Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 2, 553–557

PREPARATION, CHARACTERIZATION AND THERMAL DECOMPOSITION OF PHENYLENEDIAMMONIUM SULFATE SALTS
Part. XVI

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Three phenylenediammonium sulfate (PDAS) salts were prepared under solvent free conditions and characterized by gravimetric, spectroscopic and elemental analyses. Thermal decomposition studies of the salts have been investigated using TG (static air), TG/DTG and DSC (inert atmosphere). The thermal decomposition pathways have also been suggested and it has been found that PDAS salts on heating under vacuum in solid state give diaminobenzene sulfonic acids (DABSA) via proton transfer.

Keywords: *diaminobenzenesulfonic acid, phenylenediammonium sulfate, proton transfer, thermal decomposition*

Introduction

The decomposition of monoammonium salts has been explained on the basis of the high temperature acid base theory [1–3]. It has been reported that the base strength of the anion increases with the rise in temperature until it reaches the base strength of amine molecule. At this temperature, the anion base removes the proton from the ammonium ion. The work on thermal decomposition of transition metal nitrate and perchlorate complexes [4–6] and various ring-substituted monoammonium nitrates [7–10], perchlorates [11–13], chlorides [14–16], bromides [17, 18] and fluorides [19] have already been reported.

In our earlier studies on preparation and thermal decomposition of sulfate salts [20–24], it was suggested that the sulfate salts decomposes in solid state to ring substituted aminobenzenesulfonic acids which find applications [25, 26] in organic syntheses, dyestuffs, medicines, tanneries and detergents. Studies on ring-substituted diammonium sulfate salts are very meager. Hence, in the light of these findings it was of interest to work on preparation, characterization and thermal decomposition of phenylenediammonium sulfate (PDAS) salts.

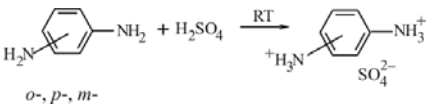
Experimental

Materials

Phenylene-1,2-diamine (Johnson), phenylene-1,4-diamine (sdfine), phenylene-1,3-diamine (Alfa Aesar) were purified by recrystallisation. Sulfuric acid (Ranbaxy), silica gel TLC grade (Merck), $BaCl_2$ (BDH) were used as received.

Preparation and characterization of PDAS

Precipitates of PDAS were obtained by reacting corresponding phenylenediamine (PDA) with conc. H_2SO_4 in 1:1 molar ratio at room temperature (Scheme 1).



Scheme 1

The precipitate were washed twice with ethyl acetate to remove unreacted amine and then recrystallised from distilled water except P-1,4-DAS which was found to dissociate in water, so it was recrystallised from slightly acidic (glc. AcOH) solution. Crystals obtained were vacuum dried. The purity of salts was checked by TLC and their characterization was made by infrared (Perkin Elmer RXI spectrometer), elemental (elemental Vario EL(III) Carlo Erba 1108 instrument), mass (JEOL SX 102/DA-6000 Mass Spectrometer) and gravimetric methods. The physical parameters, TLC, elemental and spectral data are shown in Table 1. All salts were found to decompose during melting point determination.

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1388–6150/$20.00

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Table 1 Physical parameters, TLC, elemental and spectral data of PDAS and DABSA

Compound	Color	R_f	*m.p.*/ decomp.	Yield/ %	IR frequency	*m*/*z*	Element/%		
							C	H	N
P-1,2-DAS	orange flat plates	0.80a:b:c	174 (d)	89	3434 $\upsilon_{NH_3^+}$, 2927.2 υ_{C-H}, 1599.5 δ_{N-H}, 1383 υ_{C-N}, 620, 1115 $\upsilon_{SO_4^{2-}}$	210, 211,171, 107	34.93 (34.95)	5.45 (4.85)	13.19 (13.59)
P-1,3-DAS· 4/3 H_2O	colorless rectangular crystals	0.68a:b:c	219 (d)	96	3421 $\upsilon_{NH_3^+}$, 3136 υ_{C-H}, 1630 δ_{N-H}, 1401 υ_{C-N}, 618, 1119 $\upsilon_{SO_4^{2-}}$	171,165 107	31.90 (31.30)	5.72 (5.21)	11.26 (12.17)
P-1,4-DAS	grey amorphous	0.74a:b:c	159 (d)	80	3424 $\upsilon_{NH_3^+}$, 3208 υ_{C-H}, 1492 δ_{N-H}, 1385 υ_{C-N}, 730, 1120 $\upsilon_{SO_4^{2-}}$	107, 211, 171, 324	35.73 (34.95)	4.70 (4.85)	12.05 (13.59)
3,4-DABSA	light orange amorphous	0.77a:b:c	>300	72	3342 υ_{N-H}, 1505 δ_{N-H}, 1318 υ_{C-N}, 619 υ_{C-S}	81, 107, 120, 211	38.12 (38.29)	4.81 (4.25)	15.03 (14.89)
2,4-DABSA	grey amorphous	0.64a:b:c	>294	79	3335 υ_{N-H}, 1531 δ_{N-H}, 1301 υ_{C-N}, 617.2 υ_{C-S}	81, 95, 123, 120	37.36 (38.29)	5.15 (4.25)	14.11 (14.89)
2,5-DABSA	dirty yellow amorphous	0.72a:b:c	>309	62	3334 υ_{N-H}, 1504.6 δ_{N-H}, 1298 υ_{C-N}, 618 υ_{C-S}	81, 107, 120, 165	40.01 (38.29)	4.78 (4.25)	13.75 (14.89)

R_f – Retention factor; *m.p.* – melting point; *d* – decomposition temperature
Eluent – water:chloroform:*n*-butanol (a:b:c), locating reagent-iodine

Conversion of PDAS to corresponding diaminobenzene sulfonic acids (DABSA)

The samples of phenylene-1,2-diammonium sulfate (P-1,2-DAS), phenylene-1,4-diammonium sulfate (P-1,4-DAS) and phenylene-1,3-diammonium sulfate (P-1,3-DAS) were heated respectively at 230, 170 and 210±2°C in a tube furnace for 20 min under reduced pressure (400±2 mm Hg). Each residue was washed with ethyl acetate, recrystallised from distilled water, then concentrated under vacuum and their purity was checked by TLC. The residue identified, respectively, as 3,4-diaminobenzenesulfonic acid, 2,5-diaminobenzenesulfonic acid and 2,4-diaminobenzenesulfonic acid. The physical parameters, TLC, elemental and spectral data of DABSA are given in Table 1. Moreover, all DABSA gave dye test and effervescences with aq. $NaHCO_3$.

Cross sulfonation studies

The cross sulfonation studies [27–30] were performed by heating each sample of PDAS separately at corresponding temperature with small amount of aniline under vacuum (400±2 mm Hg) for about 20 min. The sulfanilic acid was obtained in each case along with the corresponding sulfonic acid of each salt. It indicates the formation of sulfuric acid and amine molecules in situ and the former might have sulfonated the aniline to form sulfanilic acid.

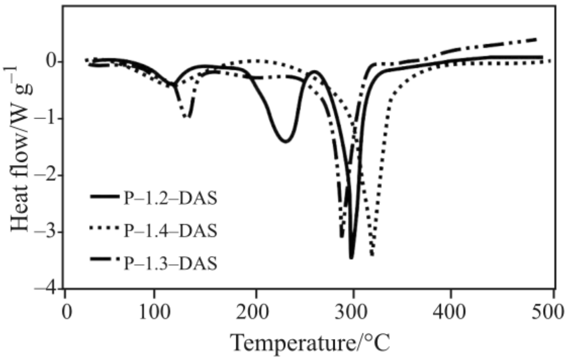


Fig. 1 DSC curves of PDAS in argon atmosphere

Thermal decomposition methods of PDAS

TG/DTG studies

Simultaneous TG/DTG analysis on the PDAS salts has been done by using DuPont 2910 TG instrument at a heating rate of 10°C min^{-1} (sample mass ~5 mg, atmosphere=flowing argon gas at a rate of 60 mL min^{-1}). The curves are shown in Fig. 1 and the phenomenological data are summarized in Table 2.

DSC studies

DSC analysis on the PDAS has been done by using DuPont 2910 DSC instrument at a heating rate of 10°C min^{-1} (sample mass ~4.3 mg, atmosphere=flowing Ar gas at a rate of 40 mL min^{-1}). The DSC thermograms are shown in Fig. 2 and data are summarized in Table 2.

Non-isothermal TG studies

Non-isothermal TG on PDAS (mass 33 mg,100–200 mesh) were undertaken in static air at a heating rate of 10°C min^{-1} using home made TG apparatus [31] fitted with temperature cum controller. The accuracy of the furnace was ±1°C. A round bottom platinum crucible was used as sample holder. The fractional decomposition (α) has been plotted *vs.* temperature (°C) and the curves are given in Fig. 3.

Results and discussion

The C, H, N data (Table 1) confirms beyond doubt the formation of phenylenediammonium sulfate salt. P-1,3-DAS crystal is formed in hydrated form with molecular formula P-1,3-DAS·4/3 H_2O which has also been proved by crystal structure [32] and other two (P-1,2-DAS and P-1,4-DAS) are present in anhydrous form. The IR data (Table 1) shows the bands in the range 3421–3434 cm^{-1} for $\upsilon_{NH_3^+}$, 618–730 and 1115–1120 cm^{-1} for $\upsilon_{SO_4^{2-}}$. Further mass spectra have also confirmed the salt prepared (*m*/*z* 107 is due to the radical by loss of one of the amino H atom of PDA;

Table 2 TG/DTG and DSC profile data of PDAS salts in Ar atmosphere

Compound	TG			DTG peak/°C	DSC peak/°C
	SDT/°C	FDT/°C	Mass/%		
P-1,2-DAS	145	220	9.5^a	210.0	224.0
	260	309	62.1^b	297.1	295.3
P-1,4-DAS	85	178	8.7^a	119.0	117.3
	228	315	53.0^b	305.7	319.9
P-1,3-DAS·4/3H_2O	78	180	18.0^a	112.3	115.0
	230	290	58.0^b	286.4	278.1

SDT – starting decomposition temperature; FDT – final decomposition temperature
a – formation of acid; b – decomposition of acid

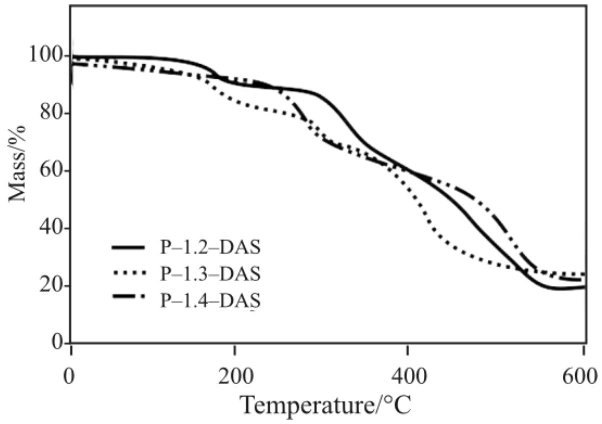


Fig. 2 TG curves of PDAS in argon atmosphere

171 is due to diphenylammonium ion radical and 211 due to dihydroazoamino phenanthrene).

Nonisothermal TG taken in static and inert atmosphere (Figs 1 and 2, Table 2) shows that mass loss occur in two steps for all the three salts. Step 1 is the solid state decomposition of salt to form corresponding acid and step 2 is concerned with the decomposition of acid. For P-1,2-DAS and P-1,4-DAS there is 9.5 and 8.7% mass loss respectively in first step, which clearly indicates that sulfonation is the first step with the release of a molecule of water. However, for the P-1,3-DAS there is 18% mass loss in the first step. This mass loss is due to the evolution of water of crystallization and a water molecule from sulfonation. The plateau in region 232–260°C for P-1,2-DAS, 180–220°C (Scheme 2) for P-1,4-DAS and for 185–225°C P-1,3-DAS·4/3H_2O show the stability of the corresponding DABSA in that particular temperature range. The second step is the decomposition of corresponding DABSA by deamination, desulfonation followed by ring rupture. DTG and

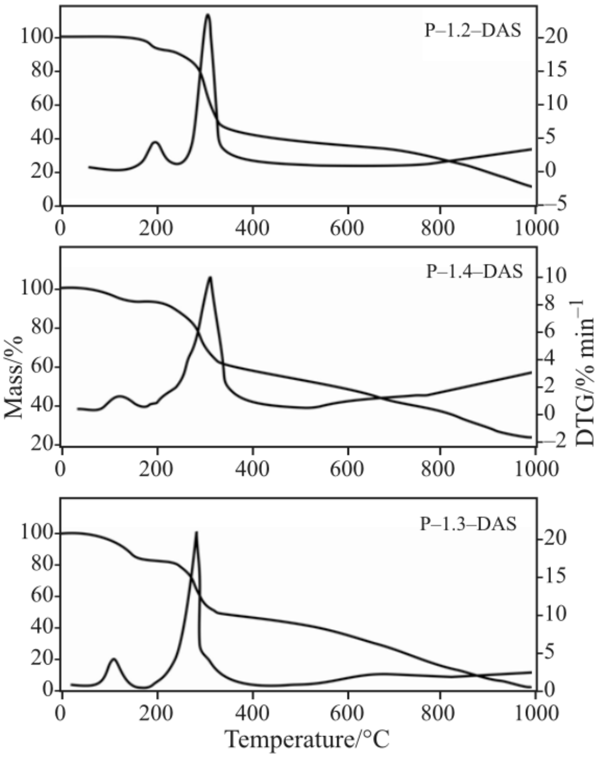
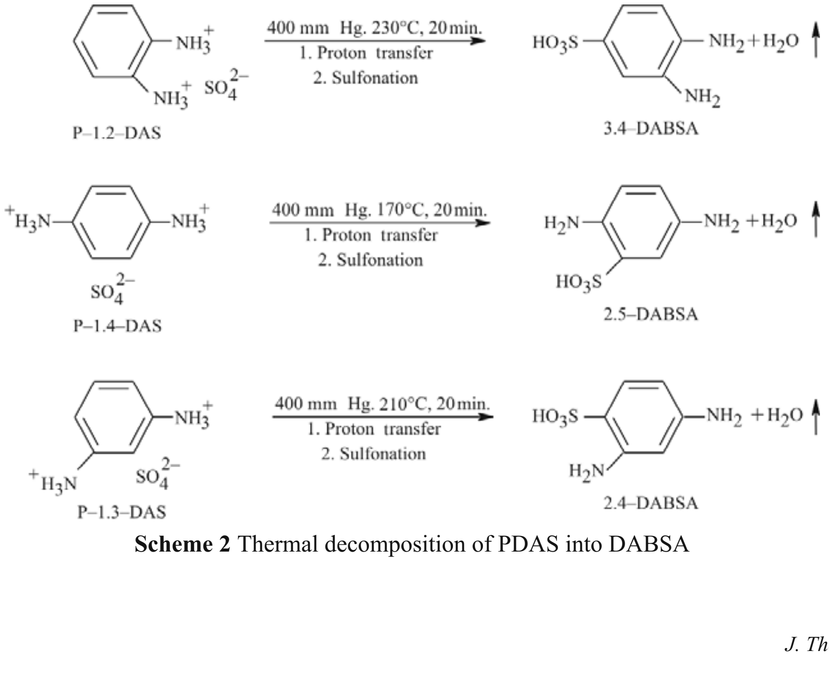


Fig. 3 Non-isothermal TG/DTG curves of PDAS in static air

DSC thermograms (Figs 1 and 2) both show two peaks which also confirm the two-step decomposition. First peak seems to be due to sulfonation process to form corresponding acid and second peak corresponds to the decomposition of DABSA.

It has been reported [1, 2] that the basicity of the anion (SO_4^{2-}) increases with rise in temperature until it reaches the base strength of phenylenediammonium anion to form PDA and H_2SO_4 molecules. Therefore, PDAS salts seem to decompose in solid state to form DABSA (confirmed by C, H, N, IR; υ_{C-S} at



Scheme 2 Thermal decomposition of PDAS into DABSA

617–620 cm^{-1} and mass spectra; *m*/*z* 81 due to –SO_3H Table 1) via proton transfer process prior to sulfonation as illustrated in Scheme 2. It has also proved by cross sulfonation studies.

Conclusions

Thermal decomposition of phenylenediammonium sulfate salt gives diaminobenzenesulfonic acid by proton transfer and a subsequent sulfonation process.

Acknowledgements

The author thanks the University Grants Commission for financial support to one of the author P. Srivastava. We are also thankful to the Head of Chemistry Department, DDU Gorakhpur University for providing laboratory facilities; Dr. D. K. Setua, Joint Director, DMSRDE, Kanpur for TG/DSC and CDRI Lucknow for elemental and spectral analyses.

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Received: September 25, 2007
Accepted: October 16, 2007
OnlineFirst: January 26, 2008

DOI: 10.1007/s10973-007-8786-0