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Sulfonation of arylamines. Part 6. Thermal decomposition of ring-substituted arylammonium sulfates

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Abstract

Ring-substituted arylammonium sulfates (RSAS) having electron donating or attracting substituents have been prepared and characterized. Thermal decomposition studies were carried out by TG, DTG and DTA techniques. Log k and decomposition temperatures (T_d) were found to have a linear relationship with pK_a values of the corresponding arylamine. Hammett equation gave positive value of p (Hammett substituent constant), which indicates that the decomposition is facilitated by electron demanding substituents. The proton transfer process seems to be the primary rate controlling step in the decomposition of these sulfates. © 1997 Elsevier Science B.V.

Keywords: Hammett equation; Proton transfer; Ring-substituted arylammonium sulfates (RSAS); Thermal decomposition

1. Introduction

The nitrogen base salts of inorganic acid, such as nitric and perchloric acids, find applications in explosive mixtures [1,2].In view of the presence of both oxidant and fuel in the same molecule, they have been used in propellant formulations. [1,3]. The thermal decomposition reactions of ring-substituted arylammonium nitrates [4] and perchlorates [5] have been explained by postulating dissociation involving proton transfer as the primary step prior to decomposition. A similar process has also been envisaged in the case of ammonium nitrate [6], ammonium perchlorate [7], ammonium chlorate [8], ammonium iodate [9], methyl-substituted ammonium nitrates [10] and perchlorates [11].

Recently, a number of ring (mono- and di-) substituted ammonium nitrates (RSAN), perchlorates (RSAP) have been prepared and characterized [12–17]. The mechanism of their thermal decomposition leading to ignition/explosion have also been proposed. In the light of these findings, thermal decomposition studies on ring-substituted arylammonium sulfates (RSAS) have been found to be most interesting.

In the present report, the thermal decomposition of RSAS has been investigated in detail, and the kinetic parameters evaluated using nonisothermal equations.

2. Experimental

2.1. Materials

The following LR grade amines were purified according to standard methods [18]; aniline (Ran-

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baxy); *m*-toluidine (Wilson Laboratory); *p*-toluidine (British Drug House); *m*-anisidine (Merck); *m*-nitroaniline (Robert Johnson); and *p*-chloroaniline (Wilson Laboratory). Conc. H_2SO_4 (A.R.) silica gel G, TLC grade (Qualigens) and Barium chloride (British Drug House) were used as received.

2.2. Preparation and characterization of RSAS

RSAS [19–23] were prepared by treating corresponding arylamine with conc. H_2SO_4 in 2 : 1 molar ratio at room temperature and the reaction is as follows:

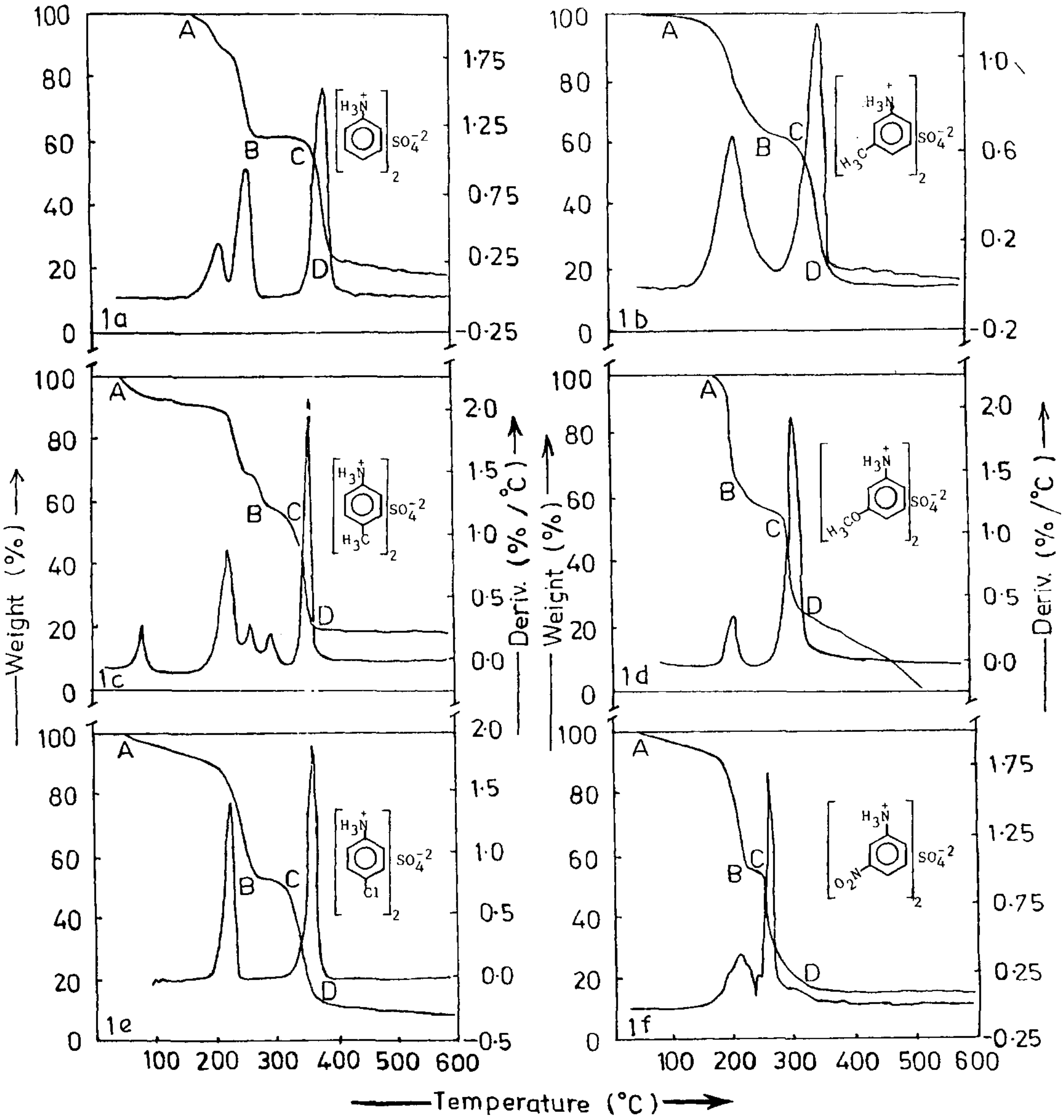

Fig. 1. TG/DTG thermograms of RSAS. (a) – DAS; (b) – *m*-DTS; (c) – *p*-DTS; (d) – *m*-DAS; (e) – *p*-CAS; and (f) *m*-NAS.

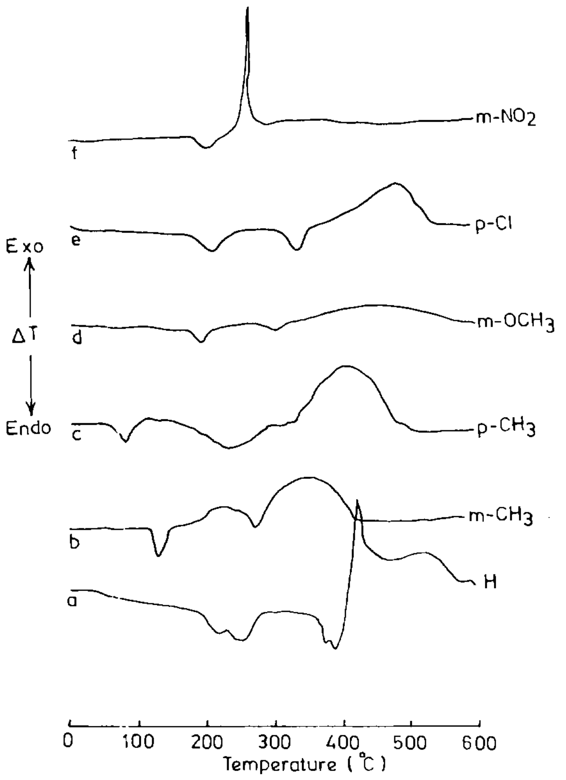

Fig. 2. DTA traces of RSAS. (a) – DAS; (b) – *m*-DTS; (c) – *p*-DTS; (d) – *m*-DAS; (e) – *p*-CAS; and (f) – *m*-NAS.

$$RC_6H_4NH_2 + H_2SO_4 \underset{2:1}{\overset{RT}{\rightarrow}} \underset{RSAS}{(RC_6H_4NH_3^+)_2SO_4^{2-}}$$

where, R = H, *m*-CH_3, *p*-CH_3, *m*-OCH_3, *p*-Cl or *m*-NO_2.

All the sulfate salts were recrystallized from aqueous solutions, concentrated under vacuum at room temperature. The crystals were vacuum dried. Salts having *m*-NO_3 and *p*-Cl substituents were found to dissociate in aqueous solution, and hence these were recrystallized from slightly acidic (glacial acetic acid) solution. Their purity was checked by TLC. These sulfates were characterized by molecular weight determination, elemental, gravimetric and spectroscopic analyses and are reported in earlier publications [19–23].

2.3. Thermal decomposition of RSAS

Studies were undertaken using the following conditions.

Table 1
Thermal analysis data for RSAS

S. No.	Compound	TG		DTA		DTG
		Theoretical wt. loss (%)	Observed wt. loss (%)	Endotherm (°C)	Exotherm (°C)	Peak Temperature. (°C)
1.	Dianilinium sulfate (DAS)	39.06	40.0	215, 245	—	215, 260
2.	*m*-Ditoluidinium sulfate (*m*-DTS)	40.06	38.0	130	225	210
3.	*p*-Ditoluidinium sulfate (*p*-DTS)	40.06	40.0	80, (190–290)	—	225, 260, 290
4.	*m*-Dianisidinium sulfate (*m*-DAS)	40.99	37.0	197	—	197
5.	*p*-Chloroanilinium sulfate (*m*-CAS)	41.22	45.0	225	—	225
6.	*m*-Nitroanilinium sulfate (*m*-NAS)	41.71	45.0	220	—	215

2.3.1. *Simultaneous TG/DTG studies*

Simultaneous TG/DTG were taken by Dupont 990 modular thermal analysis system, in conjunction with 951 thermogravimetric analyzer, using 10 mg of powdered sample (200–400 mesh), at a heating rate of 10°C min$^{-1,}$ under a controlled dynamic atmosphere of nitrogen. The data obtained are presented in Fig. 1(a–f).

2.3.2. *DTA studies*

DTA on sulfates were undertaken at a heating rate of 10°C min^{-1} in static air, and the data plotted as shown in Fig. 2(a–f).

Weight loss, exotherm, endotherm and DTG peak temperatures are noted from Figs. 1 and 2, and the values reported in Table 1.

3. Results and discussion

Figs. 1 and 2 show TG/DTG and DTA thermoanalysis of RSAS.The thermal decomposition of the individual sulfate salts are described below:

3.1. *Dianilinium sulfate (DAS)*

TG studies on DAS showed 40% wt. loss (theoretical value 39.08%) in the 180–270°C temperature range (Fig. 1a (A→B)) which confirms the formation of corresponding aminobenzenesulfonic acid (ABSA) described earlier [19,20]. This acid is stable up to 340°C (Fig. 1a(B→C)). Above 340°C, decomposition of ABSA takes place (Fig. 1a(C→D)). DTA (Fig. 2(a)) showed endotherm at 215° and 245°C, which may be due to the thermal decomposition of DAS, to form ABSA. DTG (Fig. 1(a)) showed peaks at 215° and 260°C, which shows that the overall decomposition of DAS proceeds through two steps.

3.2. *m-Ditoluidinium sulfate (m-DTS)*

TG studies on *m*-DTS showed 38% wt. loss (theoretical value 40.06%) in the 125–280°C temperature range (Fig. 1b(A→B)). Methylaminobenzenesulfonic acid (Me-ABSA) [21] seems to be formed in this temperature range and is stable up to 295°C (Fig. 1-b(B→C)). Above this temperature, the acid undergoes decomposition (Fig. 1b(C→D)). DTA (Fig. 2(b)) showed an endotherm at 130°C and an exotherm at 225°C. DTG (Fig. 1(b)) also showed maxima at 210°C in the same temperature range.

3.3. *p-Ditoluidinium sulfate (p-DTS)*

This salt undergoes thermal decomposition over the 50–300°C temperature range (Fig. 1c(A→B)) and a 40% wt. loss (theoretical value 40.06%) was observed. DTA (Fig. 2(c)) showed an endotherm at 80°C and a broad endotherm between 190° and 290°C. In DTG (Fig. 1(c)), peaks were observed at 80°, 225°, 260° and 290°C. The decomposition of *p*-DTS in the above-mentioned temperature range leads to the formation of methylaminobenzenesulfonic acid (Me-ABSA), [22] which is stable up to 320°C (Fig. 1c(B→C)). Above 320°C, Me-ABSA decomposes (Fig. 1c(C→D)). The overall decomposition of *p*-DTS takes place through several steps which has been discussed in detail in our earlier publication [22].

3.4. *m-Dianisidinium sulfate (m-DAS)*

m-DAS undergo 38% wt. loss (theoretical value 41%) in the 180–215°C temperature range (Fig. 1-d(A→B)). An endotherm in DTA (Fig. 2(d)) and a peak in DTG (Fig. 1(d)) were observed at ~200°C. A 38% wt. loss corresponds to the formation of methoxyaminobenzenesulfonic acid (MeO-ABSA) [23]. A plateau in TG curve (210–280°C) (Fig. 1d(B→C)) shows the stability of MeO-ABSA, and above 280°C (Fig. 1d(C→D)) MeO-ABSA starts decomposing.

3.5. *p-Chloroanilinium sulfate (p-CAS)*

p-CAS showed 45% wt. loss (theoretical value 41.2%) over the 50–255°C temperature range (Fig. 1-e(A→B)), which is also accompanied by an endotherm (Fig. 2(e)) and a DTG (Fig. 1(e)) peak at 225°C. The overall decomposition of *p*-CAS leads to the formation of chloroaminobenzenesulfonic acid (Cl-ABSA), confirmed by elemental and spectral data, which is stable up to 315°C (Fig. 1e(B→C)). Above 315°C (Fig. 1e(C→D)), the decomposition of Cl-ABSA takes place.

3.6. *m-Nitroanilinium sulfate (m-NAS)*

Thermal decomposition of *m*-NAS shows 45% wt. loss (theoretical value 41.7%) in the 50–220°C temperature range (Fig. 1f(A→B)). An endotherm at 220°C in DTA (Fig. 2(f)) and a maxima at 215°C in DTG curve (Fig. 1(f)) were also observed. All these studies establish the formation of nitroaminobenzenesulfonic acid (NO_2-ABSA), also confirmed by elemental and spectral data, which seems stable between 220° and 250°C (Fig. 1f(B→C)). Above this temperature it decomposes (Fig. 1f(C→D)).

The foregoing description shows that ring-substituted ABSA are formed as intermediates during thermal decomposition of RSAS [21–24]. However, ABSA decomposes further and corresponding DTG and DTA peaks are reported in Fig. 1(a–f) and Fig. 2(a–f) respectively. Hence, detailed kinetic analysis of thermal decomposition of RSAS was undertaken using integral equations, namely, Madhusudanan–Krishnan–Ninan (MKN) [25], MacCallum–Tanner (MCT) [26,27] and Coats–Redfern [28] equations.

The values of activation energies (E_a) and correlation coefficients (r) are represented in Table 2. On the basis of highest correlation coefficient values, MCT (n=1) (Eq. (1)) gave the best fit for the decomposition of DAS, *m*-DTS, *p*-DTS, *m*-DAS and *p*-CAS. However, TG data on *m*-NAS were found to fit in MCT (n=0).

$$\ln g(\alpha) = \ln[AE_a/\Theta R] - 0.485E_a^{0.435} - [0.449 + 0.217E_a] \times 10^3/T \qquad (1)$$

where $g(\alpha) = 1 - (1-\alpha)^{(1-n)}/(1-n)$, Θ the heating rate, E_a the activation energy for decomposition, α the fractional decomposition at time t, and n the order parameter.

Plots of $\ln g(\alpha)$ vs. $1/T$ for kinetic analysis of RSAS are shown in Fig. 3(a–f). Although, E_a were calculated by taking all the points given in Fig. 3(a–f), only a few points have been found to deviate from

Table 2
Correlation coefficient (r) and activation energy (E_a/kcal mol^{-1}) values for the decomposition or RSAS using non-mechanistic equations

Sr. No.	Compound	n=0		n=1		n=1/2		n=2/3	
		r	E_a	r	E_a	r	E_a	r	E_a
Madhusudanan–Krishnan–Ninan equation									
1.	DAS	0.9860	63.98	0.9902	71.01	0.9880	67.26	0.9886	68.72
2.	*m*-DTS	0.9390	44.19	0.9496	49.34	0.9443	46.52	0.9471	47.51
3.	*p*-DTS	0.8144	33.06	0.8420	38.13	0.8269	35.55	0.8319	36.30
4.	*m*-DAS	0.9828	98.01	0.9855	102.73	0.9846	100.42	0.9848	101.56
5.	*p*-CAS	0.9386	31.40	0.9461	36.80	0.9435	33.97	0.9438	34.89
6.	*m*-NAS	0.8927	8.80	0.8849	10.47	0.8886	9.64	0.8851	9.88
MacCallum–Tanner equation									
1.	DAS	0.9885	37.94	0.9923	41.69	0.9904	39.66	0.9906	40.44
2.	*m*-DTS	0.9558	26.73	0.9626	29.54	0.9597	28.02	0.9602	28.62
3.	*p*-DTS	0.8714	20.97	0.8878	23.83	0.8803	22.31	0.8811	22.82
4.	*m*-DAS	0.9849	56.69	0.9862	58.94	0.9859	57.79	0.9850	58.30
5.	*p*-CAS	0.9610	19.73	0.9630	22.59	0.9624	21.11	0.9625	21.62
6.	*m*-NAS	0.9569	6.50	0.9467	7.38	0.9518	6.92	0.9511	7.10
Coats–Redfern equation									
1.	DAS	0.9860	15.30	0.9898	16.83	0.9880	16.09	0.9888	16.30
2.	*m*-DTS	0.9388	10.49	0.9495	11.72	0.9440	11.07	0.9457	11.33
3.	*p*-DTS	0.8094	7.83	0.8382	9.02	0.8249	8.41	0.8298	8.64
4.	*m*-DAS	0.9828	23.37	0.9849	24.52	0.9839	24.12	0.9849	24.04
5.	*p*-CAS	0.9368	7.45	0.9456	8.68	0.9416	8.07	0.9431	8.27
6.	*m*-NAS	0.8900	2.07	0.8790	2.44	0.8847	2.25	0.8832	2.30

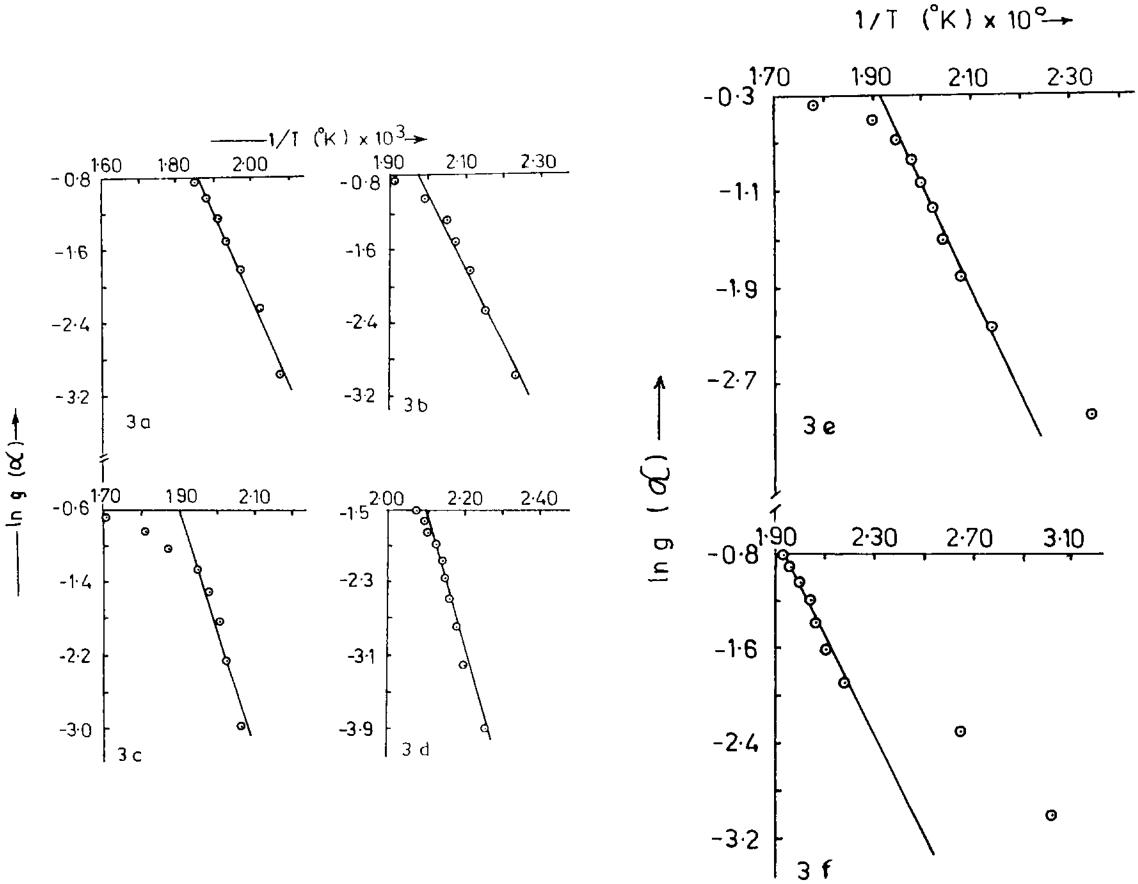

Fig. 3. Kinetics of the thermal decomposition of RSAS by MacCallum–Tanner equation. (a) – DAS; (b) – *m*-DTS; (c) – *p*-DTS; (d) – *m*-DAS; (e) – *p*-CAS; and (f) – *m*-NAS.

linearity (for *p*-DTS, *p*-CAS and *m*-NAS) (Fig. 3(c), (d) and (f)).

E_a values for these sulfates were found to follow the trend

$$m\text{-NAS} < p\text{-CAS} < p\text{-DTS} < m\text{-DTS} < \text{DAS} < m\text{-DAS}.$$

The E_a values for *m*-DTS and *p*-DTS are lower than DAS. This can be explained on account of the electron demanding behavior (–I) of $-CH_3$ group [29–33] which weakens the N–H bond in *m*-DTS and *p*-DTS. However, E_a value for *p*-DTS is less than that for *m*-DTS. It is because of the fact that $-CH_3$ group in the *para* position shows direct hyperconjugative resonance with $-NH_3^+$ group.

The highest value of E_a, i.e. 58.94 kcal/mol has been found for *m*-DAS. This salt shows very peculiar type of behavior. Though, it is found that $-OCH_3$ group generally exhibits a strong –I character, with the absence of resonance effects in *m*-DAS. Higher values can be explained on the basis of intermolecular hydrogen bonding. The E_a values for *p*-CAS and *m*-NAS are lower than DAS, which may be due to strong -I effect of –Cl and $-NO_2$ groups.

The fitting of Hammett equation [34–37] (Eq. (2)) was also tried for the thermolysis of RSAS.

$$\log(k/k_0) = p\sigma \qquad (2)$$

where log (k/k_0) is the relative rate, p the reaction constant and σ the Hammett substituents constant.

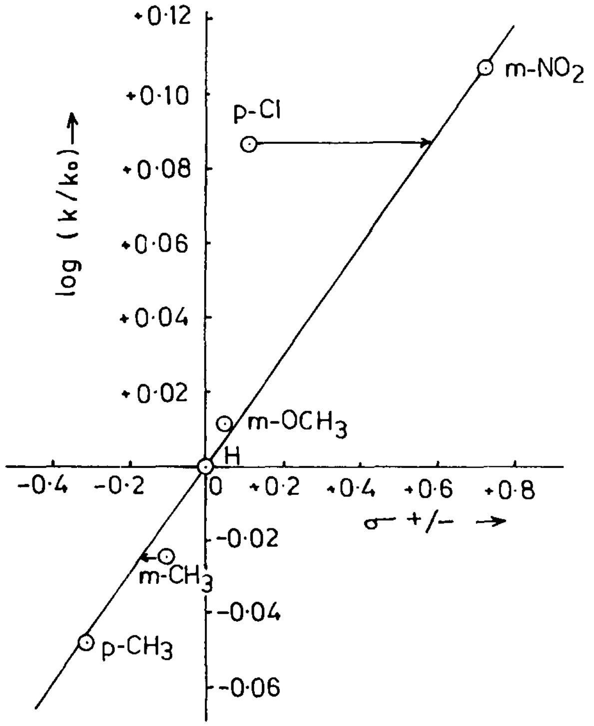

Fig. 4. Hammett plot for the thermal decomposition of RSAS.

The rate constants (k) were calculated from the TG data and log k/k_0 were plotted against $\sigma^{+/-}$ showed linear relationship (Fig. 4), whence it can be inferred that the same mechanism is operating throughout the series. The reaction constant (p), calculated by a least squares method [34,38], was found to be 0.15. The positive value of p indicates [39] that the decomposition is facilitated by electron-demanding substituents. However, p-CAS deviates from linearity which may be due to the large resonance/inductive effects of –Cl group.

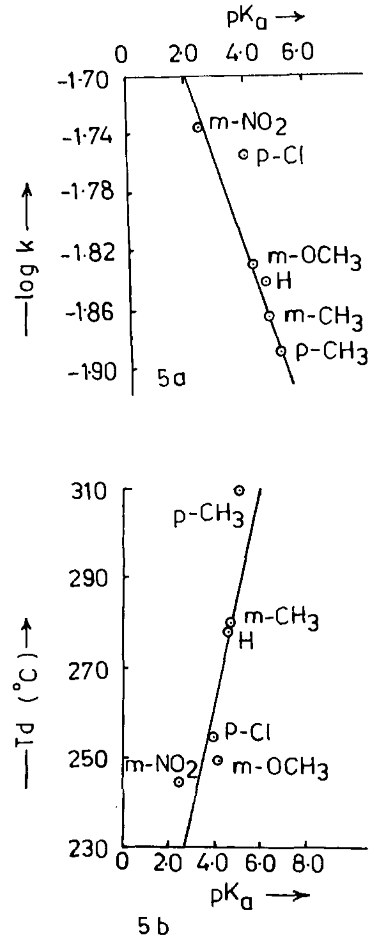

Fig. 5. (a) Log k vs. pK_a plot for RSAS. (b) T_d (°C) vs. pK_a plot for RSAS.

Based on the foregoing discussions, it can be concluded that the proton transfer process is the primary rate-controlling step in the decomposition of sulfates. The pK_a values [40] (Table 3) gave linear plots against

Table 3
Relative rates, Hammett substituents constant (σ), pK_a and decomposition temperature (T_d) of RSAS

S. No.	Compound	log (k/k_0)	$\sigma^{+/-}$	pK_a of the amine	T_d (°C)
1.	DAS	0.0	0.0	4.60	278
2.	m-DTS	−0.025	−0.10	4.71	280
3.	p-DTS	−0.048	−0.31	5.08	310
4.	m-DAS	+0.012	+0.05	4.20	250
5.	p-CAS	+0.087	+0.11	3.99	255
6.	m-NAS	+0.107	+0.73	2.45	245

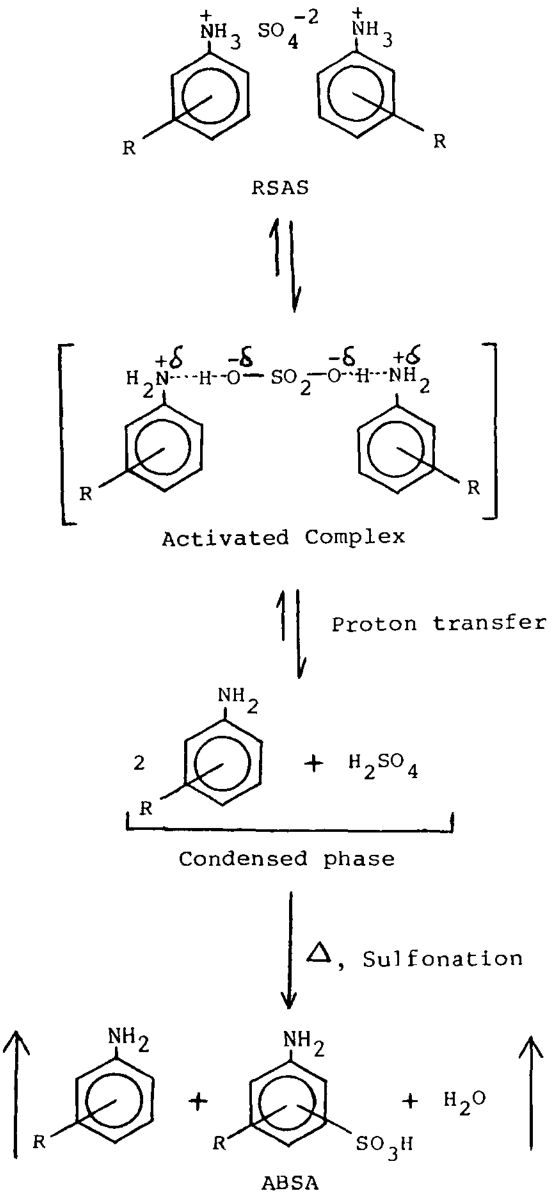

Fig. 6. Schematic representation for the thermal decomposition pathways for RSAS.

log *k* and T_d (°C) which are shown ln Fig. 5(a) and (b). Low pK_a (higher acidity) of the amine causes easy removal of proton from $-NH_3^+$ and, consequently, T_d (°C) will be lowered. All these factors, clearly indicates that thermal stability of sulfates depends upon pK_a values of the corresponding amines. The overall decomposition pathways for RSAS has been summarized in Fig. 6. It seems that RSAS decompose at high temperatures via activated complex and proton transfer to regenerate parent amine and H_2SO_4 molecules. The later than sulfonate corresponding amine to form ABSA. Unreacted amine and water are released vapors [19,21].

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