PHOTOCHEMICAL REACTIONS OF DIMETHYLANILINE
IN THE PRESENCE OF ACIDS

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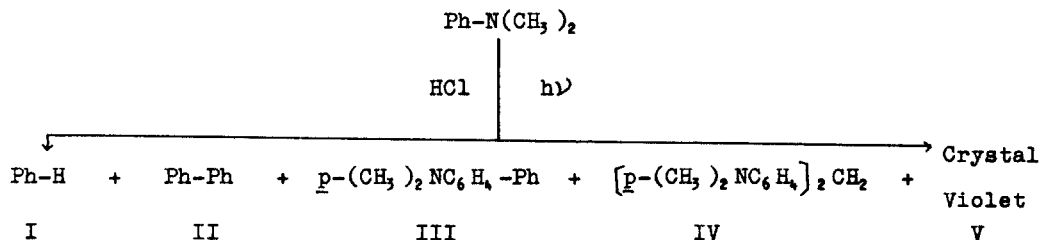Higashiasakayamacho, Sakai, Osaka, Japan

Although there have been various spectroscopic investigations on the photochemical primary processes of aromatic amines (1 - 5), less is known on the reactivities of simple aromatic amines in an electronically excited state.   The present report deals with the photochemical reactions of dimethylaniline (DMA) in the presence of acids giving phenyl radicals which are generated through charge transfer from excited DMA to anilinium cation.

Degassed samples of neat DMA and its ethanolic solution in a quartz tube were not significantly changed by a prolonged irradiation under the conditions investigated.[*]   When acetic acid was added to DMA, the solution was turned to a brownish or a blue color by the photolysis, and appreciable amounts of products could be obtained.   Table I shows the results with acetic and formic acids.   In a typical run, an ethanolic solution of DMA (0.04 mole) and hydrogen chloride (0.012 mole) in a quartz tube was irradiated for 25 hr., and there were obtained benzene (26% yield), diphenyl (21%), p-dimethylaminodiphenyl (4%), bis(p-dimethylaminophenyl)methane (8%), and crystal violet (18%) at 60% conversion of DMA.   The structure and yield of crystal

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[*]   Unless otherwise noted, the photolyses were carried out at room temperature in a quartz or a pyrex tube by a high pressure mercury arc.   All of the samples were degassed.

violet were determined by comparison of the visible absorption spectrum of
the photolysate with that of crystal violet, since the former spectrum was
superimposable on the latter.   The products III and IV were identified by di-

$$Ph-N(CH_3)_2$$

$$HCl \quad | \quad h\nu$$

$$Ph-H \quad + \quad Ph-Ph \quad + \quad \underline{p}-(CH_3)_2NC_6H_4-Ph \quad + \quad \left[\underline{p}-(CH_3)_2NC_6H_4\right]_2CH_2 \quad + \quad \text{Crystal Violet}$$

$$I \qquad\qquad II \qquad\qquad III \qquad\qquad\qquad IV \qquad\qquad\qquad V$$

rect comparison of the spectral (ir, uv, and nmr) data and of the melting po-
ints with those of the respective authentic samples and by the elemental ana-
lyses.   The yields of II, III and IV were determined by uv-spectroscopic and
gravinometric methods, while those of benzene were done by gas chromatogra-
phic measurements.   The formation of benzene and diphenyl clearly shows that
phenyl radicals were generated.

TABLE I

Acid		DMA	Irradia-tion time	Vessel[a]	Products				V[b]
					I	II	III	IV	
		g.	hr.				mg.		
AcOH	1 g.	5	25	Q	ND[c]	ND	40	220	–
	2 g.	4	25	Q	ND	ND	70	320	+
	20 ml.	5	30	Q	100	32	100	250	–
	10 ml.	2	29	P	70	25	22	300	–
HCO$_2$H	1 g.	5	25	Q	ND	ND	210	350	+
	5 g.	5	31	Q	ND	ND	200	200	–
	10 ml.	2	53	P	–	–	–	–	–

a)   Q denotes a quartz tube and P a pyrex one.
b)   The plus sign denotes the formation of crystal violet, while the
       minus sign shows no observation of the formation.
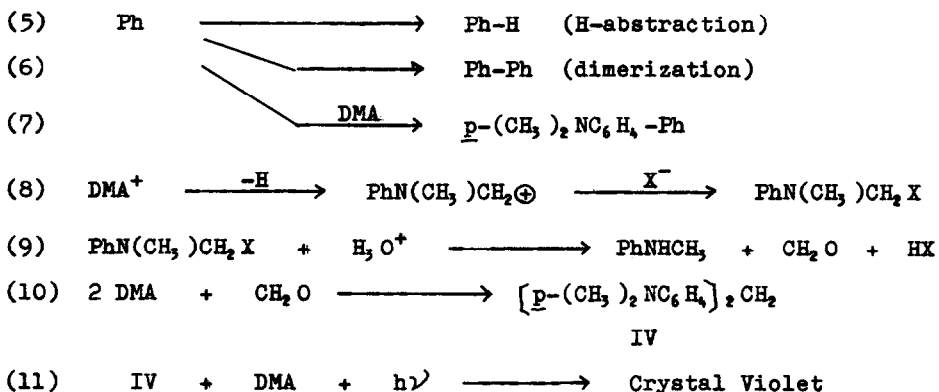c)   Not determined.

The photolysis of DMA containing an excess of hydrogen chloride in a quartz tube for 50 hr. afforded benzene in 50% yield at 10% conversion, but in a pyrex tube gave rise to no reaction.   In this case, dimethylanilinium chloride (DMAH) was present as the sole photo-reactive species.   When a less amount of hydrogen chloride was used than that of DMA, benzene was obtained by the photolysis in a pyrex tube.   Since the pyrex glass cut off the light below 2800 A, only DMA absorbed the incident light.   Table II shows that the amount of benzene formed increases with the increase of the acid concentration.   Therefore, it might be concluded that the source of the phenyl radical was DMAH, and that DMA functioned as a "sensitizer" for the decomposition of DMAH.   Similarly, trimethylanilinium bromide (TMB) and iodide (TMI) were decomposed by the sensitization of DMA.

TABLE II[*]

HCl	2×10^{-4}		5×10^{-4}	1×10^{-3}		2×10^{-3}	
TMB (mole)		2×10^{-4}			1×10^{-3}		
TMI						1×10^{-3}	
Ph-H (mg.)	10	10	25	40	40	40	65

*   Solutions were prepared from 0.017 mole of DMA and the listed amounts of HCl, TMB and TMI dissolved in a mixed solvent (5 ml. of 2-propanol + 5 ml. of t-butanol + 2 ml. of water) and were photolyzed in a pyrex tube for 29 hours.

On the basis of the energy relationships between the excited states of DMA and of the anilinium cations (AN) used, however, a simple excitation transfer from an excited DMA to AN might be highly unlikely for the sensitization effect of DMA.   The uv-absorption spectra of AN were essentially superimposable on that of benzene, while DMA had the longest absorption band at 300 mμ.   The 0-0 band of the phosphorescence spectra of DMA has been reported to lie at 26,650 cm^{-1} (ca. 76 kcal/mole) (6).   Although the energy level of the lowest triplet state of AN is not known, it may be best approximated by that of toluene (83 kcal/mole) (7).   At any rate, the lowest excited singlet and triplet states of DMA are probable to be energetically lower than

the respective states of AN. Thus either the singlet or the triplet excita-
tion transfer may be endothermic and may rarely occur, though such a mecha-
nism can not be totally excluded.

The fluorescence of DMA in ethanol was quenched with TMB (Table III).
Since the ultraviolet absorption spectra of DMA were not changed in the pre-
sence of TMB up to the concentration of 5×10^{-3} M, the quenching with TMB is
dynamic and shows that there is an interaction of TMB with the lowest excited
singlet state of DMA.

TABLE III[a]

TMB x 10^3 M	0	1.33	6.65	13	26	100
F_0/F [b]	1	1.074	1.32	1.47	2.43	very large

a) Ethanolic solutions of DMA (0.1 M) containing various amounts of
TMB were excited at 300 mμ at room temperature. TMB had no absorption
above 290 mμ. The solutions were not degassed.
b) F_0 and F denote the emission strengths at 348 mμ in the absence of
and the presence of TMB, respectively.

There have been appeared several reports on the spectroscopic investi-
gations of heteropolar excimers, and it has been known that highly polar sol-
vents facilitate electron transfer in heteropolar excimers and only the quen-
ching of the fluorescence from a fluorescer can be observed (8, 9). Thus
all of the results obtained are consistent with the electron transfer mecha-
nism comprising the formation of the charge transfer complex (a heteropolar
excimer) between DMA in the lowest excited singlet state and AN in the gro-
und state. A simple mechanism for the formation of the products is depic-
ted as follows.

Primary Processes

(1) $DMA + h\nu \longrightarrow DMA^*$

(2) $DMA^* + AN \longrightarrow [DMA^* \text{---} AN]$

(3) $[DMA^* \text{---} AN] \longrightarrow DMA^+ + AN^-$

(4) $AN^- \longrightarrow Ph\cdot + RN(CH_3)_2$

$(AN = Ph\overset{\oplus}{N}(CH_3)_2 R,\ R = H\ or\ CH_3)$

Secondary Processes

(5)   Ph $\xrightarrow{\hspace{4cm}}$ Ph-H   (H-abstraction)

(6) $\xrightarrow{\hspace{4cm}}$ Ph-Ph   (dimerization)

(7) $\xrightarrow{\hspace{1cm}DMA\hspace{1cm}}$ p-$(CH_3)_2NC_6H_4$-Ph

(8) DMA^+ $\xrightarrow{\hspace{0.5cm}-H\hspace{0.5cm}}$ $PhN(CH_3)CH_2\oplus$ $\xrightarrow{\hspace{0.5cm}X^-\hspace{0.5cm}}$ $PhN(CH_3)CH_2X$

(9) $PhN(CH_3)CH_2X$ + H_3O^+ $\xrightarrow{\hspace{2cm}}$ $PhNHCH_3$ + CH_2O + HX

(10)   2 DMA + CH_2O $\xrightarrow{\hspace{2cm}}$ $[p-(CH_3)_2NC_6H_4]_2CH_2$

                                                        IV

(11)   IV + DMA + hν $\xrightarrow{\hspace{2cm}}$ Crystal Violet

The secondary processes 5, 6, 7, 9 and 10 are well known.   Details of
the processes 8 and 11 can not be drawn at the present stage and are now
under investigation.

Recently, the photochemistry of trimethylanilinium salts has been rep-
orted by Walsh and Long (10).   The photolysis of the anilinium salts in
methanol affords benzene in good yields through charge transfer caused by the
photo-excitation of a charge transfer complex which forms in the ground state
between an anion and the anilinium cation.   An important result supporting
the charge transfer mechanism is that the photolysis of trimethylanilinium
salts is most effective in the presence of iodide anion which is well known
to be readily oxidized.   However, it can not be totally excluded that, since
intersystem crossing to triplet state may be expected to be enhanced by the
heavy atom effect of iodide anion, the photolysis will occur through the tri-
plet state.   On the basis of this point, it is of interest to note that tol-
uene, p-xylene, and anisole also "sensitized" the decomposition of DMAH, bec-
ause both of the electron transfer and the triplet excitation transfer mecha-
nism may be quite possible for the sensitization effect of the above three
aromatic compounds on account of their high triplet energy (11).

In summary, it is emphasized that the excited singlet state of DMA has
an ability to donate the electron to AN under the conditions where the gro-
und state DMA can not do so.

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