Synthesis, characterization and thermal decomposition of di-(2,4,6-trimethylanilinium) sulphate†

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Di-(2,4,6-trimethylanilinium) sulphate [2,4,6-TMAS] was synthesized by reaction of 2,4,6-trimethylaniline with concentrated sulphuric acid at room temperature. The crystal structure of this salt was determined using single crystal X-ray diffraction. It crystallizes in orthorhombic space group Pna2$_1$, a= 7.7115(1) Å, b= 30.3746 (6) Å, c=16.9251 (3)Å , α=β=γ [°]=90°, V=3964.43 (12)A and Z=8. The structure contains 2,4,6-trimethylanilinium ions that share vertices through intermolecular H- bonds with sulphate ions and a water molecule. Notably thermal and microwave heatings of di-(2,4,6-TMA)S have afforded 3-amino-2,4,6-trimethylbenzenesulphonic acid (3-A-2,4,6-TMBSA) with release of a molecule of amine and water. It has been suggested that the proton transfer from anilinium to SO$_4^{2-}$ ion is a primary and rate controlling step. Further di-(2,4,6-TMA)S and 3-A-2,4,6-TMBSA were characterized by infrared, mass spectrometry, elemental and thermogravimetric- differential scanning calorimetric (TG-DSC) analyses. The mean value for the energy of activation (83.0 kJ mol^{-1}) for the conversion of di-(2,4,6-TMA)S to 3-A-2,4,6-TMBSA has been determined from isothermal thermogravimetry data.

Keywords: 2,4,6-trimethylaniline, X-ray diffraction, Thermal, Microwave, 3-Amino-2,4,6-trimethylbenzenesulphonic acid

Sulphonation of arylamines has been conventionally achieved by "baking process"[1-3], which involves multi-step reactions and use of organic solvents[2,3]. Singh *et al*.[4-9] have carried out sulphonation of various mono and di-substituted arylamines in solid state via an intermediate salt formation. Proton transfer process[10,11] plays an important role in the thermal decomposition of amine salts. Solid state sulphonation is simple, convenient and ecofriendly, because no solvent is required. In this process, the sulphate salts are subjected to thermal and microwave energy by which the corresponding aminobenzenesulphonic acids are formed which have a wide range of applications[12] in organic syntheses, dyestuffs, medicines, detergents and tanneries. Compared to thermal process, microwave irradiations[13] gave their sulphonated product in lesser time.

In the line of these findings, we have prepared and characterized di-(2,4,6-TMA)S which on thermal and microwave treatment, in solid state, forms (3-A-2,4,6-TMBSA) .

Kinetic parameters for solid-state sulphonation are of practical interest as the data may be helpful for prediction of conditions for manufacture and storage. Thermo-analytical techniques can provide important measure of kinetics of thermally stimulated reactions, which permit a deeper insight into the mechanism of solid-state decomposition reactions. Further, kinetics of thermal decomposition of di-(2,4, 6-TMA)S have also been evaluated by isothermal and isoconversional methods.

Experimental Procedure

Materials and apparatus

2,4,6-trimethylaniline (Merck), conc. H$_2$SO$_4$ (Merck), ethyl acetate (Merck), silica gel (TLC grade, Qualigens) and BaCl$_2$ were used as received.

A commercial household microwave oven model (MS 1921 HE, LG electronics private Ltd) and homemade tube furnace[14] for conventional (under vacuum) heating purpose were used.

Preparation and characterization

White amorphous precipitate of di-(2, 4, 6-TMA) S were obtained immediately at room temperature (RT) when 2,4,6-trimethylaniline mixed with conc. H$_2$SO$_4$ in 2:1 molar ratio as shown in Scheme 1.
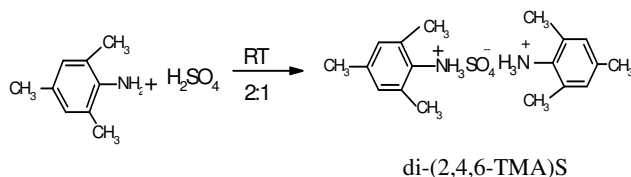
Scheme 1—Preparation of di-(2,4,6-TMA)S from 2,4,6-trimethylaniline

The precipitates were washed with ethyl acetate to remove any excess of amine and recrystallized from double distilled water. Transparent long needle shaped crystals were obtained on keeping the above solution for 48 h at room temperature. The purity of the salt was checked by TLC and identified by single X-ray crystallography, elemental and spectral analyses. The physical parameters are given in Table 1.

X-rays crystallography

Suitable transparent needle shaped, single crystals of di-(2,4,6-TMA)S with approximate dimension of 0.35×0.30×0.06 mm were obtained by recrystallizing the crude product by slow evaporation of their aqueous solution. The data collection was done at low temperature (223 K) using a Nonius Kappa CCD diffractometer equipped with a rotating anode generator Nonius FR 591. The programs that were used involve data collection by Hooft and Nonius[15] and data reduction by Otwinowski and Minor[6]. The structure was solved by direct methods (program SHELXS-97)[17] and refined by the full matrix least squares method on all F^2 data using SHELXL-97[18]. Hydrogen atoms were placed in geometrically

calculated positions by using a riding model. Images were created with the SCHAKAL program[19]. Refinement with anisotropic thermal parameters for non-hydrogen atoms led to R values of 0.051.

The crystal structure of salt is shown in Fig. 1; whereas its crystal data and structure refinement and hydrogen bond parameters are summarized in Tables 2 and 3.

Elemental and spectroscopic analyses

The C, H, N analyses were done with elemental Vario EL (111) Carta Erba 1108 instrument. The FTIR spectra were recorded with Perkin-Elmer RXL spectrometer in the range of 4000-450 cm^{-1}.The FAB mass spectra was recorded on J60LQ SX 102/Da-6000 mass spectrometer using Xenon gas.

Conversion of sulphate salt into corresponding aminobenzenesulphonic acid

Thermal study

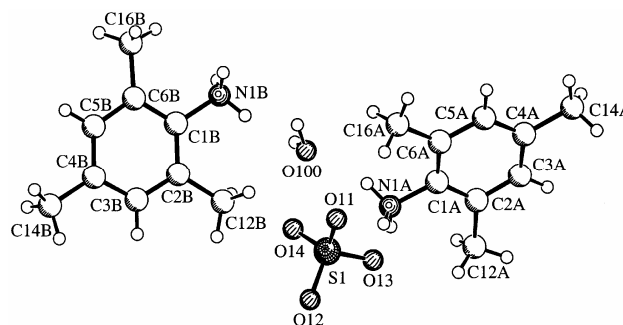The sample was heated, in a tube furnace at 230°C for 20 min under reduced pressure, a gray colour

Fig. 1—Crystal structure of di-(2,4,6-TMA)S

Table 1—Physical parameters,TLC, CHN, IR, and mass analyses of di(2,4,6 TMA)S and 2,4,6-TMABSA

Compound	Structural formula	Crystal colour	M.P °C	TLC	R_f	Yield %	C H N (calculated)	IR (cm^{-1})	Mass (m/z)
Di (2,4,6-TMA)S		White needles	194	a:b:c	0.98	78	56.7 7.7 7.1 (58.77.67.6)	3400υ(⁺NH₃), 3027(v)=CH 1618(v), 1585(v), 1500(v), 1483(v) C=Cstr.,1121,738 υ (SO₄⁻), 2950υ(CH str.), 1299 υ(C-N)	369,368(80) 271(60),95(20) 602(60),135(100
3-A-2,4,6-TMBSA		Gray amorphous	170	a:b:c	0,0.92	57	51.27.56.7 (50.06.9 6.5)	3448,3346 (m) N-str., 1579 (m-s) N-Hbending, 1280 (m-s) C-Nstr, 1114 υ (SO₃H), 2800 (m) C-Hstr.	135(100),93(20) 154(20),271(30),

Eluent a= DMSO, b=ethylacetate , c= H₂O; locating reagent- Iodine

Table 2—Crystal data and structure refinement for di-(2,4,6-TMA)S

Empirical formula	$C_{18} H_{30} N_2 O_5 S$
Formula weight	386.50
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
space group	$Pna2_1$ (No.33)
Unit cell dimensions	a =7.7115 (1) Å
	b = 30.3746(6) Å
	c = 16.9251(3) Å
Volume	3964.43(12) Å^3
Z, Calculated density	8,1.295 mg/m^3
Absorption coefficient	0.194 mm^{-1}
F(000)	1664
Crystal size	0.35 × 0.30× 0.06 mm
Theta range for data collection	1.34 to 27.87°.
Limiting indices	-8<=h<=10,-39<=k<=37,
	-10<=l<=22
Reflections collected / unique	23200 / 6692 [R(int)= 0.059]
Completeness to theta = 27.87	99.4 %
Max. and min. transmission	0.989 and 0.935
Refinement method	Full-matrix least squares on F^2
Data/restraints / parameters	6692 / 1 / 469
Goodness-of-fit on F^2	0.992
Final R indices [$I>2\sigma(I)$]	R1 = 0.051, wR^2 = 0.117
R indices (all data)	R1 = 0.090, $w R^2$ = 0.143
Absolute structure parameter	0.45(9)
Largest diff. peak and hole	0.32 and-0.55 eÅ^{-3}

Table 3—Hydrogen bonds with H.A < r(A) + 2.000 Å and <DHA > 110°

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1A-H1A1	0.900	1.777	177.62	2.677	O13
N1A-H1A1	0.900	2.788	153.80	3.618	S1
N1A-H1A2	0.900	1.948	164.21	2.824	O100
N1A-H1A3	0.900	1.957	154.42	2.796	O22 [a]
N1A-H1A3	0.900	2.879	139.13	3.608	S2 [a]
N1B-H1B1	0.900	1.883	164.45	2.761	O22
N1B-H1B1	0.900	3.022	154.78	3.856	S2
N1B-H1B2	0.900	1.795	177.78	2.694	O13 [b]
N1B-H1B2	0.900	2.944	155.93	3.784	S1 [b]
N1B-H1B3	0.900	2.125	140.00	2.873	O101
N1C-H1C1	0.900	1.972	152.68	2.802	O12
N1C-H1C1	0.900	2.922	135.38	3.618	S1
N1C-H1C2	0.900	1.968	157.73	2.821	O101 [c]
N1C-H1C3	0.900	1.785	162.46	2.657	O23 [a]
N1C-H1C3	0.900	2.734	161.47	3.599	S2 [a]
N1D-H1D1	0.900	2.112	136.43	2.833	O100
N1D-H1D2	0.900	1.837	171.46	2.730	O23 [a]
N1D-H1D2	0.900	2.998	149.01	3.798	S2 [a]
N1D-H1D3	0.900	1.857	172.44	2.752	O12 [d]
N1D-H1D3	0.900	2.983	162.52	3.852	S1 [d]
O100-H101	0.997	1.783	168.82	2.767	O21
O100-H101	0.997	2.826	162.84	3.790	S2
O100-H102	0.847	1.941	168.37	2.776	O11 [d]
O100-H102	0.847	3.017	157.29	3.812	S1 [d]
O101-H103	0.997	1.807	161.54	2.771	O11
O101-H103	0.997	2.815	165.62	3.789	S1
O101-H104	0.946	1.837	163.17	2.756	O21
O101-H104	0.946	2.947	143.91	3.753	S2

Symmetry code	[a]: [-x+2, -y+1, z-1/2]
	[b]: [-x+1, -y+1, z+1/2]
	[c]: [-x+1, -y+1, z-1/2]
	[d]: [x+1, y, z]

residue was obtained. The residue was then washed with a solvent, recrystallized from water, concentrated under vacuum and their purity was checked by TLC. The reaction products was identified as 3-A-2,4,6-TMBSA by spectral and elemental analyses (Table 1). Moreover, this acid gave effervescences with aq. $NaHCO_3$.

Microwave study

The salt was powdered, placed in a Pyrex test tube and then loaded into a microwave oven (domestic) and irradiated for appropriate times with a power of 700 W. After completion of the reaction (monitored by TLC), contents were cooled to remove impurity and recrystallized from water to get acids in a pure form.The acid was characterized by elemental and spectral analysis (Table 1).

Thermal analysis

Simultaneous TG-DTG-DSC analysis on the salt (sample weight 5.8 mg,100-200 mesh) has been done by using Perkin Elmer (Pyris Diamond) instrument at a heating rate of 10°C/min (heat flow from 40-700°C in nitrogen atmosphere). The thermogram is shown in Fig. 2.
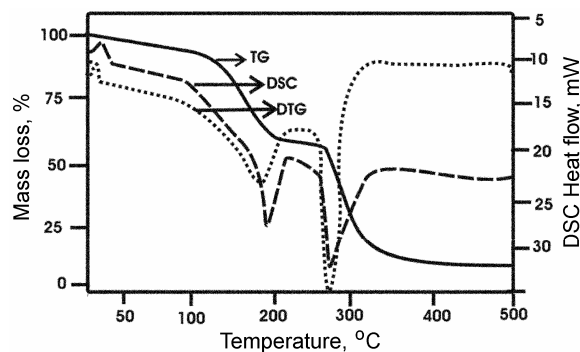

Fig. 2—Non-isothermal TG- DSC curves of di-(2,4,6-TMA)S

Isothermal TG

Isothermal TG studies (wt. 20 mg, 100-200 mesh) were undertaken in static air using indigenously fabricated TG apparatus[20] at appropriate temperatures. The accuracy of furnace was ±1°C. A round bottom
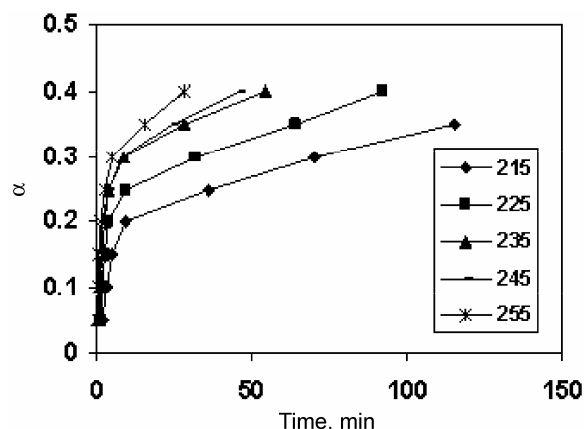
Fig. 3—Isothermal TG of di- (2,4,6- TMA)S in static air

Table 4—Arrhenius parameters for isothermal decomposion of di-(2,4,6-TMA) S salt

S.No.	Reaction model	r	E, kJ/mol
1	Power law	0.9883	74.5
2	Power law	0.9889	75.0
3	Power law	0.9898	76.1
4	Power law	0.9920	83.0
5	One-dimensional diffusion	0.9914	86.5
6	Mampel (first order)	0.9920	81.9
7	Avrami-Erofeev	0.9910	77.9
8	Avrami-Erofeev	0.9900	76.4
9	Avrami-Erofeev	0.9908	77.7
10	Contracting sphere	0.9919	81.1
11	Three-dimensional diffusion	0.9721	89.3
12	Contracting cylinder	0.9919	80.7
13	Prout-Tomkins	0.9886	74.8
14	Ginstling-Brounshtein	0.9620	66.8

gold crucible was used as a sample holder. The fraction decomposition (α) has been plotted against time (min) and the plots are shown in Fig. 3.

Kinetic analysis

Kinetic analysis of solid state decomposition is usually based on a single step kinetic equation[21]

$$d\alpha / dt = k\,(T)\,f\,(\alpha) \qquad\qquad \dots\ (1)$$

where t is the time, T is the temperature, α is the extent of conversion ($0 < \alpha < 1$), $k\,(T)$ is the rate constant and $f\,(\alpha)$ is the reaction model[21], which describes the dependence of the reaction rate on the extent of reactions. The value of α is experimentally derived from the global mass loss in TG experiments. The reaction model may take various forms, some of which are shown in Table 4. The temperature dependence of $k\,(T)$ can be satisfactorily described by the Arrhenius equation, whose substitution into Eq. (1) yields

$$d\alpha / dt = A \exp\,(-E/RT).f\,(\alpha) \qquad\qquad \dots\ (2)$$

where, A is pre-exponential factor, E is activation energy and R is the gas constant.

Model fitting method

Rearrangement and integration of Eq. (1) for isothermal conditions gives

$$g_j(\alpha) = k_j(T)t \qquad\qquad \dots\ (3)$$

where $g(\alpha) = {_0\int^{\alpha}} [f\,(\alpha)]^{-1}\,d\alpha$ is the integrated form of the reaction model. The subscript j has been introduced to emphasize that substituting a particular reaction model in Eq. (3) results in evaluating the

corresponding rate constant, which is determined from the slope of a plot of $g_j(\alpha)$ verses t. For each reaction model selected, the rate constants are evaluated at several temperatures T_i and Arrhenius parameters are determined using the Arrhenius equation (4) in its logarithmic form

$$\ln k_j(T_i) = \ln A_j - E_j/RT_i \qquad\qquad \dots\ (4)$$

Arrhenius parameters were evaluated for isothermal experimental data by the model fitting method.

Isoconversional method

This method allows the activation energy to be evaluated without making any assumptions about the reaction model. Additionally, the method evaluates the effective activation energy as a function of the extent of conversion which allows one to explore multi-step kinetics.

The basic assumption of the isoconversional method[22] is that the reaction model as defined in Eq. (1) is not dependent on temperature or heating rate. Under isothermal conditions, on combining Eqs (3) and (4) we get

$$-\ln t_{\alpha,i} = \ln [A_\alpha/g\,(\alpha)] - E_\alpha/RT_i \qquad\qquad \dots\ (5)$$

where E_α is evaluated from the slope of the plot of $-\ln t_{\alpha,i}$ against T_i^{-1}. Thus, E_α at various α_i for di-(2, 4, 6-TMA)S have been evaluated and the E_α dependencies are shown in Fig. 4.

Results and Discussion

The X-ray crystallography, elemental and spectral data clearly confirm the formation of di-(2,4, 6-TMA)S salt when 2,4,6-trimethylaniline reacts with
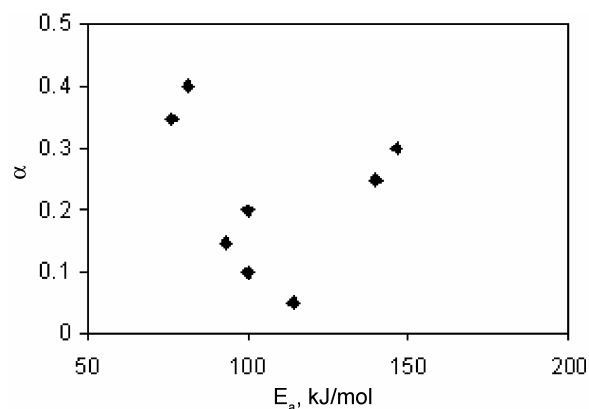
Fig. 4—Dependence of the activation energy (E_a) on the extent of conversion (α)

concentrated H_2SO_4 in 2:1 molar ratio. Elemental data obtained from di-(2,4,6-TMA)S match with theoretically calculated values with an accuracy of ± 1%. FTIR spectrum of salt show (γ^+NH_3) at 3432 cm^{-1}, (δ N-H) at 1483, (γ C-H)at 3208, (γ C-N) at 1381.5 cm^{-1}, C=C stretching at 1618, 1585, 1561, 1483 , while sharp peaks at γ 738 and 1121 cm^{-1} are due to SO_4^{2-}. The mass spectroscopy shows base peak at *m/z* 135 (100%) may be due to 2, 4, 6 trimethyl anilinium cation and at 368 molecular ion peak of di-(2,4,6-TMA)S.

The compound crystallizes from slow evaporation of their aq. solution in the orthorhombic crystal system, space group Pna 2$_1$ with unit cell dimension *a*=7.7115(1) Å, *b*=30.3746 (6) Å, *c*=16.9251(3) Å, Z=8, D_x=1.295 g cm^{-1} (Table 1). It is very clear from X-ray analyses (Fig. 1) that it confirms to the molecular formula ($C_9H_{14}N_2SO_4$) H_2O having one molecule of water of crystallization. The two moieties of anilinium cation are bonded to one sulphate ion by electrostatic as well as intermolecular hydrogen bonds. Further, one molecule of water is also intermolecular hydrogen bonded with –NH$_2$ of amine moieties (Table 3).

The TG thermograms (Fig. 2) in nitrogen atmosphere shows that di-(2,4,6-TMA)S undergo mass loss of 42% (41.5% calculated) by the evolution

of amine and a water molecule (temperature range of 90-190°C) and corresponding sulphonic acid is formed. This was also confirmed by Co-TLC and chemical analyses. The stability of corresponding sulphonic acid is shown by the plateau in TG curves (190-280°C). Heating the sample beyond this temperature resulted in the decomposition of corresponding sulphonic acid by deamination, desulphonation, dealkylation followed by ring rupture. It has also been observed that heating this sulphate salt in air at higher temperature gave black products which contain their acid. This is presumably due to the formation of quinonoid like materials arising from hydroxylation, oxidation and polymerization of amino compounds. DSC (Fig. 2) shows two peaks which also confirm the two step decomposition. First peak seems to be due to sulphonation process to form corresponding sulphonic acid and second peak corresponds to the decomposition of acid form.

In order to prepare the pure form, it was thought best to remove the corresponding amine, while heating under low pressure which is formed along with their acids. Thus, the sample was heated at 230°C for 20 min in Hg pressure were found to contain 3-A-2,4,6-TMBSA. Solid residues were washed with appropriate solvent and the purity was then confirmed by TLC. Further, the acid is confirmed by elemental and spectral analyses (Table 1).

In order to get the same product (3-A-2,4,6-TMBSA) in shorter time, the salt was subjected to microwave irradiation at 700 W for 4 min, to form the acid. It has been observed that compare to classical methods, the MW irradiation took a short time (Scheme 2).

The isothermal TG in static air has been done to know the kinetics of the thermal decomposition of above salt, using 14 mechanism based kinetic models. In the model fitting method, the kinetics is analyzed by choosing a best fit model based on the value of the correlation coefficient *r* close to 1. The corresponding
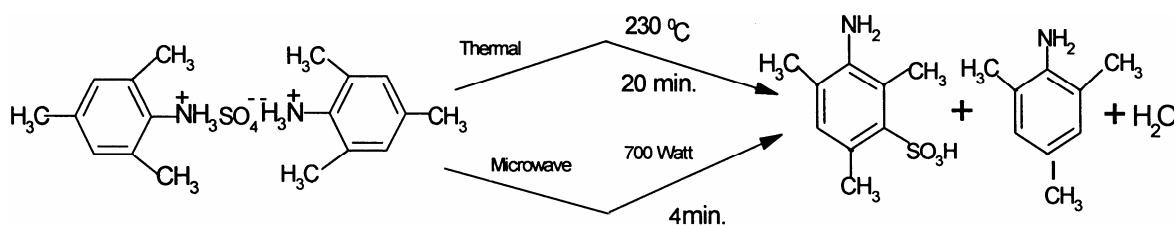
Scheme 2—Synthesis of 3-A-2,4,6- trimethylbenzenesulphonic acid

values of E_a from different models for a particular sample are nearly equal irrespective to the equation used. Average value of activation energy is 83.0 kJ/mol from isothermal TG data (Table 4).

In addition another method, called isoconversional method is known to permit estimation of activation energy independent of the model used. In this method, activation energy corresponding to the extent of conversion of the sample is evaluated. As is clear from the Fig. 4, activation energy has different value at different α.

The conversion of salt to corresponding ring substituted aminobenzenesulphonic acid by thermal and microwave treatment is shown in Scheme 2. It is inferred that under both treatments salt decompose to regenerate amine and acid by proton transfer[7,9,10] from substituted anilinium ion to the sulphate ion in condensed phase. Further interaction between amine and sulphuric acid at higher temperature yields sulphonated product (acid).

Conclusions

Thermal and microwave decomposition of di-(2,4, 6-TMA)S gives 3-A-2,4,6-TMBSA by proton transfer and a subsequent sulphonation process. Compared to thermal, the microwave irradiation takes a short time to form corresponding acid.

Acknowledgements

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