{PhD}$$

$$\mathrm{Ph}\cdot + \text{Hydrogen donor} \rightarrow \text{largely PhH}$$

Table 7 shows the proportions of benzene-d_1 obtained from the photochemical reactions of DMA-d_6 with halobenzenes which increase in the order: iodobenzene, bromobenzene, and chlorobenzene. In the case of iodobenzene, however, it should be noted that the proportion of benzene-d_1 is remarkably low in comparison with the other two cases, in analogy with the ratio (IV+V)/II. The low proportion of benzene-d_1 might be evidence of the free radical nature of the phenyl radical generated by electron transfer to iodobenzene and suggests that ETR occurs in a long range type[23] between ^{1}DMA and iodobenzene. On the other hand, a high proportion of benzene-d_1 is obtained from the photochemical reaction with chlorobenzene. This indicates that the cage reaction is dominant in the formation of benzene and suggests that ^{1}DMA donates the electron to chlorobenzene in close contact, *i.e.* in a short range type.[23] Since the proportion of benzene-d_1 obtained from the reaction with bromobenzene is nearer the case of chlorobenzene than iodobenzene, it can be suggested that the ETR distance for bromobenzene is in somewhat shorter range, but longer than the distance for chlorobenzene.

The results are in good parallelism with electron affinities of halobenzenes. The electron affinity of iodobenzene is the highest (0.5$_7$ eV) in the three halobenzenes,[24] while the electron affinities of chloro-

TABLE 7. CONTENTS OF BENZENE-d_1 OBTAINED FROM PHOTOREACTIONS OF DMA-d_6 WITH HALOBENZENES

	m/e	C_6H_6	PhX		
			X=Cl	X=Br	X=I
Rel. intensities	78	100	15	25	34.5
	79	8.2	22.8	17.9	10.2
Benzene-d_1	(%)	—	66	42	12

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[22] a) J. A. Stockdale and G. S. Hurst, *J. Chem. Phys.*, **41**, 255 (1964); W. E. Wetworth, R. S. Becker, and R. Tung, *J. Phys. Chem.*, **71**, 1652 (1967). b) This suggests only a qualitative measure, since the proportion of benzene-d_1 cannot represent the fraction of the cage reaction; the phenyl radical in the solvent cage might abstract the hydrogen atom of the wall of the solvent cage even in small proportions, while free phenyl radical might also abstract the deuterium atom from DMA-d_6.

[23] T. Okada, H. Oohari, and N. Mataga, This Bulletin, **43**, 2750 (1970).

[24] G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

benzene and bromobenzene are identical (0.4 eV)[24] or similar.[25] It is resonable to expect that ETR takes place in a long range type for iodobenzene with a high electron affinity,[23] while the acceptors having similar electron affinities may abstract electron from a donor in similar distances.

As regards quenching behavior to DMA fluorescence, halobenzenes are classified into two groups, one involving chlorobenzene and bromobenzene, and the other iodobenzene. It is of interest to note that the same classification of halobenzenes is made from both fluorescence data and product distribution.

With chlorobenzene and bromobenzene, exciplex formation in non-polar solvents is evident from the following observations; 1) appearance of new emissions,[2-4] 2) endothermic and dynamic property of the fluorescence quenching[26] and 3) solvent dependency of the fluorescence quenching on solvent polarity.[27] Moreover, the charge-transfer character of the emission entities is supported by the fact that the new emission maxima are shifted to longer wavelength with the decrease of ionization potentials of the aromatic amines (Table 4).[28] It might be suggested that the fluorescence quenching with chlorobenzene and bromobenzene is ascribed to the formation of the exciplexes between ^{1}DMA and the ground state halobenzenes, at least in non-polar solvents.

On the other hand, the exciplex formation with iodobenzene is negative. Therefore, the fluorescence quenching with iodobenzene is governed by a different mechanism from an exciplex one even in non-polar solvents. If a complex were assumed, it would have a configuration differing from the exciplexes discussed above and might be totally non-emissive as in the case of pyrene-tetracyanoethylene.[23] In polar solvents, in particular, no exciplex mechanism can be suggested, since exciplexes even if formed in non-polar solvents are non-existent[3] or quite shorter-lived[4] in polar solvents. A direct electron transfer mechanism is preferred for the fluorescence quenching. Since the kinetic data show the identity of the mechanism between the fluorescence quenching and the photochemical reaction, the mechanism is supported by the long range type character of the reaction deduced from the product distribution. It is unreasonable to assume that a long range type electron transfer takes place by way of a discrete intermediate such as an exciplex. The direct electron transfer mechanism is shown in Scheme 2.

$$^1\text{DMA} + \text{PhI} \xrightarrow{k_r'} \text{DMA}^+ + \text{Ph}\cdot + \text{I}^- \qquad (16)$$

$$^1\text{DMA} + \text{PhI} \xrightarrow{k_q} \text{DMA} + \text{PhI} \qquad (17)$$

$$1/\phi = \left(1+\frac{k_q}{k_r'}\right)+\frac{k_d}{k_r'}\frac{1}{[\text{PhI}]} \qquad (18)$$

$$F_0/F = 1 + (k_r' + k_q)\tau[\text{PhI}] \qquad (19)$$

$$k_r'/k_d = 50\,\text{M}^{-1}, \quad k_q/k_r' = 0.25$$

$$(k_r' + k_q)\tau = k_r\tau = 42\,\text{M}^{-1}$$

Scheme 2.

On the other hand, all the results clearly show that the mechanism for chlorobenzene and bromobenzene differs from the case of iodobenzene. The short range character of ETR suggested from the product distribution may imply such a close contact intermediate as an exciplex or an ion pair shown in Scheme 1. The fluorescence data on the formation of exciplexes suggest an exciplex intermediacy, though the exciplex formation in non-polar solvents may exhibit no direct evidence for the exciplex intermediacy in methanol.[29]

For mechanistic elucidation, the rate data obtained from the quantum yield measurements will be briefly discussed. Although the life of ^{1}DMA has not been reported, it can be approximately replaced with the singlet life of aniline (3.2 nsec in ethanol).[30] If this is the case, the reaction rates (k_r and k_r') for chlorobenzene, bromobenzene and iodobenzene can be estimated to be respectively 1.8×10^9, 5.1×10^9 and $19\times10^9\,\text{M}^{-1}\,\text{sec}^{-1}$, which are close to the diffusion rate in methanol (ca. $10^{10}\,\text{M}^{-1}\,\text{sec}^{-1}$). Since it is well established that the formation of exciplexes and ETR occur in a diffusion or a near diffusion rate,[2-4,23] the rate data can support also the mechanisms in Schemes 1 and 2. The fact that k_r increases in the order of chlorobenzene, bromobenzene, and iodobenzene may reflect the order of the electron affinities of the halobenzenes.

Singlet excitation transfer, if it occurs, is endothermic, since the absorption of DMA appears at a longer wavelength than in any halobenzenes. If this is the case, near diffusion rates cannot be obtained, and the singlet excitation transfer mechanism can be excluded. A triplet excitation transfer mechanism can be also ruled out by sensitization experiments (*vide supra*).

Experimental

General. Spectroscopic analyses of the organic products were carried out as follows; the NMR spectra with a high Hitachi Perkin-Elmer R-20 spectrophotometer, IR

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[25] The electron affinities might correlate with polarographic half-wave potentials $E_{1/2}$. If this is the case, the electron affinities of bromobenzene will be slightly higher than that of chlorobenzene, since the half-wave potentials are reported to be -2.58 V for chlorobenzene and -2.32 V for bromobenzene; M. F. Thomas and B. Stevens, "Molecular Luminescence," ed. by E. C. Lim, W. A. Benjamin, Inc., New York (1969), p. 158.

[26] No evidence could be obtained on the formation of EDA-complexes in the ground state. The UV spectra of DMA were the same in both the presence and the absence of 0.1 M halobenzenes. Even though chlorobenzene and bromobenzene were used as solvent, the maximum of ^1L_b band shifted only 2—3 nm to longer wavelength, and no new absorption could be observed.

[27] K. Kaneta and M. Koizumi, This Bulletin, **40**, 2254 (1967).

[28] a) Since all of the fluorescence spectra were uncorrected, no explicit first order correlation between ionization potentials and the emission maxima could be obtained. b) P. G. Farrel and J. Newton, *J. Phys. Chem.*, **69**, 3506 (1965).

[29] The fluorescence quenching mechanism in polar solvents has not been established satisfactorily. Weller stated direct electron transfer mechanism,[3] while Mataga suggested exciplex mechanism for a short range type of ETR.[4,23]

[30] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York and London (1965), p. 60.

spectra with a Hitachi EPI-S2 spectrophotometer, UV spectra with a Hitachi 124 spectrophotometer, fluorescence spectra with a Hitachi MPF-2A spectrofluorometer and mass spectra with a Hitachi RMS-4 spectrometer. Yields and the product ratios were determined by vpc with a Simadzu GC-2C under the conditions described previously.[12] Solvents were purified as usual. TEA was refluxed over potassium hydroxide and distilled. Chlorobenzene and bromobenzene were washed three times with concentrated sulfuric acid, three times with water, dried over anhydrous calcium chloride and distilled through a column packed with stainless steel helices. Iodobenzene was washed twice with a dilute aqueous solution of sodium thiosulfate, three times with water, dried over calcium chloride and distilled through the column. The tertiary aromatic amines were refluxed with an excess of acetic anhydride and acidified with hydrochloric acid. The acidified solutions were treated five times with ether and basified with sodium hydroxide. The amines separated from the aqueous layers were then treated as usual. All of the amines were distilled under nitrogen stream *in vacuo* before use. Acetone was purified by the ordinary method.[31] Acetophenone and propiophenone were purified by fractional distillation under reduced pressure.

Quantum Yields. Methanolic solutions (5 m*l*) containing 1.0 M DMA, 0.1 M TEA and 0.025—0.2 M halobenzenes were degassed and sealed in 10 mm o. d. Pyrex tubes, which were then irradiated on a merry-go-round apparatus at room temperature through a filter solution with a path length of 1 cm containing 0.2 g potassium chromate made up to 1 *l* with distilled water with a high pressure mercury arc. After the relative quantum yields were determined, the quantum yields at 0.2 M chlorobenzene, 0.2 M bromobenzene and 0.025 M iodobenzene were determined to be 0.26_4, 0.41_3, and 0.49 by potassium ferrioxalate actinometry,[19] respectively. The values were constant at 0.5—10% conversion within 10% experimental errors.

Sensitization Studies. Samples of *t*-butyl alcohol solutions containing 0.1 M halobenzenes and 0.1 M ketones were prepared, degassed and irradiated through a Pyrex glass with a high pressure mercury arc. The amounts of benzene formed and halobenzenes consumed were determined by vpc.

Photochemical Reaction in Preparative Scale. As a typical run, the photochemical reaction of DMA with bromobenzene will be described. A methanolic solution (30 m*l*) containing 4 g DMA, 4 g bromobenzene and 5 m*l* TEA in a Pyrex tube was irradiated for 45 hr with a high pressure mercury arc. The amounts of the products and of bromobenzene consumed were determined by vpc analyses of an aliquot of the photolysate (5 m*l*). It was found that 450 mg of benzene, 790 mg of *o*-dimethylaminodiphenyl and 96 mg of *p*-dimethylaminodiphenyl were formed at about 50% consumption of bromobenzene. After removal of the solvent fraction under reduced pressure at room temperature, 5 m*l* of benzene was added to the residue and cooled on an ice bath. TEA hydrobromide (2.32 g) was then filtered off, washed with benzene and recrystallized from 2-propanol. Found: C, 39.67; H, 9.09; N, 7.68; Br, 43.70%. Calcd for $C_6H_{16}NBr$: C, 39.59; H, 8.85; N, 7.69; Br, 43.90%.

After removal of benzene and the unreacted materials from the filtrate, further distillation gave crude *o*-dimethylaminodiphenyl, which was redistilled, bp 80°C/1 mmHg; $\tau(CCl_4)$ 7.5 (s, 6H) and 3.1—2.3 (m, 9H). The product was converted into its picrate, mp 184—186°C (dec.). Found; C, 56.72; H, 4.12; N, 13.09%. Calcd for $C_{20}H_{18}N_4O_7$; C, 56.34; H, 4.26; N, 13.14%.

Finally, the residue was chromatographed on silica gel. After *o*-dimethylaminodiphenyl was eluted with 10% of benzene in hexane, further elution with 1 : 1-mixture of benzene - hexane gave *p*-dimethylaminodiphenyl, which was recrystallized from methanol, mp 118—119°C. Found: C, 85.30; H, 7.63; N, 6.84%. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10%.

Preparation of DMA-d_6. DMA-d_6 was obtained by alkylation of aniline[32] with perdeuterated trimethyl phosphate prepared from methanol-d_4 and phosphorus oxychloride, and purified by preparative vpc on a 3 m Apiezon column at 160°C, bp 84°C/15 mmHg. The IR spectrum showed a characteristic absorption of aromatic C–H bond at 3030 cm^{-1} and aliphatic C–D bond at 2000—2200 cm^{-1} (4 peaks), while absorption of aliphatic C–H at 2900 cm^{-1} region could not be observed. The NMR spectra showed only the signals of aromatic protons at τ 2.8—3.7 as a multiplet.

Photochemical Reaction of DMA-d_6. A methanolic solution containing 0.7 M DMA-d_6, 0.7 M TEA and 2 M chlorobenzene or bromobenzene was prepared. In the case of iodobenzene, the concentration was set in 0.2 M in order to avoid direct photolysis of iodobenzene. The samples (4 m*l*) were degassed and irradiated in the same way as in the quantum yield measurements. The photolysates were subjected directyl to vpc-mass spectrometric analyses. The vpc was operated with an 1 m ODPN column plus an 1 m PEG-200 column at 70°C. Table 7 lists the relative intensities at *m/e* 78 and 79 of benzene-h_6 and of the benzene fractions obtained from the photolyses, from which the contents of benzene-d_1 were determined.

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[31] A. Bramley, *J. Chem. Soc.*, **59**, 10 (1916).

[32] J. H. Billman, A. Radike, and B. W. Mundy, *J. Amer. Chem. Soc.*, **64**, 2977 (1942); D. G. Thomas, T. H. Billman, and C. E. Davis, *ibid.*, **68**, 895 (1964).