

## Sulfonation of arylamines : Part VII—Kinetics of thermal decomposition of tetramethyldianilinium sulfates

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Tetramethyldianilinium sulfates (TMDAS) have been prepared and characterised. Thermal decomposition of these salts has been studied by TG and kinetics evaluated using Prout-Tompkins equation. Activation energies of these salts are found to be linearly related to the  $pK_a$  of the corresponding amine. It has been found that TMDAS give dimethylaminobenzenesulfonic acids (DMAB-SA) via solid state reaction induced by heat. A reaction scheme representing the thermal decomposition pathways of these salts has been suggested. The proton transfer (unimolecular elementary reaction) seems to be the primary step which is followed by a bimolecular step (sulfonation) for the decomposition of these salts.

Extensive studies have been made on the preparation, characterisation and thermal decomposition of ring monosubstituted arylammonium sulfates<sup>1-7</sup>. It has also been found that these sulfates undergo decomposition to ring substituted aminobenzene-sulfonic acids which find applications<sup>8</sup> in organic syntheses, dyestuffs, medicines and tanneries. Recently, we have investigated the thermolysis of dimethylanilinium nitrates<sup>9</sup> and perchlorates<sup>10</sup>. Not much work has been reported on tetramethyldianilinium sulfates<sup>11-12</sup> (TMDAS). As a part of our ongoing research programme, TMDAS have been prepared and characterised. The kinetics of thermal decomposition of these salts have also been undertaken.

### Materials and Methods

Materials like 3, 4-, 2, 5- and 2, 4-dimethylanilines (DMA) (E. Merck); sulfuric acid (AR Qualigens); silica gel G TLC grade (Qualigens) and barium chloride (BDH) were used as received.

**Preparation and characterisation of TMDAS.**—White precipitates of the sulfates of 3, 4-, 2, 5- and 2, 4-dimethylanilines were obtained immediately on reacting conc. sulfuric acid with the corresponding amine in 2:1 molar ratio at room temperature (RT), and the reaction is shown in Scheme I.

The precipitates were washed thrice with ethyl acetate to remove the unreacted amine. All sulfates were recrystallised from doubly distilled water after concentration (under vacuum), the crystals vacuum dried, and the purity was checked by

TLC. These salts were characterised by microanalysis and spectroscopy<sup>13-15</sup>. They were found to decompose before melting, and are nonhygroscopic and quite stable at room temperature.

**3, 4, 3', 4'-TMDAS** : Anal. Calcd for  $C_{16}H_{24}N_2SO_4$ : C, 56.47; H, 7.06; N, 8.24. (Found: C, 56.50; H, 7.50; N, 8.04%; UV( $H_2O$ ): 332.8 (log  $\epsilon$  0.08), 288.0 (0.33), 268 (0.87), 260 (1.12), 235.6 (1.61), 216.4 (3.42) nm; MS (relative intensity) : m/z 120(100), 121(30.7), 106(49.6), 92(15.9), 79(23.0), 77(70.0), 59(17.0), 53(62.0), 50(25.0), 43(29.0); IR(KBr): 3390-3465 br, 2580 m, 1945 m, 1600 s, 1568 m, 1494 s, 1450 m, 1382 s, 1330 m, 1288 s, 1245 m, 1215 m, 1185 m, 1100 br, 1072 m, 1038 m, 874 s.

**2, 5, 2', 5'-TMDAS**: Anal. Calcd for  $C_{16}H_{24}N_2SO_4$ : C, 56.47; H, 7.06; N, 8.24. Found: C, 56.49; H, 7.35; N, 8.12%; UV ( $H_2O$ ): 281.6 (log  $\epsilon$  0.28), 271.2 (0.31), 232 (0.65) and 208.8 (2.97) nm; IR(KBr): 3300-3500 br, 2840-3040.br, 2565 m, 1570 br, 1504 m, 1290 m, 1190 m, 1100 m, 1042 br, 985 s, 962 m, 872 m, 800 s; <sup>1</sup>H NMR (DMSO- $d_6$ ):  $\delta$  6.70-7.40 (6H, aromatic), 4.3 (6H,  $NH_3$ ); 2.3(12H, Me).

**2, 4, 2', 4'-TMDAS**: Anal. Calcd for  $C_{16}H_{24}N_2SO_4$ : C, 56.47; H, 7.06; N, 8.24. Found: C, 56.52; H, 7.34; N, 8.16%; MS (relative intensity): m/z 104(100) 229(24.1), 197(16.0), 180(20.0), 153(36.0), 151(20.0), 121(43.0), 120(88.0), 119(60.0), 105(60.0), 90(29.0), 77(92.0), 75(18.0), 64(15.0), 53(16.0), 52(15.0), 51(33.0), 42(15.0); <sup>1</sup>H NMR ( $D_2O$ ):  $\delta$  2.1(12H, Me), 6.68-6.94(6H, aromatic).

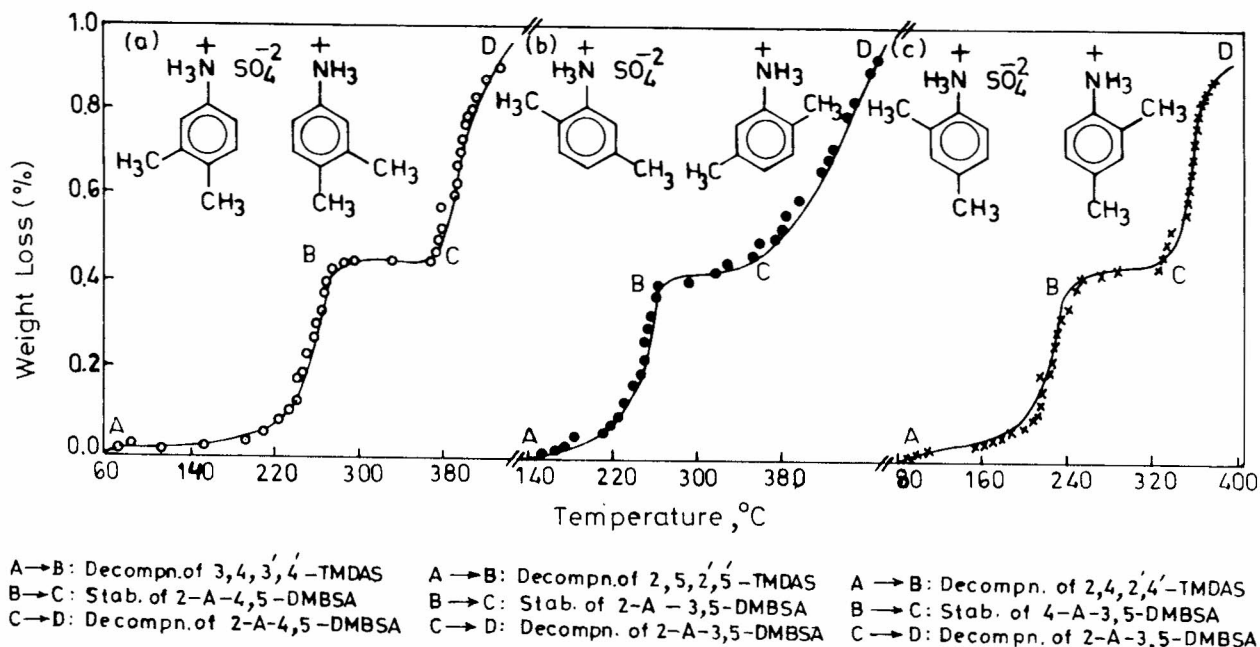


Figure 1—TG curves of (a) 3, 4, 3', 4'-TMDAS, (b) 2, 5, 2', 5'-TMDAS, (c) 2, 4, 2', 4'-TMDAS

**Conversion of TMDAS to dimethylaminobenzenesulfonic acid (DMABSA).** The samples of 3, 4, 3', 4', 2, 5, 2', 5'- and 2, 4, 2', 4'-TMDAS were heated respectively at 155°, 195° and 180° ± 2°C in a tube furnace<sup>16</sup> for 50 min at 60 ± 2 mm Hg pressure. Each residue was washed with ethyl acetate and dissolved in water which on concentration under vacuum gave an amorphous solid. Their purity was checked by TLC. These compounds were also found to decompose during melting and were identified as 2-A-4, 5-DMBSA, 4-A-2, 5-DMBSA, and 2-A-3, 5-DMBSA. The structure, physical parameters, and  $R_f$  values (TLC) of TMDAS and DMABSA are given in Table I.

**Cross-sulfonation studies<sup>3-6</sup>.** The samples of all the three sulfates were heated separately in a tube furnace with small amount of aniline at the same temperature and pressure given above for 35 min. The products were separated by preparative TLC using glacial acetic acid, chloroform, abs. ethanol and *n*-butanol (1.8:2.6:0.6:1.0) as eluent and identified as sulfanilic acid, 2-A-4, 5-DMBSA, 4-A-2, 5-DMBSA, 2-A-3, 5-DMBSA, 3, 4-DMA, 2, 5-DMA, 2, 4-DMA and aniline.

**Thermogravimetry (TG) studies on TMDAS:**  
**(a) Dynamic TG.** Analyses of these sulfates (wt 30 mg, 200-400 mesh) were carried out in static air at a heating rate of 5°C min<sup>-1</sup> using an indigenously fabricated apparatus<sup>17</sup>. The plots showing wt loss (%) versus temperature (°C) are shown in

Figure 1.

**(b) Isothermal TG.** Isothermal TG analyses of TMDAS were carried out in static air using the same apparatus and 30 mg of the sample (200-400 mesh) at appropriate temperatures: 270°, 285°, 300°, 315°C for 3, 4, 3', 4'-TMDAS; 240°, 255°, 270°, 285°, 300°C for 2, 5, 2', 5'-TMDAS; and 210°, 220°, 230°, 240°, 250°C for 2, 4, 2', 4'-TMDAS. Wt loss (%) versus *t* (min) plots are shown in Figure 2.

## Results and Discussion

**Weight loss.** Temperature curves (Figure 1) and decomposition pathways reported in Scheme I suggest that the thermal decomposition of TMDAS salts involves more than one steps. It seems that all salts (Scheme I) decompose in the solid state (1) via proton transfer (N-H) bond heterolysis to form the corresponding amine and sulfuric acid molecules in condensed phase (3, step ii). However, the N-H bond heterolysis (a unimolecular elementary reaction) occurs through an activated complex (2, step i). It is reported<sup>18,19</sup> that the basicity of the anion SO<sub>3</sub><sup>2-</sup> increases with temperature until it reaches the base strength of the dimethylaniline. At this temperature, the anion base removes a proton from the dimethylanilinium ion to form the corresponding dimethylaniline and sulfuric acid molecules in condensed phase (3). The proton transfer has been confirmed by adding a drop of sulfuric acid or amine to the

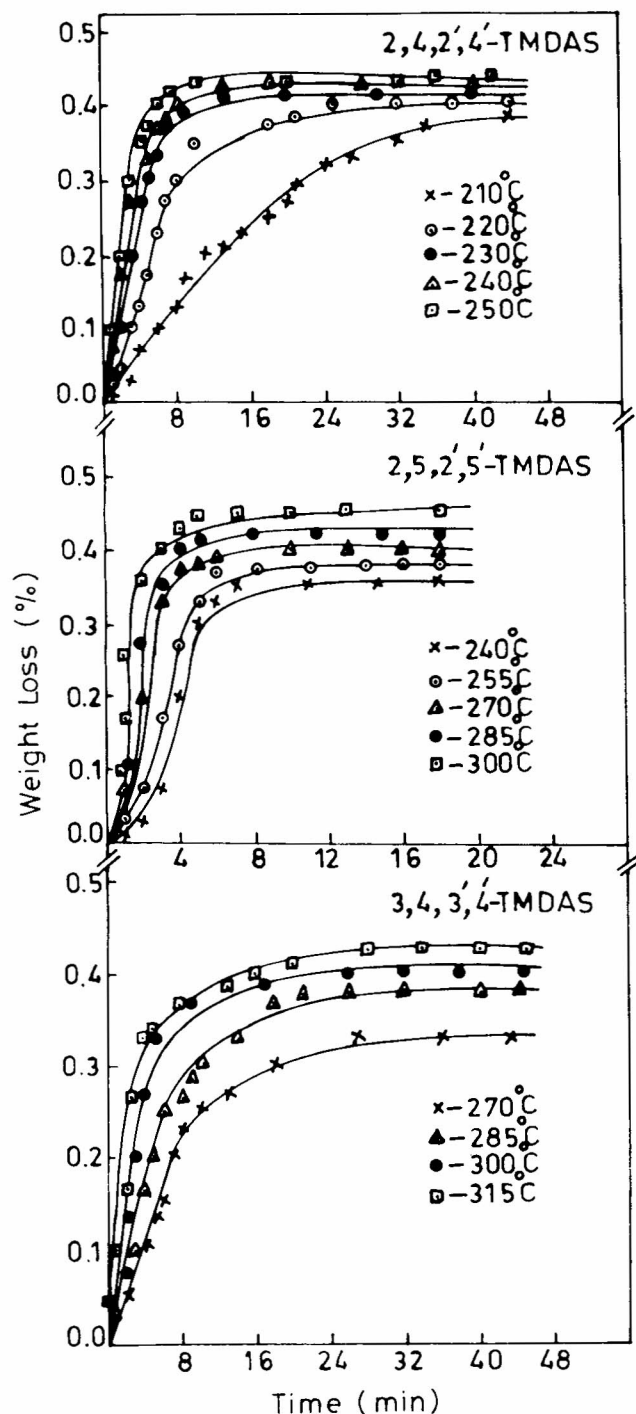
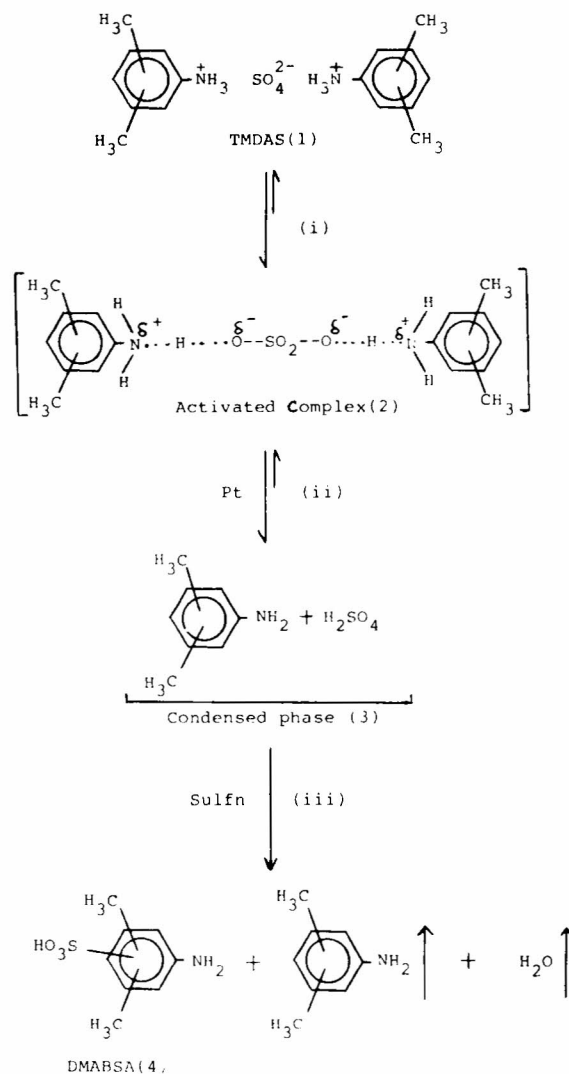


Figure 2—Isothermal TG curves of (a) 3, 4, 3', 4'-TMDAS, (b) 2, 5, 2', 5'-TMDAS, (c) 2, 4, 2', 4'-TMDAS

sample during TG. Lower values of  $\alpha$  were obtained which suggest the shifting of equilibrium to the left. Such N-H bond heterolysis has also been reported by many workers<sup>3-6, 20-24</sup> for various ammonium and substituted ammonium salts. The dissociation involving proton transfer seems to be the primary step in the decomposition of



Pt - Proton transfer, Sulfn - sulfonation

Scheme I—Thermal decomposition pathways of tetramethyldianilinium sulphate

TMDAS. Moreover, cross-sulfonation studies have proved the formation of the corresponding dimethylaniline and sulfuric acid molecules in the condensed phase (3).

Sulfur trioxide (liberated from  $H_2SO_4$ ) seems to sulfonate dimethylanilines at higher temperatures by bimolecular C-sulfonation in the condensed phase (3, Scheme I, step iii) and the corresponding DMABSA 4 are formed.

Dynamic TG curves, presented in Figure 1, clearly show that all sulfates decompose in different temperature ranges; 3, 4, 3', 4'-TMDAS decompose between 75° and 270°C (Table II, Figure 1a part A  $\rightarrow$  B) to form 2-A-4, 5-DMBSA (Table I) which is stable between 275° and 368°C (part A  $\rightarrow$  C Table II). A wt loss of 43.0% was observed

Table I—Structure, physical parameters and TLC data of tetramethyldianilinium sulfates and dimethylaminobenzenesulfonic acids

Sulfate taken				Aminobenzenesulfonic acid formed					
Compd	Crystals	$R_f^*$	$pK_a$	Structure	Crystals	Yield (%)	Decomp. temp. (°C)	Tlc	
								Eluent†	Spot† ( $R_f$ )
3,4,3',4'-Tetramethyldianilinium sulfate (3,4,3',4'-TMDAS)	Light yellow needles	0.79	5.17	2-Amino-4,5-dimethylbenzenesulfonic acid (2-A-4,5-DMBSA)	White flakes	58.5	366	a:b:c (3.5:2:1.5)	Yellow (0.83)
2,5,2',5'-Tetramethyldianilinium sulfate (2,5,2',5'-TMDAS)	Gray amorphous	0.85	4.53	4-Amino-2,5-dimethyl-benzenesulfonic acid (4-A-2,5-DMBSA)	Dark green amorphous	58.1	342	a:b:d (4:2:1)	Brown (0.82)
2,4,2',4'-Tetramethyldianilinium sulfate (2,4,2',4'-TMDAS)	White rectangular plates	0.90	4.89	2-Amino-3,5-dimethyl benzenesulfonic acid (2-A-3,5-DMBSA)	Yellow plates	57.8	320	a:d (2:1.5)	Brownish yellow (0.75)

\* Eluent, chloroform; locating reagent, iodine; spots, yellowish green

† a = Gl.acetic acid; b = benzene; c = acetone; d = abs. ethanol

‡ With iodine..

Table II—Thermogravimetric analysis of tetramethyldianilinium sulfates

Compd	Decomposition of TMDAS*		Stability range of DMABSA
	Sdt (°C)	Fdt (°C)	
3, 4, 3', 4'-TMDAS	75	275	275-363°C
2, 5, 2', 5'-TMDAS	157	264	264-320°C
2, 4, 2', 4'-TMDAS	87	250	250-326°C

\* Sdt = starting decomposition temperature; Fdt = final decomposition temperature

which is comparable with the theoretical wt loss of 40.9%. The decomposition temperature range of 2, 5, 2', 5'-TMDAS is 157-264°C (Figure 1b, part A → B) and the corresponding acid (4-A-2,5-DMBSA, Table 1) does not decompose between 264° and 320°C (plateau B → C). The ob-

served wt loss is 41.0% which is quite comparable with the theoretical value (40.9%). 2, 4, 2', 4'-TMDAS was found to decompose between 87° and 250°C (Figure 1c part A → B) giving 2-A-3,5-DMBSA (Table I) which does not decompose, and remains stable in the temperature range 250-326° (part B → C) (observed wt loss, 42.0%. Calcd, 40.9%). Thus, TG studies confirmed the formation of DMABSA from their corresponding salts. Amines and water formed during decomposition escape as vapours at higher temperatures, and DMA were characterised by co-TLC, chemical analyses, and water by Karl Fischer reagent<sup>25</sup>.

All TMDAS when heated in air at higher temperatures gave brownish black material containing DMABSA. It was difficult to isolate DMABSA from the above material. Thus, to obtain DMABSA in a pure form, samples of TMDAS were

Table III—Kinetic parameters for the thermal decomposition of tetramethyldianilinium sulfates

Salt	$k(10^{-2}/\text{min})(\text{temp. } ^\circ\text{C})$					$E_a$ (kcal/mol)
3, 4, 3', 4'- TMDAS	9.06 (270)	11.92 (285)	25.82 (300)	31.92 (315)	—	18.4
2, 5, 2', 5'- TMDAS	35.00 (240)	41.14 (255)	42.70 (270)	50.78 (285)	64.29 (300)	6.0
2, 4, 2', 4'- TMDAS	6.3 (210)	13.54 (220)	19.12 (230)	28.46 (240)	36.15 (250)	16.8

heated in vacuum at a constant temperature in an indigenously fabricated tube furnace. The probable structures of DMABSA's are given in Table I. Heating 2-A-4, 5-DMBSA (Figure 1a, part C  $\rightarrow$  D), 4-A-2, 5-DMBSA (Figure 1b part C  $\rightarrow$  D) and 2-A-3, 5-DMBSA (Figure 1c part C  $\rightarrow$  D) beyond 368°, 320° and 326°C, respectively brings about decomposition by deamination, desulfonation, dealkylation, followed by ring rupture.

Isothermal TG of TMDAS in static air gave acceleratory curves (Figure 2). The kinetics of the thermal decomposition of these salts ( $\alpha = 0.05 - 0.30\%$ ) were evaluated using Prout and Tompkins equation<sup>26</sup> (Eq. 1).

$$\log \alpha/(1 - \alpha) = kt + C \quad \dots (1)$$

The kinetic parameters are presented in Table III. The values  $E_a$  (Table III) for the thermal decomposition of TMDAS were found in the order 3, 4, 3', 4'-TMDAS > 2, 4, 2', 4'-TMDAS > 2, 5, 2', 5'-TMDAS. Linear relationship was obtained when  $E_a$  was plotted against acid dissociation constant ( $pK_a$ <sup>27</sup>) (Figure 3) which clearly indicates that a salt having higher dissociation constant (low  $pK_a$ ) has a lower value of  $E_a$ .

It is reported that *ortho*<sup>28-30</sup> and *meta*<sup>23,24,31-32</sup> methyl groups exert *-I* effects and *para*-methyl activates the benzene ring due to *+I* and hyperconjugative<sup>28</sup> effects. Thus, in 2, 4, 2', 4'- and 2, 5, 2', 5'-sulfates, *-I* effect together with the *ortho*<sup>28-30</sup> and steric strain<sup>28</sup> effects causes weakening of the N-H bond thereby favouring N-H bond heterolysis. The low value of  $E_a$  for 2, 5, 2', 5'-TMDAS seems to be due to strong *-I* effect of *m*-CH<sub>3</sub> alongwith *ortho* and steric strain which causes easy removal of proton (low  $pK_a$  4.53) from  $-\dot{N}H_3$  to  $SO_4^{2-}$  whereas in 2, 4, 2', 4'- and 3, 4, 3', 4'-TMDAS, the strengthening of N-H bond is due to hyperconjugative (*+I*) electron release from *p*-CH<sub>3</sub>.

### Conclusions

The kinetic parameters for the thermal decom-

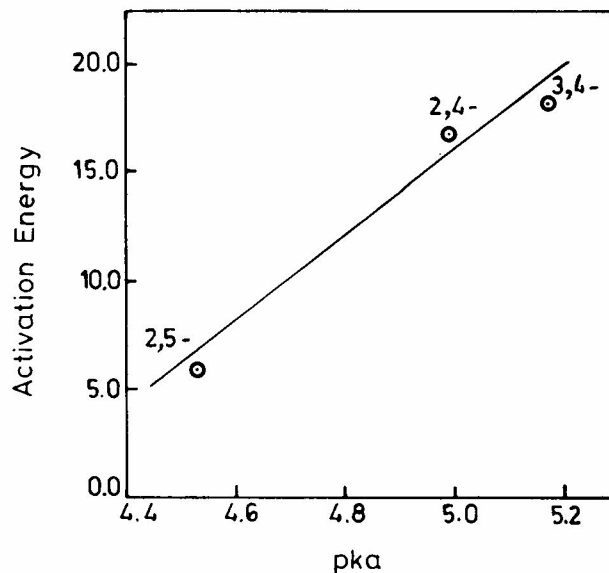


Figure 3—Plot of  $E_a$  versus  $pK_a$  of TMDAS

position of TMDAS have been found to be related to  $pK_a$  of arylamines. The N-H bond heterolysis seems to be the primary step for the decomposition of salts. An abnormal behaviour of electron-donating group ( $-\text{CH}_3$ ) was also observed within a class of compounds.

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