Formations and Reactions of Cation Radicals from Compounds Possessing a *p*-Dimethylaminophenyl Group by Reactions with *o*-Sulfobenzoic Anhydride

Toshikazu NAGAI, Tadao SHINGAKI, and Hirokazu YAMADA*
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560

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It was found that cation radicals were formed from a number of substrates bearing a *p*-dimethylaminophenyl group, such as *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and *N,N,N',N'*-tetramethylbenzidine (TMB), by reactions with *o*-sulfobenzoic anhydride (*o*-AH). The systems, bis(*p*-dimethylaminophenyl)methane (BMM) and tris (*p*-dimethylaminophenyl)methane (TMM) with *o*-AH, gave their cations in the presence of oxygen, showing that the oxygen eliminates the hydrogen atoms of the cation radicals derived from BMM and TMM. The reactions of *N,N*-dimethylaniline (DMA) with *o*-AH gave rise to isolations of BMM and *N*-methylaniline, along with the formations of the cation radical of TMB and the crystal violet cation (TMM^+). The mechanisms of the reactions are proposed.

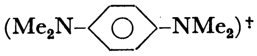
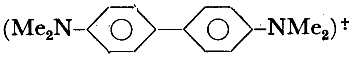
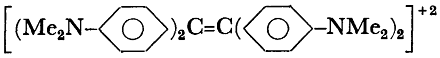
Cation radicals are familiar as transient species in mass spectrometry or anodic oxidation.[1] However, the chemical behaviors of cation radicals have not, until recently, received much attention.[2] Previously, we reported that the radical cations of some aromatic hydrocarbons, triethylamine, triphenylamine or *N*-vinylcarbazole arose in liquid sulfur dioxide in the presence of oxygen; in these cases, the existence of the radical cations was proved from the electronic or ESR spectra and from the chemical follow-up reactions.[3] The values of the electron affinity and the dielectric constant of liquid sulfur dioxide are not so much higher than those of the usual acceptors or polar solvents. Hence, sulfur dioxide probably plays a role of a polarizable electrophilic reagent, using the available 3d orbitals of the sulfur atom, rather than that of a polar solvent. Keeping these consideration in mind, we have examined the reaction of some sulfones with substrates possessing a *p*-dimethylaminophenyl group. It was found that mixed sulfonic–carboxylic anhydrides provided a convenient means of generating cation radicals from the substrates.

Results and Discussion

Formation of Cation Radicals and Cations. In the reactions of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), *N,N,N',N'*-tetramethylbenzidine (TMB) and tetrakis(*p*-dimethylaminophenyl)ethylene (TMPE) with *o*-sulfobenzoic anhydride (*o*-AH) in acetonitrile, the formations of their cation radicals were investigated spectrophotometrically. The absorption maxima in the 340—1400 nm range for the cation radicals or dication are summarized in Table 1, being compared with those reported by some authors.

These values were in fair agreement with those reported,[4–11] though the peak positions for TMPE shifted slightly. The reaction of TMPE with *o*-AH in acetonitrile underwent double electron transfer to form the diamagnetic dication (TMPE^{2+}), whose absorption band was in essential agreement with that observed in the reaction of TMPE with iodine in acetonitrile.[11] These results are coincident with those reported by Foster and Thomson:[12] that the ease of the complete

TABLE 1. ABSORPTION MAXIMA OF CATION SPECIES

Cation species	$\lambda_{\max}$ (nm)	Medium	Method of prepn.	Ref.
 $(\mathrm{TMPD}^{\cdot+})$	566 615	CH_3CN	Chem	This work
	569 619	CH_3CN	Chem[c)]	4
	575 625	$(C_2H_5)_2CHCH_3$[a)]	Photo	5
	575 635	CCl_4[a)]	γ.	6
	560 606	H_2O	Chem[d)]	7
	575 615	EPA[a,b)]	Photo	8
 $(\mathrm{TMB}^{\cdot+})$	438 458 472	CH_3CN	Chem	This work
	910 1050			
	436 458 472	$(C_2H_5)_2O$	Chem[e)]	9
	900 1050	CCl_4[a)]	γ.	6
	435 458 472	CH_3CN	Anodic	10
 (TMPE^{+2})	489 534 640—900	CH_3CN	Chem	This work
	469 540 650—900	CH_3CH_2Cl	Chem	11

a) These experiments were carried out at −196 °C. b) Mixture solvent; ether: isopentane: ethanol 5:5:2 (volume ratio). c—f) In the preparations, c) tetrachloro- or tetrabromo-*o*-benzoquinone, d) perchloric acid, e) tris (*p*-bromophenyl)ammonium perchlorate, and f) iodine were used as acceptors.

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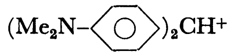
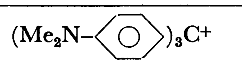
* Present address: Dai Nippon Ink and Chemicals Industrial Co., Ltd., Takaishi, Osaka 592.

Table 2. Absorption maxima of cations

Cation	Solvent	$\lambda_{\max}$ (nm)	Ref.
 (BMM$^+$)	CH_3CN	560(sh) 607	This work
	H_2O	608	15
	acid C_2H_5OH	560(sh) 610	16
	C_2H_5OH	605	17
 (TMM$^+$)	CH_3CN	550(sh) 592	This work
	H_2O	542(sh) 590	18
	dil HCl	599	15
	C_2H_5OH	545(sh) 591	16
	CH_3OH	550(sh) 590	19

electron transfer is TMPE>TMPD>TMB.

An investigation by ESR also was undertaken for the reaction of TMPD with *o*-AH in acetonitrile. The hyperfine coupling constants of TMPD$^{\dot{+}}$ were assigned as follows: $a_{\mathrm{CH_3}}=6.65$ G; $a_{\mathrm{N}}=6.85$ G; $a_{\mathrm{ringH}}=1.98$ G. These couplings are very similar to those reported by Carrington[13)] and Taft.[14)]

The reactions of bis(*p*-dimethylaminophenyl)methane (BMM) and tris(*p*-dimethylaminophenyl)methane (TMM) with *o*-AH were investigated spectrophotometrically in acetonitrile. The absorption maxima observed are due to those of bis(*p*-dimethylaminophenyl)methyl cation (BMM$^+$) and tris(*p*-dimethylaminophenyl)methyl cation (TMM$^+$, Crystal Violet cation) by reference to the literature values (Table 2). These cations are to be derived from the corresponding cation radicals (BMM$^{\dot{+}}$ and TMM$^{\dot{+}}$): the cation radicals are then able to release a hydrogen atom to afford highly stabilized BMM$^+$ and TMM$^+$ respectively.

Table 3. Effect of oxygen on formation of cation species

Amine	Cation species	Yield (mol %)[a)]	
		undegassed	degassed
TMPD	TMPD$^{\dot{+}}$	20	18
TMM	TMM$^+$	59	29

a) Calculated from molar extinction coefficients. TMPD$^{\dot{+}}$: 1.1×10^4 at 615 nm.[7)] TMM$^+$: 1.1×10^5 at 592 nm.[18,19)]

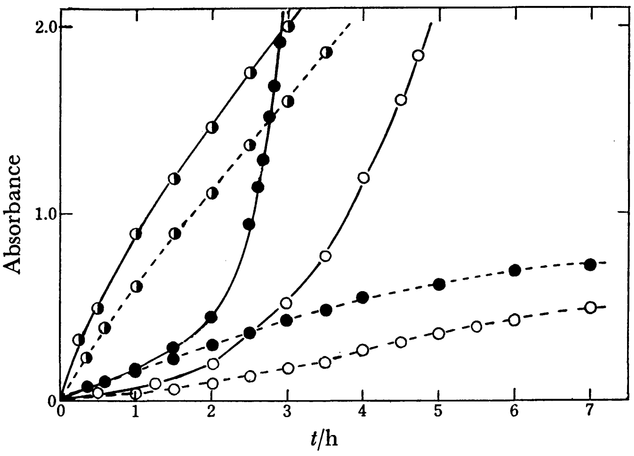
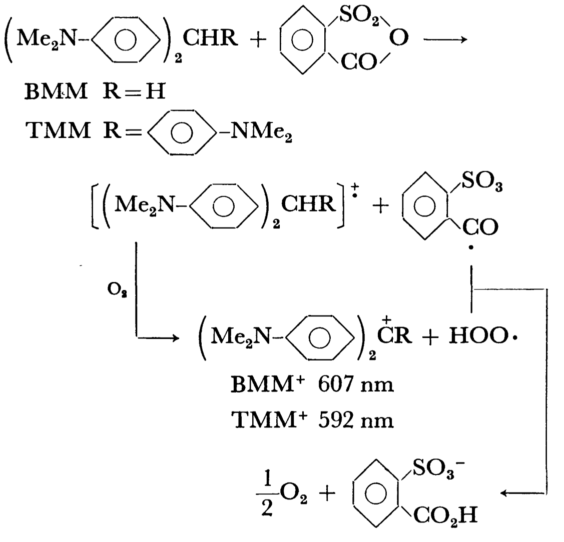


Fig. 1. Effect of oxygen on the rate of formation of cation species in acetonitrile at 8 °C. [TMPD], [BMM], and [TMM]: 7.6×10^{-3} M, [*o*-AH]: 1.3×10^{-3} M. ◑: TMPD$^{\dot{+}}$, ○: BMM$^+$, ●: TMM$^+$. ——: under undegassed, ------: under degassed.

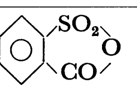
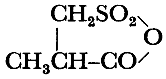
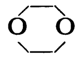


Scheme 1.

An intervention of oxygen, here, was considered important for the elimination of the hydrogen atoms. Influences of oxygen on the formation of such cation species have not been investigated to date, though they have been mentioned in Refs. 2b and 9. And so, the reactions with *o*-AH were carried out under a degassed condition. As shown in Table 3, the reaction of TMM with *o*-AH gave a decreased yield of the cation under a degassed atmosphere, in contrast to that of TMPD. Effects of oxygen on the formation rates of the cation species were also studied for the reactions of TMPD, BMM, and TMM with *o*-AH in acetonitrile (Fig. 1). The formation rates of the cations were remarkably accelerated in the presence of oxygen, in contrast to those of the cation radical (TMPD$^{\dot{+}}$). These results show that the cations are formed from the cation radicals, which are derived from BMM and TMM which have some available hydrogen atoms, by hydrogen abstraction with oxygen (Scheme 1). To explain the retarded formation of the cations under the degassed atmosphere, a following alternative pathway can be considered: the cation radicals (BMM$^{\dot{+}}$ and TMM$^{\dot{+}}$) give their protons to the counter anion radical shown in Scheme 1, and are transformed into the radicals (BMM· and TMM·), which are then oxidized by *o*-AH to the highly stabilized cations (BMM$^+$ and TMM$^+$).

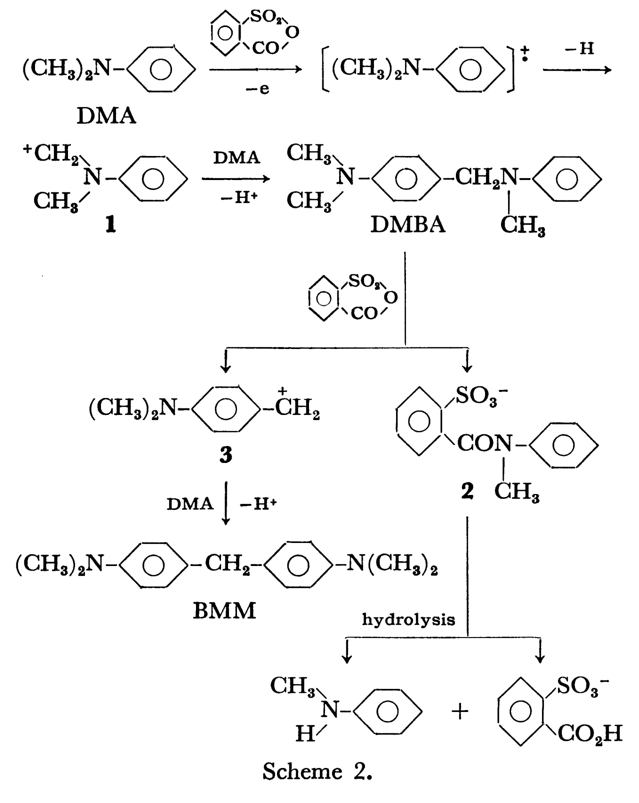
Reaction of N,N-*Dimethylaniline with* o-*AH.* *N,N*-Dimethylaniline (DMA) has no blocked *para*-position in contrast to the amines used so far. Studies of the cation radical (DMA†) formation from DMA have been done by many researchers.[2b,9,19–23] In their studies,[2b,19] it was recognized that the cation radical converted to tris(*p*-dimethylaminophenyl)methyl cation (Crystal Violet cation). However, none of the reports clarified the reaction path to the Crystal Violet cation from the cation radical (DMA†) at all.

TABLE 4. EQUIMOLECULAR REACTIONS BETWEEN DMA AND ANHYDRIDES

Amine	Anhydride	Medium		Yield (%)[a)] BMM	Yield (%)[a)] C_6H_5-$NHCH_3$
DMA		CH_3CN	O_2	49	20
		CH_3CN	N_2	10	6
		C_6H_6	O_2	20	4
DMA		CH_3CN	O_2	45	12
			O_2	13	7

a) Calculated based on triple the molar quantity of the amine used.

An equimolar amount of DMA and *o*-AH was allowed to react in a solvent. Table 4 shows the results. These products are the same as those obtained from the gamma-radiolysis[20] of DMA. This fact and the formation of TMB†, as described below in detail, suggest that DMA† is formed in this reaction. A reaction of DMA with *β*-sulfoisobutyric anhydride (*β*-AH) also gave the same products as the reaction with *o*-AH (Table 4).



Scheme 2.

The mechanism for this reaction, outlined in Scheme 2, is similar to that reported previously by Grodowski and Latowski[21] from the study of the photoxidation of DMA with bromobenzene. A hydrogen atom of the cation radical derived from DMA is abstracted by oxygen to give *N*-methylanilinomethyl cation (**1**). This cation attacks the *para*-position of unoxidized DMA to afford *N*-(*p*-dimethylaminobenzyl)-*N*-methylaniline (DMBA). In a subsequent reaction step, DMBA is decomposed by sulfonic carboxylic anhydride giving the anilide derivative (**2**) and *p*-dimethylaminobenzyl cation (**3**). This carbocation (**3**), in the presence of DMA, forms the isolated product BMM. The anilide derivative **2** is hydrolyzed by treatment in an alkali solution to yield *N*-methylaniline. On the other hand, when DMA was treated with *o*-AH in the presence of authentic DMBA, the same products, BMM and *N*-methylaniline, were also obtained. In this reaction, it was confirmed by means of NMR and thin-layer chromatography that the DMBA used had been consumed completely. These results support the reaction mechanism shown in Scheme 2.

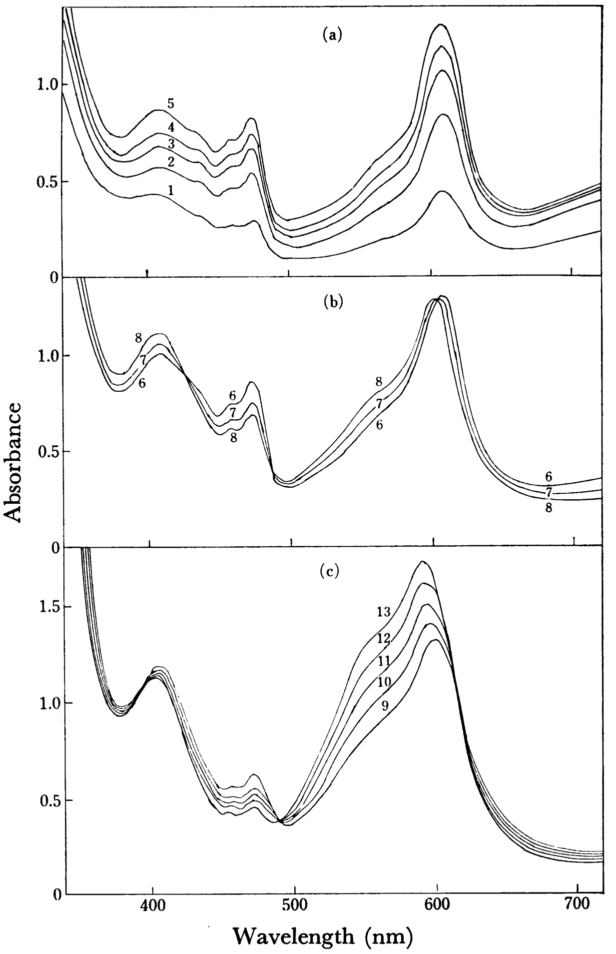
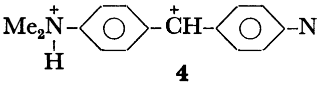


Fig. 2. Spectroscopic course of the reaction of DMA with *o*-AH in acetonitrile. [DMA]$=4.1\times10^{-2}$ M, [*o*-AH]$=4.1\times10^{-2}$ M. After mixing:
(a) 1, 10 min; 2, 20 min; 3, 30 min; 4, 40 min; 5, 60 min;
(b) 6, 110 min; 7, 160 min; 8, 210 min;
(c) 9, 300 min; 10, 420 min; 11, 540 min; 12, 660 min; 13, 900 min.

Reaction Course from DMA to TMM$^+$. In the reaction of DMA with *o*-AH, it was confirmed by the optical spectra that *N,N,N′,N′*-tetramethylbenzidine cation radical (TMB$^{+\cdot}$) and Crystal Violet cation (TMM$^+$) were formed. When an acetonitrile solution of DMA was mixed with an acetonitrile solution of *o*-AH, the reaction mixture rapidly assumed a yellowish-green color, then turned to a green color (stage 1). The green color gradually changed to a bluish-green color (stage 2) and finally to a purple color (stage 3). Figure 2 shows the absorption spectra of the reaction mixture of DMA and *o*-AH corresponding to stages 1, 2, and 3.

The addition of an acetonitrile solution of *o*-AH to an acetonitrile solution of DMA gave rise to a new series of absorptions in the visible region at 438, 458, and 472 nm, due to the TMB$^{+\cdot}$, and at 607 nm due to BMM$^+$. In addition, a new absorption at 408 nm was also observed. This band was assigned to a dication (**4**) protonated at one nitrogen atom of BMM$^+$, because the same absorption band was also obtained by the addition of *o*-sulfobenzoic acid to an acetonitrile solution of BMM$^+$, which had been prepared by the reaction of BMM and *o*-AH.



$\mathrm{Me_2\underset{H}{\overset{+}{N}}-C_6H_4-\overset{+}{C}H-C_6H_4-NMe_2}$

4

In stage 1, each of these absorptions due to TMB$^{+\cdot}$, BMM$^+$, and the dication (**4**) increased in intensity over a period of one hour, as shown in Fig. 2a. In stage 2 (Fig. 2b), it was observed that the intensity of the absorption at 592 nm due to TMM$^+$ increased while those of TMB$^{+\cdot}$ and BMM$^+$ decreased, showing the isosbestic points at 426, 490, and 602 nm. In stage 3 (Fig. 2c), the absorption of TMM$^+$ showed further increased intensity, with an isosbestic point at 490 nm, with the lapse of time, while the absorptions in the 430—480 nm region, on the contrary, decreased in intensity. Such spectral changes were observed as well by the use of *β*-AH instead of *o*-AH.

From these changes of the absorption spectra, it is suggested that the oxidation of DMA to TMM$^+$ by the sulfonic carboxylic anhydrides proceeds through BMM$^+$ and TMB$^{+\cdot}$. On the other hand, the addition of DMA to the solution of BMM$^+$, which had been prepared by the reaction of BMM with *o*-AH in acetonitrile, showed a new absorption band at 592 nm due to TMM$^+$, together with a decrease in the intensity of the absorption at 607 nm due to BMM$^+$. The presence of the isosbestic point at 490 nm, in Fig. 2c, shows that a one-electron transfer reaction occurs between TMM and TMB$^{+\cdot}$. This was confirmed also from the result that the spectrum of a mixture of TMM and TMB$^{+\cdot}$, which had come from the reaction of TMB with *o*-AH in acetonitrile, changed with the isosbestic point at 492 nm, as shown in Fig. 3.

Finally, we here propose a mechanism for the oxidation of DMA to TMM$^+$ by the sulfonic carboxylic anhydrides, as shown in Scheme 3, which is different

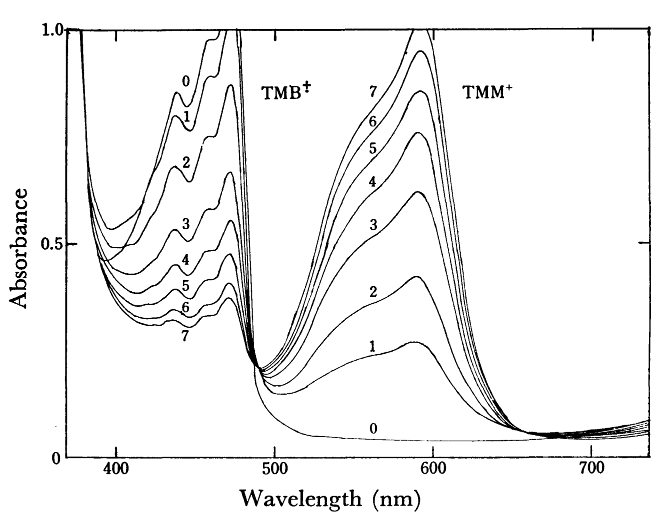
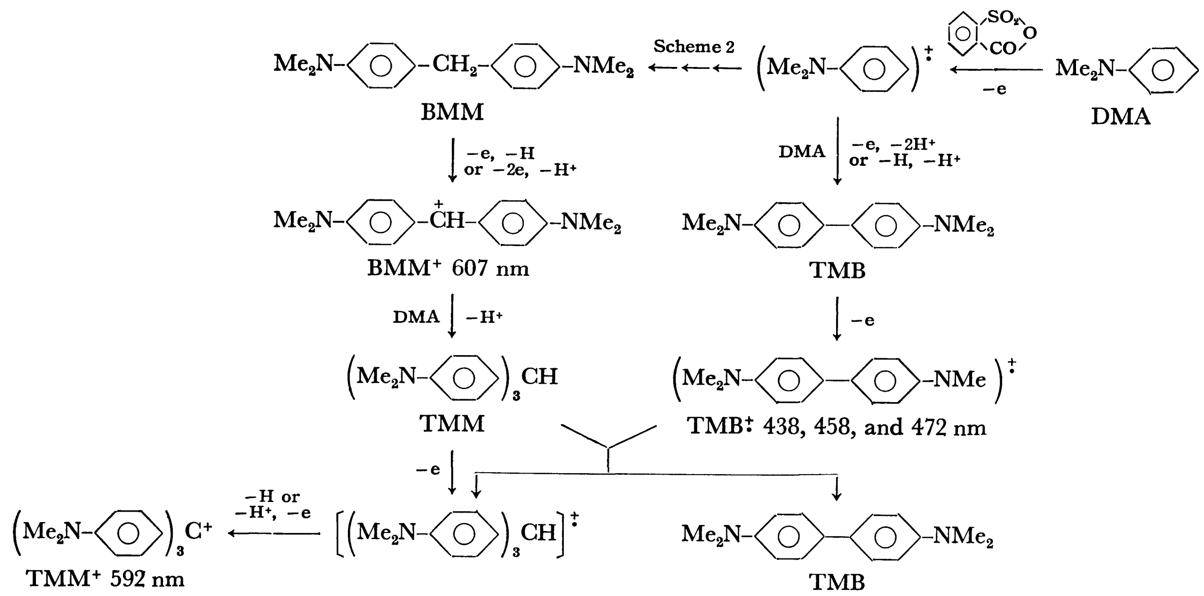


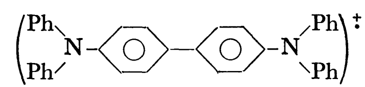
Fig. 3. Spectroscopic course of the reaction of TMB$^{+\cdot}$ with TMM in acetonitrile. 0, TMB$^{+\cdot}$ alone. After addition of TMM: 1, immediately; 2, 10 min; 3, 20 min; 4, 30 min; 5, 40 min; 6, 50 min; 7, 60 min.



Scheme 3.

from the mechanism proposed in the system of DMA and chloranil.[24] The BMM^+ derived from BMM attacks the *para*-position of the unoxidized DMA, giving TMM. Alternatively, the cation radical of DMA dimerizes or reacts with the parent to form $\text{TMB}^{+\cdot}$. Then, the one-electron transfer reaction between TMM and $\text{TMB}^{+\cdot}$ occurs to afford TMM^+.

Reaction of Triphenylamine with o-*AH.* A reaction of triphenylamine with *o*-AH was studied spectrophotometrically in a similar manner. An absorption band appeared at 480 nm. This broad band is apparently due to the *N*,*N*,*N'*,*N'*-tetraphenylbenzidine cation radical (**5**), whose spectral assignment has been reported by Hasegawa,[25] Dollish, and Hall.[26]



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Triphenylamine is not blocked at the *para*-positions and doesn't contain a labile hydrogen atom such as the *N*-methyl group of DMA. Thus, the cation radical derived from triphenylamine recombines or reacts with the parent exclusively at the *para*-position to give the cation radical **5**.

Experimental

The optical absorption spectra in the 340—740 nm and 650—1400 nm ranges were recorded on a Union SM-401 and a Shimadzu MPS-50L recording spectrophotometer. The quartz cell used was 1.0 cm in length. If necessary, each of the sample solutions of an electron donor and an acceptor was mixed into the cell after repeated freeze-pump-thaw-cycles. The NMR spectra were obtained on a Varian EM-360 (60 MHz) analytical spectrometer with tetramethylsilane as an internal standard. The IR and ESR spectra were taken on an Hitachi EP-S and a JEOL JES-NE2X instrument. Gas chromatography was done on a Yanagimoto GCG-5DH unit, employing as adsorbent 10% Apiezon Grease M on Celite (60—80 mesh).

Solvents. Acetonitrile, benzene, and dioxane were used after the commercial reagents were purified according to the published directions.[27]

Materials. *o*-Sulfobenzoic anhydride (*o*-AH) was prepared from acid ammonium *o*-sulfobenzoate,[28] which had been obtained by the hydrolysis of *o*-sulfobenzoic imide (saccharin insoluble);[29] mp 127 °C (lit,[28] 128 °C). The preparation of *β*-sulfoisobutyric anhydride (*β*-AH) was the same as that reported by Kharasch *et al.*[30] *N*,*N*,*N'*,*N'*-Tetramethyl-*p*-phenylenediamine (TMPD) was obtained by alkalizing an aqueous solution of its dihydrochloride salt with a potassium hydroxide aqueous solution. The amine was purified by means of sublimation; mp 51 °C (lit,[31] 51 °C). The white crystalline solid thus obtained was kept at about −20 °C in the dark until used. *N*,*N*,*N'*,*N'*-Tetramethylbenzidine (TMB) was recrystallized twice from 1-pentanol; mp 196 °C (lit,[12] 196 °C). Tetrakis(*p*-dimethylaminophenyl)ethylene (TMPE) was prepared according to the method given in the literature,[32] and recrystallized from a benzene–ligroin mixture; mp 314.5—315.0 °C (lit,[32—33] 314—316 °C). Bis and tris(*p*-dimethylaminophenyl)methanes (BMM and TMM) respectively were recrystallized twice from ethanol. BMM: mp 90 °C (lit,[34] 91 °C). TMM: mp 176 °C (lit,[35,36] 177—178 °C). *N*,*N*-Dimethylaniline (DMA) was refluxed with acetic anhydride, followed by neutralization, separation of the organic layer, and repeated distillation under reduced pressure. The colorless oil was dried over pellets of sodium hydroxide, and distilled *in vacuo* before use. Triphenylamine was recrystallized from absolute ether, followed by recrystallization from ethanol; mp 127 °C (lit,[37] 128 °C). *N*-(*p*-Dimethylaminobenzyl)-*N*-methylaniline (DMBA) was prepared in the following way. A solution of benzoyl peroxide (12 g) in benzene (100 ml) was added dropwise to a solution DMA (24 g) in benzene (20 ml) with stirring, keeping the temperature at 25 °C. The reaction mixture was refluxed for 14 h. The benzene solution was washed with a sodium hydroxide solution, followed by washing with water and drying with sodium sulfate. Then the benzene and unchanged DMA were removed by distillation under a pressure of 2 Torr. The residue (6 g) was chromatographed on alumina (90 g), and DMBA (1.5 g) was eluted with light petroleum ether. The white crystal was recrystallized from ethanol; mp 67.5—68.0 °C (lit,[23] 68 °C). NMR (CCl_4, δ): 2.80 (s, 6H, $-\text{CH}_3$), 2.85 (s, 3H, $-\text{CH}_3$), 4.30 (s, 2H, $-\text{CH}_2-$) and 6.50—7.20 (m, 9H, aromt.).

Reaction of DMA with Sulfonic Carboxylic Anhydrides. A solution of 3 g of DMA in an absolute solvent (25 ml) was added to an equimolecular solution of sulfonic carboxylic anhydride in the absolute solvent (25 ml). The reaction mixture, protected in the usual way from atmospheric moisture, was stirred for a week in the dark at room temperature. The reaction mixture was evaporated to a deep green syrup under reduced pressure. A sodium hydroxide solution was added to the residue and an insoluble oily substance was extracted with ether; the ether extract was dried over sodium hydroxide. Removal of the solvent gave a brown crystalline residue, which was recrystallized from ethanol. The IR, NMR, and mass spectra of this product were identical with those of the authentic sample, BMM. On the other hand, after the alkali aqueous solution was heated at about 90 °C for 6 h, the solution was extracted with ether. Concentration of the ether solution gave an oily substance, which was analyzed by the use of gas chromatography. The IR and NMR spectra of the product were identical with those of the authentic sample, *N*-methylaniline.

Reaction of DMA with o-*AH in the Presence of DMBA.* A solution of *o*-AH (38.5 mg) in anhydrous acetonitrile (2 ml) was added to a solution of DMA (20 mg) and DMBA (8.6 mg) in absolute acetonitrile (2 ml). The reaction mixture was introduced into a cell and then sealed. The visible spectrum of the final product was identical to that of TMM^+, whose yield was five times that of the reaction in the absence of DMBA. A procedure similar to that described above was carried out.

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