

## Kinetics of Thermal Decomposition of Dianilinium Sulphate

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The thermal decomposition of arylammonium sulphate (dianilinium sulphate) has been investigated; sulphanilic acid is found to be the decomposition product. The mean value for the energy of activation ( $28.27 \pm 0.46 \text{ kcal mol}^{-1}$ )† for the decomposition has been determined from isothermal TGA data [fitted in the Avrami–Erofeev ( $n = 2, 3$ )], contracting area, contracting cube, and Jacobs–Kureishy equations. Thus, the decomposition of dianilinium sulphate seems to be controlled by a random nucleation process. The results suggest that the primary step (prior to sulphonation) in the decomposition of this salt is a proton-transfer process.

Thermal decomposition of ring-substituted aryl ammonium nitrates<sup>1</sup> and perchlorates<sup>2</sup> has been explained by postulating dissociation involving proton transfer as a primary process prior to decomposition. A similar process has also been envisaged in the case of ammonium nitrate,<sup>3</sup> ammonium perchlorate,<sup>4</sup> ammonium chlorate,<sup>5</sup> ammonium iodate<sup>6</sup> and methyl-substituted ammonium nitrates<sup>7</sup> and perchlorates.<sup>8</sup>

In the light of these findings it was of interest to make a systematic investigation of the thermal decomposition of aryl ammonium sulphates. Such studies are not reported in the literature. The reaction product (a readily precipitated white crystalline solid) of aniline and concentrated sulphuric acid (2:1) at room temperature was isolated and characterized in our laboratory and was found to be dianilinium sulphate (DAS). It was confirmed by molecular weight determination (Beckman method), gravimetric, spectroscopic and elemental analyses. Isothermal TGA studies on DAS were undertaken and data were found to fit the Avrami–Erofeev, contracting area, contracting cube, and Jacobs–Kureishy equations. Kinetic parameters were estimated and activation energy ( $E_a$ ) for the decomposition of DAS to sulphanilic acid was found to be  $28.27 \pm 0.46 \text{ kcal mol}^{-1}$ .

### Experimental

**Materials.**—Aniline (purified by distillation), conc.  $\text{H}_2\text{SO}_4$  (A.R.), silica gel G (for t.l.c. studies) were supplied by Merck; barium chloride (BDH) was used without further purification.

**Preparation and Characterisation of Dianilinium Sulphate.**—A white crystalline precipitate of dianilinium sulphate was obtained immediately at room temperature when aniline and sulphuric acid were mixed in 2:1 molar ratio as previously reported,<sup>9</sup> it was recrystallized from aqueous solution and characterized by molecular weight determination, elemental, gravimetric, and spectroscopic analyses.

The compound was found to decompose without melting (Found: C, 48.80; H, 5.30. Calc. for  $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_4\text{S}$ : C, 50.70; H, 5.63%). Molecular weight and sulphur percentage were found to be 283.7 (calc. 284) and 11.90 (calc. 11.26) respectively. U.v. spectra were taken using a Bausch and Lomb Spectronic 2000 Spectrophotometer,  $\lambda_{\text{max}}$  ( $\text{H}_2\text{O}$ ) 207.9, 230.0, and 281.0 n.m. I.r. spectra were recorded using a Beckman Spectrophotometer  $\nu_{\text{max}}$  3 035br s, 2 860as, 2 560m, 2 080w  $\text{cm}^{-1}$  are due to  $\nu_{\text{NH}}$ ; 1 550as, 1 490as are due to  $\delta_{\text{NH}}$  and 1 080vs due to  $\text{SO}_4^{2-}$  ion.

**TGA Studies on Dianilinium Sulphate.**—Isothermal TGA on dianilinium sulphate (200–400 mesh) was taken at temperatures

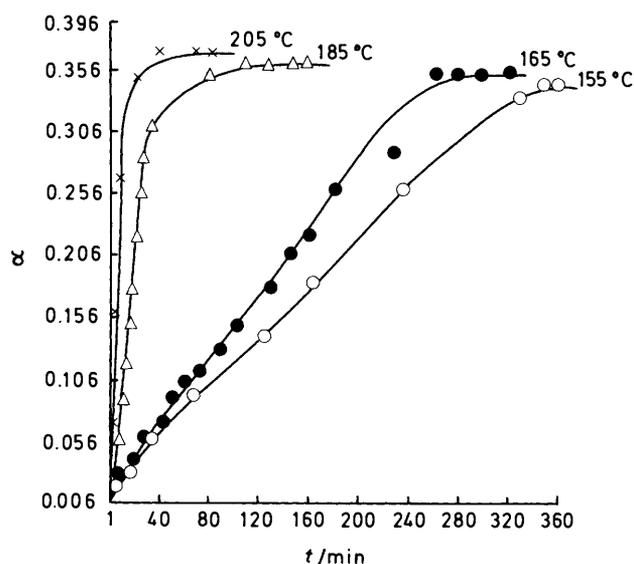


Figure 1. Thermal decomposition of dianilinium sulphate (200–400 mesh), sample weight 30 mg.

155, 165, 185, and 205 °C using an indigenously fabricated TGA apparatus<sup>10</sup> and the data are plotted in Figure 1. The accuracy of the TGA furnace was  $\pm 1$  °C.

### Results and Discussion

Elemental analysis, molecular weight determination, gravimetric, and spectroscopic analyses have proved beyond doubt that dianilinium sulphate is formed when aniline is treated with concentrated  $\text{H}_2\text{SO}_4$  in the ratio of 2:1 at room temperature. I.r. spectra of dianilinium sulphate were found to be identical with the data reported in Ref. 11. Therefore, it was deemed to be of interest to undertake detailed kinetic studies of the thermal decomposition of dianilinium sulphate.

The Avrami–Erofeev equation was used to analyse TGA data (Figures 2 and 3) and proves the contention that the rate-controlling step in dianilinium sulphate decomposition may be random nucleation and growth<sup>12</sup> (these properties being the major concepts used in the derivation of the equation). Over a large period of the decomposition process some of the potential sites ( $N_0$ ) are used up by incorporation in to the

† 1 cal = 4.184 J.

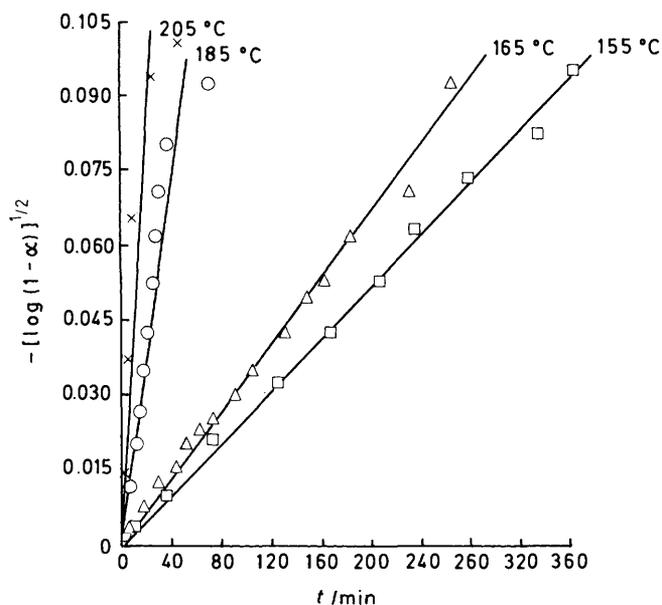


Figure 2. Kinetic analysis of dianilinium sulphate by the Avrami-Erofeev equation ( $n = 2$ ).

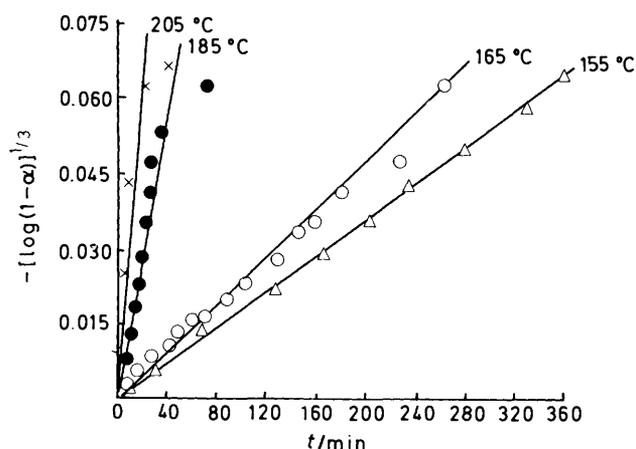


Figure 3. Kinetic analysis of dianilinium sulphate by the Avrami-Erofeev equation ( $n = 3$ ).

growth of other nuclei within close range.<sup>13</sup> However, a considerable simplification was carried out by Avrami<sup>14</sup> in a special case of random nucleation<sup>15</sup> and the following equation was suggested [(equation (1)) where  $\alpha$  = Fraction decomposi-

$$-\ln(1 - \alpha) =$$

$$\frac{6\sigma N_0 k_g^3}{V_0 k^3} \left[ \exp(-kt) - 1 + kt - \frac{(kt)^2}{2} + \frac{(kt)^3}{6} \right] \quad (1)$$

tion,  $\sigma$  = Shape factor,  $N_0$  = Total number of potential nucleus,  $k_g$  = Rate constant for linear growth,  $k$  = Rate constant for nucleus formation,  $V_0$  = Final volume of product after complete decomposition.

When  $t$  is large, equation (1) reduces to equation (2) which is

$$-\ln(1 - \alpha) = k^3 t^3 \times \text{Constant} \quad (2)$$

of the same form as the Erofeev equation<sup>16</sup> derived by a different procedure. Thus a general equation can be written as equation (3) where  $k_1$  is a rate constant.

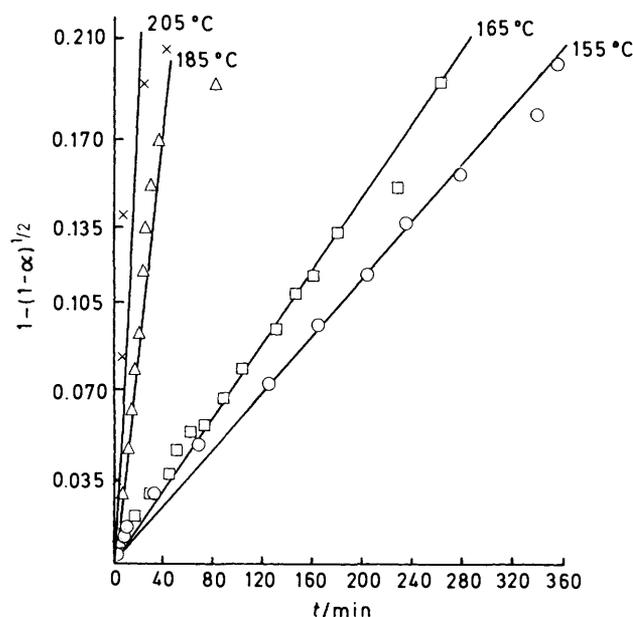


Figure 4. Kinetic analysis of dianilinium sulphate by the contracting-square equation ( $n = 2$ ).

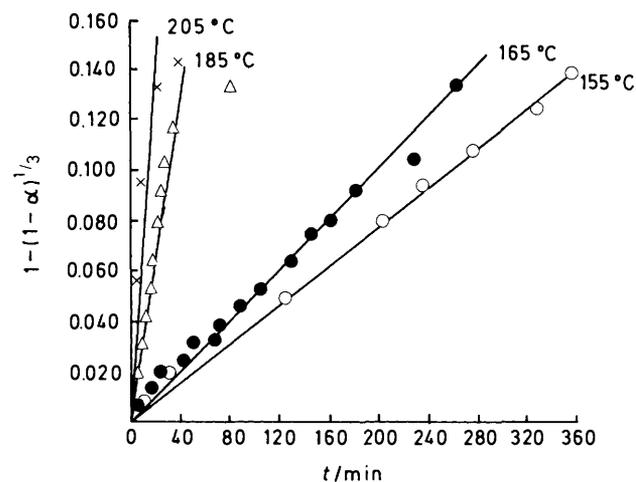


Figure 5. Kinetic analysis of dianilinium sulphate by the contracting-cube equation ( $n = 3$ ).

$$-\ln(1 - \alpha)^{1/n} = k_1 t \quad (3)$$

This equation is termed the Avrami-Erofeev equation and rate constants ( $n = 2$  and  $3$ ) are given in the Table.) TGA data were also found to give best fits for contracting area ( $n = 2$ ) and contracting cube ( $n = 3$ ) equations<sup>12,17</sup> as is clear from Figures 4 and 5, respectively. The theoretical basis of these equations is summarized below.

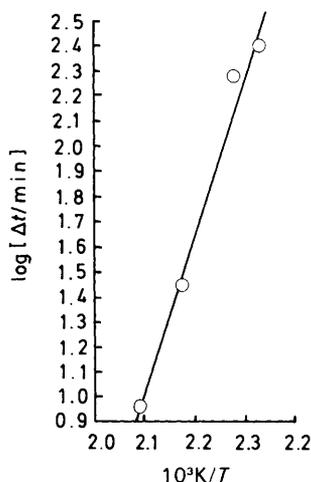
The initial nucleation steps occur rapidly over all surfaces for a single cube of reactant and the interface is established, thereafter, in the direction of the centre of the crystal; the reaction is deceleratory since the reaction interface progressively decreases throughout. If the edges of the initial cube are of length  $x$  then after reaction time  $t$  they would be  $(x - 2k't)$ , it follows that<sup>18</sup>

$$\alpha = \frac{x^3 - (x - 2k't)^3}{x^3}$$

Where  $k'$  is a constant.

**Table.** Kinetic parameters for thermal decomposition of DAS.

Temp/°C	Avrami-Erofeev equation $k_1/10^{-4} \text{ min}^{-1}$		Contracting cube equation $k_2/10^{-4} \text{ min}^{-1}$		Jacobs-Kureishy equation $E_a/\text{kcal mol}^{-1}$
	$n = 3$	$n = 2$	$n = 3$	$n = 2$	
155 ± 1	1.7	2.6	3.82	5.71	
165 ± 1	2.3	3.4	5.37	7.30	
185 ± 1	13.0	19.0	32.50	45.00	
205 ± 1	29.0, 27.91 <sup>a</sup>	42.0, 27.56 <sup>a</sup>	65.00, 28.18 <sup>a</sup>	100.00, 28.74 <sup>a</sup>	28.96

<sup>a</sup>  $E_a/\text{kcal mol}^{-1}$ .**Figure 6.** Plot of  $\log \Delta t$  versus  $1/T$  for decomposition of dianilinium sulphate.

$$\text{or } (1 - \alpha)^{1/3} = 1 - 2k't/x$$

Thus the contracting-cube equation can be written as equation (4) where  $k_2$  is a rate constant and the data are given

$$1 - (1 - \alpha)^{1/3} = k_2 t \quad (4)$$

in the Table. The contracting-area equation was also derived from a model similar to that used for the contracting-cube equation except that it is assumed that the contact area decreases progressively during reaction. Hence, equation (5) where  $k_3$  is a

$$1 - (1 - \alpha)^{1/2} = k_3 t \quad (5)$$

rate constant and the values are given in the Table. The  $E_a$  values for thermal decomposition of dianilinium sulphate have been calculated from Arrhenius plots and data are given in the Table.

The decomposition data were not found to fit the Prout-Tompkins<sup>13,15</sup> equation (6).

$$\log \left( \frac{\alpha}{1 - \alpha} \right) = k_4 t + c_1 \quad (6)$$

Where,  $k_4$  is the rate constant and  $c_1$  is a constant. This equation is based on the chain-branching radical processes which had been described for gas-phase reactions. It may, thus, be inferred that no gas-phase reactions are operative during the decomposition of dianilinium sulphate.

Further, the  $E_a$  value for dianilinium sulphate decomposition

has also been estimated using the Jacobs-Kureishy technique<sup>19</sup> [equation (7)]. The time-interval ( $\Delta t$ ) for 5–30% decomposition

$$\log \Delta t = \frac{E}{2.303RT} + c_2 \quad (7)$$

was determined from Figure 1 and  $\log \Delta t$  was plotted against  $1/T$  (Figure 6), a straight line was obtained, the slope of which gave  $E_a$  (Table). Activation-energy values reported in the Table are almost the same in each case within experimental error. This proves the applicabilities of equations (3), (4), (5), and (7) for the study of the kinetics of dianilinium sulphate decomposition.

Reported in Figure 1, are the results of TGA studies on the formation of sulphanilic acid from dianilinium sulphate in the temperature range of 155–205 °C which account for the fact that 37% weight loss was observed which is comparable with the theoretical value of 39%. One may argue that orthanilic acid may also be formed when dianilinium sulphate is heated at higher temperatures. However, orthanilic acid was not one of the end products. Many workers<sup>20</sup> have also reported that orthanilic acid rearranges to sulphanilic acid at higher temperatures.

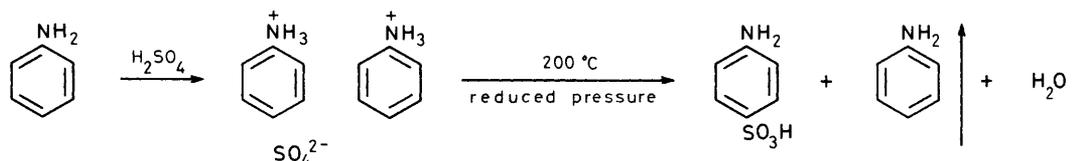
It has also been observed that heating dianilinium sulphate in air at higher temperatures, gave brownish-black products which contains sulphanilic acid. This is presumably due to the formation of quinonoid-like materials arising from hydroxylation, oxidation, and polymerisation of amino compounds. In order to prepare the pure form, it was thought best to remove the aniline, while heating under low pressure which is formed along with sulphanilic acid while heating dianilinium sulphate. Thus, the sample of dianilinium sulphate heated at 200 °C for 1 h at 40 mmHg pressure was found to contain sulphanilic acid. It was confirmed by t.l.c., chemical, and spectroscopic analyses, i.r. spectra of the prepared sample of sulphanilic acid were found to be identical with the data reported in reference 21.

Thus the formation and decomposition of dianilinium sulphate may be illustrated as in Scheme 1. However, some workers have reported<sup>20,22–25</sup> that sulphanilic acid is formed by baking anilinium hydrogensulphate at 190–200 °C. Anilinium hydrogensulphate is obtained as an intermediate in the reaction of aniline with concentrated  $\text{H}_2\text{SO}_4$ .

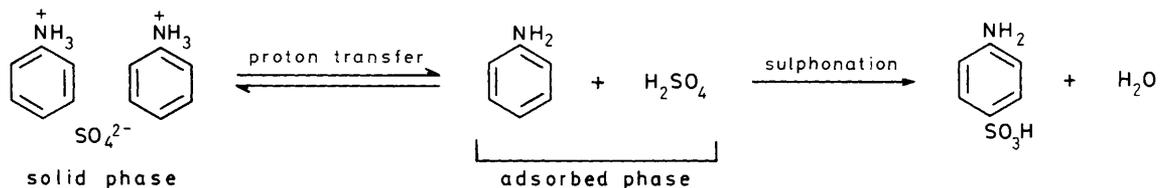
Aniline and water will be given off as vapours at higher temperatures under reduced pressure. In order to confirm the formation of aniline, droplets were collected from the cold, upper side of the sample tube and were found to contain aniline (t.l.c. and chemical analysis). The overall decomposition process seems to commence by the transfer of a proton from an anilinium ion to  $\text{SO}_4^{2-}$  ion, forming aniline and  $\text{H}_2\text{SO}_4$  molecules in the adsorbed state for a finite period prior to sulphonation as illustrated in Scheme 2.

This type of proton transfer in the case of nitrates and perchlorates was also reported by some workers<sup>26,27</sup> which are structurally analogous to the sulphate of aniline.

Dianilinium sulphate, on heating forms sulphanilic acid by a



Scheme 1.



Scheme 2.

sulphonation process whereas anilinium nitrates or perchlorates do not form nitroanilines or perchlorylanilines. Rather nitrate and perchlorate oxidise aniline to other decomposition products. It seems that the sulphonation process is more predominant than the oxidation process when arylammonium sulphates are heated at higher temperatures.

### Conclusions

Dianilinium sulphate is formed when aniline is treated with concentrated  $\text{H}_2\text{SO}_4$ . Thermal decomposition of dianilinium sulphate gives sulphanilic acid by proton transfer and a subsequent sulphonation process. Isothermal TGA data are found to fit the Avrami–Erofeev, contracting area, contracting cube, and Jacobs–Kureishy equations; and a mean value of activation energy  $28.27 \pm 0.46 \text{ kcal mol}^{-1}$  was obtained.

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