Kinetics of Thermal Decomposition of Arylammonium Sulfates. Part 2.[1] *m*-Ditoluidinium Sulfate

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The thermal decomposition of *m*-ditoluidinium sulfate (*m*-DTS) has been studied and 2-methylsulfanilic acid (2-MSA) has been found to be the decomposition product. Isothermal TGA data on *m*-DTS were fitted in Avrami-Erofeev (n = 2, 3), Contracting area, Contracting cube and Ginstling Brounshtein equations. The Contracting cube equation was found to give the best fit and the mean value for the energy of activation for *m*-DTS decomposition is 31 ± 1 kcal mol^{-1}. The proton-transfer process seems to be the primary step during decomposition of *m*-DTS.

It has been reported in our earlier paper[1] that dianilinium sulfate (DAS) is formed when aniline is treated with concentrated sulfuric acid in 2:1 molar ratio at room temperature. The thermal decomposition of DAS commences by the proton transfer process prior to sulfonation and sulfanilic acid was found to be the end product.

Sulfanilic acid[2] and substituted sulfanilic acids[3] find applications in dyestuffs, medicines, and organic syntheses. In the present communication, the preparation, characterization and thermal decomposition of *m*-ditoluidinium sulfate (*m*-DTS) is described. Isothermal TGA data on *m*-DTS were fitted in various kinetic equations and the mechanism of thermal decomposition of *m*-DTS has also been discussed.

Experimental

Materials.—*m*-Toluidine (Wilson, purified by distillation), conc. H_2SO_4 (A.R.), silica gel G, TLC grade (Qualigens) and barium chloride (BDH) were used.

m-*Ditoluidinium Sulfate*.—The grey coloured crystalline precipitates of *m*-DTS were obtained immediately on treating *m*-toluidine with H_2SO_4 (95–98%) at room temp. in 2:1 molar ratio. It was recrystallised from aq. solution (concentrated under vacuum) and the crystals were vacuum dried. Its purity was checked by TLC and was characterized by molecular weight determination, elemental, gravimetric and spectroscopic analyses. The compound was found to decompose without melting (Found: C, 53.3; H, 6.8; N, 8.8; S, 10.8%; M, 312.3. Calc. for $C_{14}H_{20}N_2O_4S$: C, 53.8; H, 6.4; N, 9.0; S, 10.3%; *M*, 312); IR spectrum (Perkin-Elmer spectrometer), ν_{max}(KBr)/cm^{-1} 2870, 2560, 1510, 1490 and 1570 (NH), 1110 and 675 (SO_4^{2-}) and 1450 (CH_3); UV spectrum (Hitachi-U-2000 spectrometer), λ_{max}(H_2O)/nm 279, 266, 232 and 212; NMR spectrum (Perkin-Elmer spectrometer), δ_H(90 MHz; solvent D_2O; standard $SiMe_4$) 2.6 (3 H, s, Me) and 7.3–7.7 (4 H, q, $C_6H_4\overset{+}{N}H_3$); mass spectrum (JEOL SX-102 mass spectrometer), m/z 149 (100%), 108 (62), 154 (50.3), 391 (43.7), 77 (40.1), 107 (36.5), 91 (28.7), 41 (26.7), 55 (23.2) and 178 (13).

TG Studies on m-*DTS*.—Dynamic TGA on *m*-DTS (30 mg) was undertaken in static air at a heating rate of 2 °C min^{-1} using an indigeneously fabricated TGA apparatus[4] and the data are plotted in Fig. 1. Isothermal TGA (200–400 mesh, 30 mg) was taken at 175, 185, 200 and 215 °C and the fractional decomposition (α) *vs.* time has been plotted in Fig. 2. The accuracy of the TGA furnace was ± 1 °C.

DTA Studies on m-*DTS*.—DTA was carried out on the sample (10 mg) at a heating rate of 10 °C min^{-1}. The differential thermogram (Fig. 3) was recorded using a two pen potentiometric strip chart recorder.

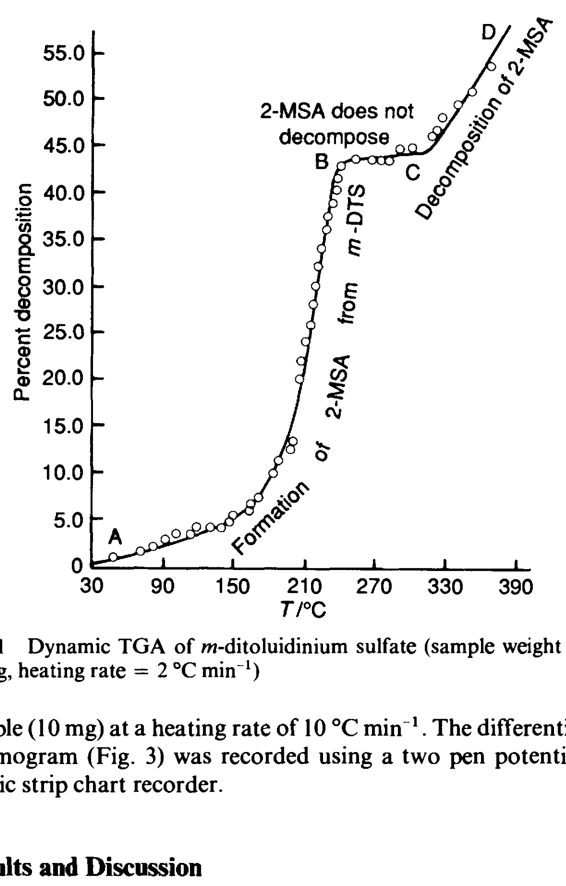


Fig. 1 Dynamic TGA of *m*-ditoluidinium sulfate (sample weight = 30 mg, heating rate = 2 °C min^{-1})

Results and Discussion

A TGA taken in static air clearly shows that *m*-DTS undergoes weight loss of 43.3% (40.0% wt. loss observed with isothermal TGA) in the temperature range 50–240 °C (Fig. 1, A→B) which proves the evolution of water and *m*-toluidine from *m*-DTS. It seems that the residual product is 2-methylsulfanilic acid (2-MSA) as the weight loss is also very much comparable with the theoretical wt. loss (40.7%). A plateau in the temperature range 240–290 °C (Fig. 1, B→C) indicates the stability of 2-MSA. Heating the sample beyond 290 °C resulted in the decomposition of 2-MSA (Fig. 1, C→D). DTA (Fig. 3) in static air showed an endotherm at 130 °C, which may be indicative of water loss. An exotherm (I) at 225 °C may be due to the sulfonation and subsequent formation of 2-MSA. The broad exotherm (II) at 345 °C shows the oxidative decomposition of the 2-MSA.

It has also been observed that *m*-DTS is formed when *m*-toluidine is treated with concentrated sulfuric acid in the molar ratio of 2:1 or 1:1. Thus, it was thought of interest to take

Table 1 Mechanism-based equations

Eqn.	Form of $g(\alpha)$	Rate controlling process
(1)	$-\ln(1-\alpha)^{1/2}$	Random nucleation; Avrami–Erofeev eqn. ($n = 2$)
(2)	$-\ln(1-\alpha)^{1/3}$	Random nucleation; Avrami–Erofeev eqn. ($n = 3$)
(3)	$1-(1-\alpha)^{1/2}$	Phase boundary reaction, cylindrical symmetry; Contracting area eqn.
(4)	$1-(1-\alpha)^{1/3}$	Phase boundary reaction, spherical symmetry; Contracting cube eqn.
(5)	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion, spherical symmetry; Ginstling-Brounshtein eqn.

Table 2 Regression analysis (R^2) of the thermal decomposition data on *m*-DTS by various kinetic models

Model	175 °C	185 °C	200 °C	215 °C
1 Avrami–Erofeev eqn. ($n = 2$)	0.97	0.91	0.93	0.95
2 Avrami–Erofeev eqn. ($n = 3$)	0.95	0.84	0.96	0.83
3 Contracting area eqn. ($n = 2$)	0.97	1.0	0.97	0.81
4 Contracting cube eqn. ($n = 3$)	0.84	1.0	1.0	1.0
5 Ginstling–Brounshtein eqn.	0.54	1.0	0.99	0.97

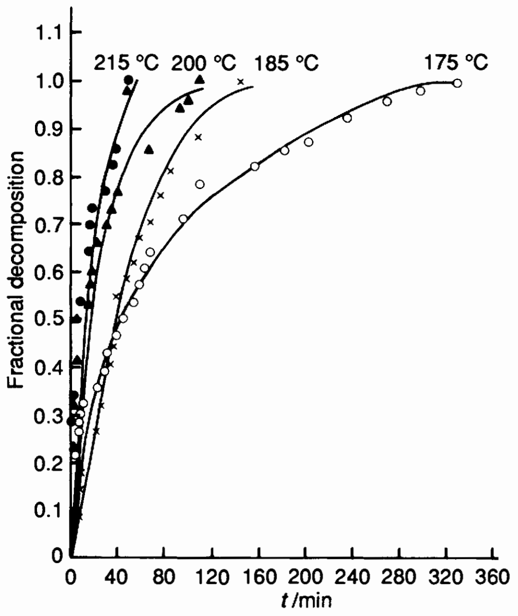


Fig. 2 Thermal decomposition (fractional weight loss = α) of *m*-ditoluidinium sulfate (200–400 mesh, sample weight = 30 mg)

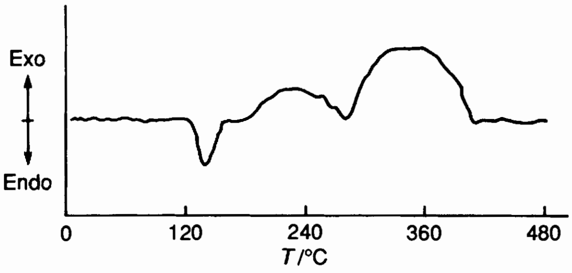


Fig. 3 DTA thermograms of *m*-ditoluidinium sulfate in static air

detailed kinetic studies on the thermal decomposition of *m*-DTS. The reaction mechanism can be derived by applying mechanism based kinetic models[5–7] and the mechanism[8] is ascertained by the equation which gives the best fit with the experimental TG data. Thus the kinetics of thermal decomposition of *m*-DTS are evaluated using five kinetic models reported in literature[9–17] (Table 1). The linearity of these kinetic models was checked by using the following equation suggested by Mahapatra *et al.*[18] and R^2-values for each model

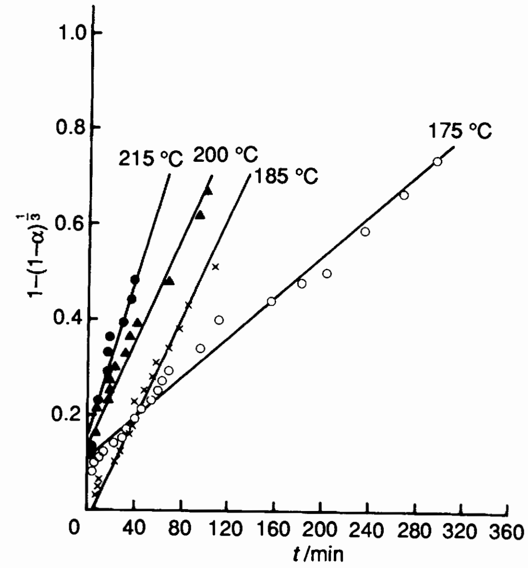


Fig. 4 Kinetic analysis of *m*-ditoluidinium sulfate by Contracting cube eqn. ($n = 3$)

$$R^2 = \frac{[\Sigma XY - n\bar{X}\bar{Y}]^2}{[\Sigma X^2 - n\bar{X}^2][\Sigma Y^2 - n\bar{Y}^2]}$$

are given in Table 2, where n is the number of readings, $\bar{X}$ and $\bar{Y}$ are average values of X and Y. The calculated kinetic parameters are given in Table 3. The Contracting cube equation has been found to give the best fit (Fig. 4).

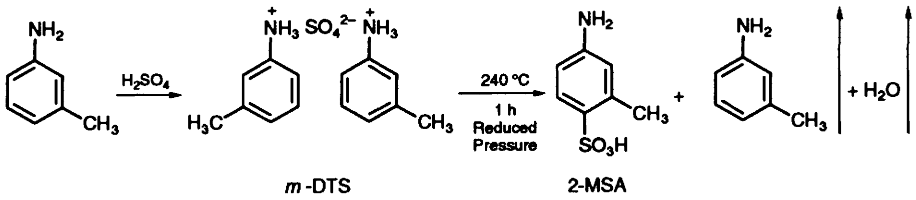
The calculated E_a for thermal decomposition of *m*-DTS is higher as compared to DAS reported in our earlier publication.[1] This may be due to the strengthening of N–H bond on account of electron donating behaviour of the Me group.

A brownish-black product containing 2-MSA was obtained when *m*-DTS was heated in air at higher temperatures, which may be due to the formation of quinonoid-like materials arising from hydroxylation, oxidation and polymerisation of amino compounds. It was difficult to separate 2-MSA from the brownish-black product. Thus, in order to prepare 2-MSA in pure form, it was necessary to remove the water and *m*-toluidine which is formed along with 2-MSA when *m*-DTS is heated at higher temperature under reduced pressure. The sample of *m*-DTS heated at 240 °C for 1 h at 60 mmHg was found to contain 2-MSA [yield 58% (calc. 59.3%)], 2-MSA was purified by preparative TLC. It gave the dye test and effervescences with $NaHCO_3$. It was also found to decompose without melting. The microanalysis and spectroscopic studies also confirmed 2-MSA (Found: C, 44.6; H, 5.0; N, 6.8. $C_7H_9NO_3S$ requires C, 44.9; H, 4.8; N, 7.5%); ν_{max}(KBr)/cm^{-1} 2930 and 1450 (CH_3), 1600 and 3380 (NH), 1235, 1170 and 1150 (SO_2–O); λ_{max}(H_2O)/nm 247 and 205; δ_H(90 MHz; solvent D_2O; standard $SiMe_4$) 2.8 (3 H, s, Me) and 7.2, 7.9–8.1 (3 H, br, $HO_3SC_6H_3NH_2$).

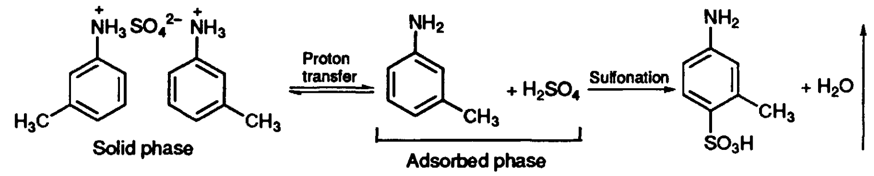
Based on the above studies, the decomposition of *m*-DTS can be proposed as given in Scheme 1. 2-MSA was found to be the major product and *m*-toluidine and water will be given off as vapours at higher temperatures under reduced pressure. The formation of *m*-toluidine was confirmed by TLC, GLC and

Table 3 Kinetic parameters for thermal decomposition of *m*-DTS

Model	$k/10^{-3}$ min^{-1}				
	175 ± 1 °C	185 ± 1 °C	200 ± 1 °C	215 ± 1 °C	E_a/kcal mol^{-1}
Avrami–Erofeev eqn. ($n = 2$)	5.93	10.8	13.5	23.3	29
Avrami–Erofeev eqn. ($n = 3$)	3.52	7.58	8.62	11.4	30
Contracting area eqn. ($n = 2$)	2.59	6.82	7.14	9.375	33
Contracting cube eqn. ($n = 3$)	2.14	5.17	5.36	7.895	32
Ginstling–Brounshtein eqn.	0.98	2.12	2.50	4.17	32



Scheme 1



Scheme 2

chemical analyses (collecting the droplets from the cold upper side of the sample tube). MS fragmentation at $m/z = 107$, also corresponds to the formation of the *m*-toluidine radical cation. Therefore, *m*-DTS seems to decompose to *m*-toluidine and H_2SO_4 molecules in adsorbed phase, *via* proton transfer, prior to sulfonation as illustrated in Scheme 2. It has been reported[19,20] that basicity of the anion (SO_4^{2-}) increases with rise in temperature until it reaches the base strength of the *m*-toluidine. At this temperature the anion base removes the proton from *m*-toluidinium cation to form *m*-toluidine and H_2SO_4 molecules.

The dissociation involving proton-transfer seems to be the rate determining step during decomposition of *m*-DTS. It was confirmed by adding a drop of *m*-toluidine or H_2SO_4 (during TGA measurements) to *m*-DTS samples and α-values were found to be lowered from 40% to 32% or 20% respectively. This clearly indicates the suppression of forward reaction. Such a type of proton transfer process has also been envisaged by many workers[21–26] in the case of arylammonium perchlorate and nitrates, which are structurally analogous to arylammonium sulfates. Brill *et al.*[27–34] have also reported the proton transfer profess in the decomposition of ammonium nitrate and aliphatic amine nitrates and perchlorates.

Further, to confirm the formation of H_2SO_4 and *m*-toluidine, cross-sulfonation of 1-naphthylamine was done. A small amount of 1-naphthylamine was heated along with *m*-DTS at 60 mmHg for 1 h. The products isolated were found to be *m*-toluidine, 1-naphthylamine, 2-MSA, and 1-naphthylamine sulfonic acids (confirmed by TLC and chemical analyses). Evolution of water during the thermal decomposition of *m*-DTS was also confirmed by using Karl-Fischer reagent.[35]

Summarizing the results, it seems that phase boundary reactions occur during thermolysis of *m*-DTS. Reactive species, such as *m*-toluidine and H_2SO_4 are formed *via* proton transfer process in adsorbed phase prior to sulfonation.

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