

Sulphonation of arylamines

Part 10: thermal decomposition of di-*ortho*-substituted arylammonium sulphates

Gurdip Singh*, Inder Pal Singh Kapoor, Jyotsna Singh

Department of Chemistry, DDU Gorakhpur University, Gorakhpur 273009, India

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Abstract

Six di-*ortho*-substituted arylammonium sulphates (di-*o*-SAS) have been prepared and characterised. The thermal decomposition of these salts was investigated by TG, DTA and DSC techniques and kinetics evaluated using mechanisms based on the kinetic equations. The parabolic law equation was found to give the best fits based on the correlation coefficients. An activation energy (35–75 kJ mol⁻¹) for the decomposition of di-*o*-SAS was found to be less than dianilinium sulphate (118 kJ mol⁻¹) and the *meta*- and *para*-substituted salts. It seems that the basicity is lowered by steric effects in di-*o*-SAS and the decomposition rates are enhanced. A reaction scheme representing the thermal decomposition pathways of these salts has also been proposed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Di-*ortho*-substituted arylammonium sulphates; Thermal decomposition

1. Introduction

The thermal decomposition studies of various ring-substituted arylammonium nitrates [1–3], perchlorates [4–6], sulphates [7–14] and chlorides [15] have been reported in our earlier publications. It was found that the sulphate salts decompose to ring-substituted aminobenzenesulphonic acids (RSABSA) which find applications in organic syntheses, dyestuffs, medicines and tanneries. Studies on thermal decomposition of di-*ortho*-substituted arylammonium sulphates (di-

o-SAS) are quite meagre and their decomposition pathways have not yet been reported. As a part of our ongoing research programmes, the di-*o*-SAS have been prepared and characterised. The thermal decomposition of these sulphates was undertaken by isothermal and non-isothermal TG, DTA and DSC techniques.

2. Experimental

2.1. Materials

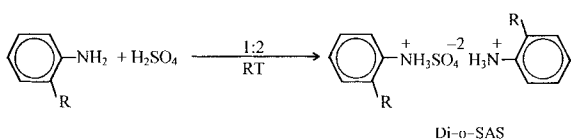
The following LR grade amines were purified according to standard methods. Aniline (Ranbaxy),

*Corresponding author. Tel.: +91-0551-200745; fax: +91-0551-340459
E-mail address: ssdas@ndf.usnl.net.in (G. Singh)

2-methylaniline (Merck), 2-chloroaniline (Ranbaxy), 2-nitroaniline (Johnsons Chemicals), 2-aminobenzoic acid (Central Drug House), Silica gel G TLC grade (Qualigens) and barium chloride (British Drug House) were used as received.

2.2. Preparation and characterisation of the di-*o*-SAS

Di-*o*-SAS were prepared by reacting corresponding arylamine with conc. H_2SO_4 in 1 : 2 molar ratio at room temperature, as follows:



where R = $-\text{CH}_3$, $-\text{Cl}$, $-\text{OC}_2\text{H}_5$, $-\text{OCH}_3$, $-\text{NO}_2$ and $-\text{COOH}$.

All these sulphates were recrystallised from water and concentrated under vacuum at room temperature. The crystals were vacuum dried. Salts having $-\text{NO}_2$ substituents were recrystallised from slightly acidic (glacial acetic acid) solution. Purity of these salts was checked by TLC and their characterisation was made by elemental, gravimetric and spectroscopic analyses. Details of synthesis and characterisation of di-*o*-SAS and their conversion to *o*-SABSA have already been reported in the preceding paper [16].

The thermal decomposition of di-*o*-SAS was investigated by TG, DTA and DSC techniques (Table 1). Isothermal and non-isothermal TG on di-*o*-SAS were carried out on fine powder (30 mg, 200–400 mesh) in static air (Figs. 1 and 2). Non-isothermal TG was undertaken in an inert atmosphere at a heating rate of 10 K min^{-1} (Fig. 3).

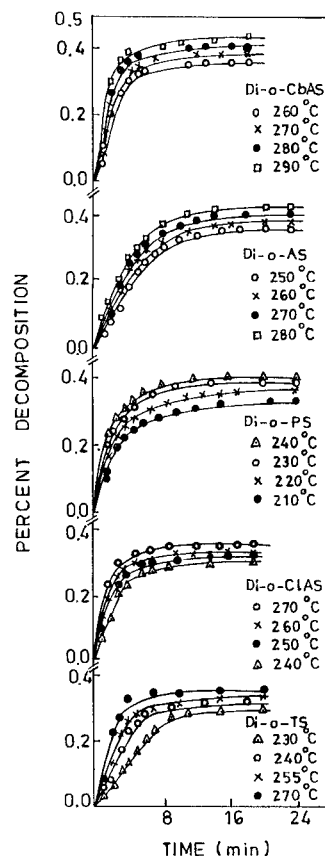


Fig. 1. Isothermal TG curves for di-*o*-SAS in static air.

DTA was carried out in static air using $\sim 10 \text{ mg}$ (200–400 mesh) of the sample at a heating of 10 K min^{-1} and plots are given in Fig. 4. DSC (Mettler) data on all the sulphates were made using $\sim 2 \text{ mg}$ (200–400 mesh) sample at 10 K min^{-1} under nitrogen atmosphere (rate of flow = $45 \text{ cm}^3 \text{ min}^{-1}$) and plots are given in Fig. 5.

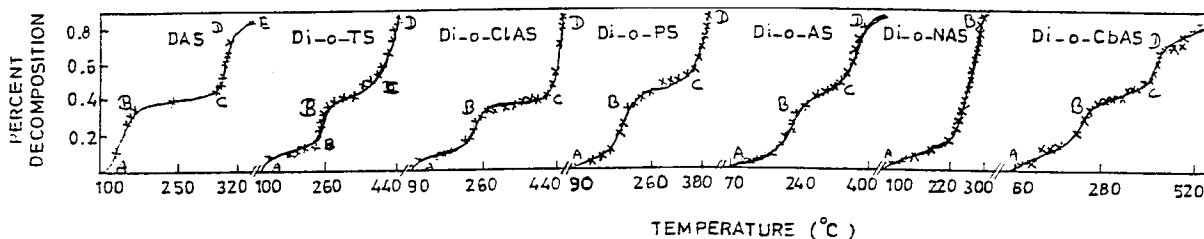
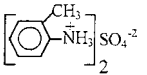
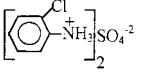
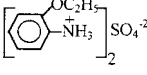
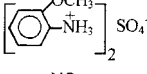
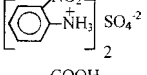
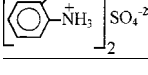


Fig. 2. Non-isothermal TG curves for di-*o*-SAS in static air (heating rate 5 K min^{-1}).

Table 1
Structure and thermal analysis data for di-*o*-SAS

Compound No.	Compound (acronym)	TG		Endothermic peaks (K)				
		Plateau temperature range (K)		DSC		DTA		
		N ₂	Air	I	II	I	II	
	1	2,2'-Dimethyldianilinium sulphate (2,2'-DMeDAS)	403–493	397–506	497	613	475	612
	2	2,2'-Dichlorodianilinium sulphate (2,2'-DCIDAS)	363–488	368–488	454	610	452	610
	3	2,2'-Diethoxydianilinium sulphate (2,2'-DEtDAS)	338–478	338–433	440	563	438	575
	4	2,2'-Dimethoxydianilinium sulphate (2,2'-DMtDAS)	338–478	338–433	440	563	438	575
	5	2,2'-Dinitrodianilinium sulphate (2,2'-D-NtDAS)	–	–	338	552	342	522
	6	2,2'-Dicarboxydianilinium sulphate (2,2'-DCbDAS)	336–488	331–501	454	636	466	628

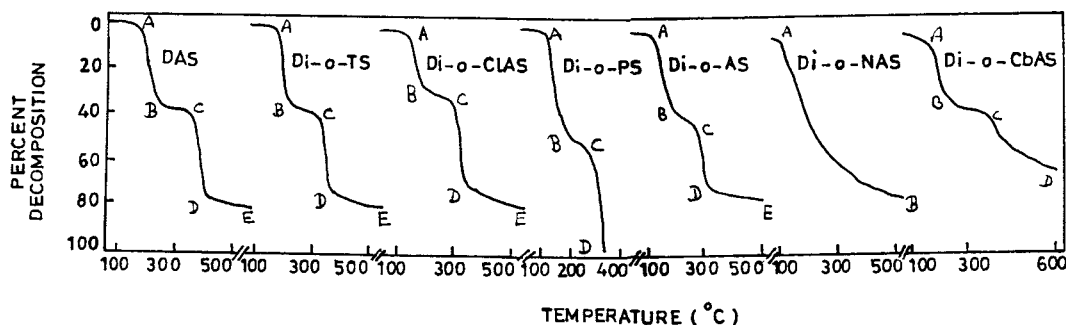


Fig. 3. Non-isothermal TG curves for di-*o*-SAS in an inert atmosphere.

3. Kinetic analysis

The study of reaction kinetics in the solid state is very important to gain information about the kinetic parameters and associated mechanisms of the process. Sestak and Berggren [17] have reported a correlation between reacted fraction (α) and time of reaction (t) usually derived for isothermal studies and variables are given in a complex form of Eq. (1).

$$\alpha = f(V, N, \theta, r, p, t)_T = \text{const}, \quad (1)$$

where V is the reacting volume of material, N the number of nuclei, θ the specific surface, r the geometric factor of particles and p the partial pressure of gaseous products.

They have paid detailed attention to the probable mechanisms of individual cases of solid state reactions expressed in integral forms of kinetic equations given in Table 2. Reaction controlled by the movement of phase boundaries, by nucleation followed by nuclei growth and by diffusion, have also been discussed.

Thus a combined form of differential equation for the preliminary appraisal of the possible mechanism has been suggested.

$$d\alpha/dt = k\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p, \quad (2)$$

where m , n and p are empirically obtained exponent factors and proper combination of them have led mathematical descriptions of majority of [18,19] possible mechanisms (Table 2).

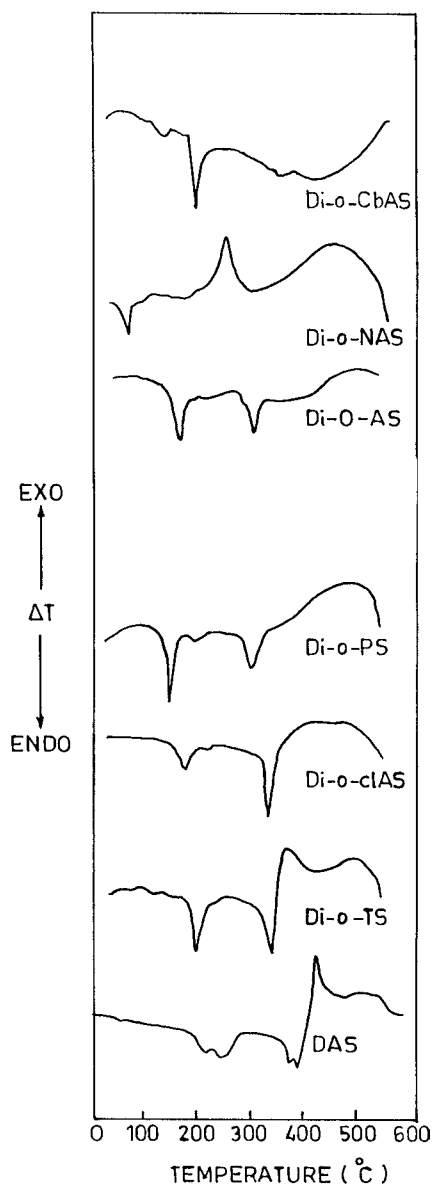
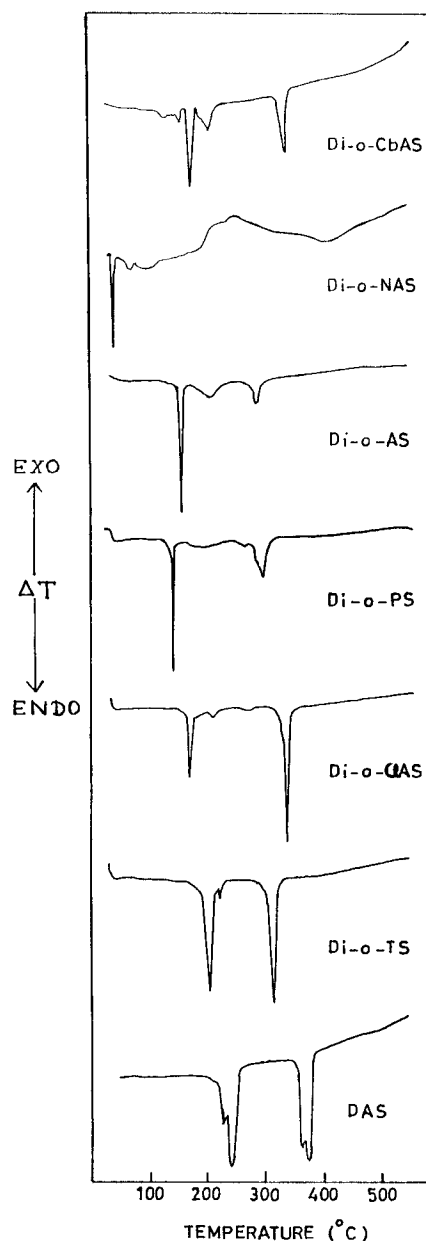
The kinetics of thermal decomposition of di-*o*-SAS (except di-*o*-NtAS) have been evaluated using the equations reported in Table 2 and only parabolic law (D_1 , Eq. (3)) was found to give best fits in temperature range 503–563 K ($\alpha = 0.05$ –0.35):

$$\alpha^2 = kt. \quad (3)$$

The estimated kinetic parameters alongwith the correlation co-efficients (r) are given in Table 3. It seems that sulphonation of di-*o*-SAS is predominantly a diffusion controlled process (Fig. 6).

Table 2
Mechanism based kinetic models

Equation number	Name of function	Form of $g(\alpha)$	Symbol	Rate controlling process
(1)	Parabolic law	α^2	D_1	One-dimensional diffusion
(2)	Valensi (Barrer) equation	$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
(3)	Jander equation	$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion spherical symmetry
(4)	Ginstling–Brounshtein equation	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion spherical symmetry
(5)	Contracting area equation	$1-(1-\alpha)^{1/2}$	R_2	Two-dimensional phase boundary reaction
(6)	Contracting cube equation	$1-(1-\alpha)^{1/3}$	R_3	Three-dimensional phase boundary reaction
(7)	Mampel equation	$-\ln(1-\alpha)$	F_1	First-order reaction
(8)	Avrami–Erofeev equation ($n = 2$)	$[-\ln(1-\alpha)]^{1/2}$	A_2	Random nucleation
(9)	Avrami–Erofeev equation ($n = 3$)	$[-\ln(1-\alpha)]^{1/3}$	A_3	Random nucleation

Fig. 4. DTA thermograms for di-*o*-SAS in air.Fig. 5. DSC thermograms for di-*o*-SAS in an inert atmosphere.

4. Discussion

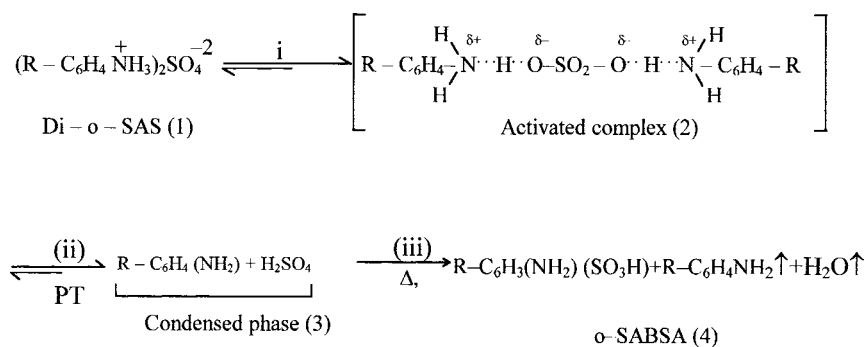
It is clear from the TG plots presented in Figs. 2 and 3 that all di-*o*-SAS (except di-*o*-NtAS) show plateau in various temperature ranges (Table 1), which suggest the formation of *o*-SABSA. It seems that di-*o*-SAS(1) dissociate via an activated complex (2) and corre-

sponding *o*-arylamine and sulphuric acid are formed in condensed phase (3) through proton transfer prior to sulphonation (Fig. 6) [9–12]. The very active H₂SO₄ [20] thus formed would sulphonate the arylamines to *o*-SABSA. The sulphonation does not take place in case of di-*o*-NtAS.

Table 3
Kinetic parameters for thermal decomposition of di-*o*-SAS

Compound Number	Rate constants $\times 10^{-3}$ (temperature, K)				E_a (kJ mol $^{-1}$)	Correlation co-efficient	ln A (min $^{-1} \times 10$)
1	9.80 (503)	18.90 (513)	21.30 (528)	35.00 (548)	68	0.9473	2.9
2	14.60 (513)	16.70 (523)	21.70 (533)	33.30 (543)	68	0.9722	2.9
3	12.50 (483)	15.30 (493)	22.10 (503)	30.00 (513)	62	0.9900 ^a	3.4
4	16.60 (523)	20.00 (533)	23.00 (543)	25.00 (553)	35	0.9933 ^a	2.6
6	22.20 (533)	30.00 (543)	40.00 (553)	53.30 (563)	72	0.9940 ^a	4.5

^a Statistically best fits.



PT – Proton transfer
Sulfn. – Sulfonation

Fig. 6. Schematic representation of thermal decomposition of di-*o*-SAS.

The plateau temperature range for di-*o*-SAS decomposition in N₂ and air atmospheres are reported in Table 1. All di-*o*-SAS (except di-*o*-NtAS) showed two endotherms (see DTA and DSC; Figs. 4 and 5, respectively). First endotherm may be due to formation of *o*-SABSA via sulphonation. The broad endotherm (II peak) may be due to the subsequent oxidative decomposition of *o*-SABSA by deamination, desulphonation and ring rupture. A brownish/black residue was observed in TG crucible in each case which may be a carbonaceous residue. The activation energies for the decomposition of di-*o*-SAS (35–75 kJ mol $^{-1}$) are less than *meta*- and *para*-substituted dianilinium sulphates (118 kJ mol $^{-1}$) [7]. It is reported [21] that all *ortho*-substituents exert the same kind of effect (base weakening) whether they are electron demanding or donating. Further, the addition of proton to nitrogen atom leads to greater internal strain in cation than in the neutral molecule and hence base weakening occurs

[21]. Although resonance and inductive effects operates in di-*o*-SAS molecules but proton transfer reactions seems to be controlled by steric factors. Thus the E_a values of di-*o*-SAS are less than DAS [7].

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