

THERMAL DECOMPOSITION KINETICS OF *p*-TOLUENESULPHONAMIDE AND SOME OF ITS N-HALOGENO AND N-METAL DERIVATIVES

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ABSTRACT

The TG, DTG and DTA traces of *p*-toluene sulphonamide, chloramine-T, dichloramine-T, dibromamine-T and the Ag and Hg derivatives of *p*-toluene sulphonamide are given and interpreted. The kinetic parameters (energies and entropies of activation and pre-exponential factors) for the main decomposition stages have been calculated.

INTRODUCTION

The sodium salt of N-monochloro-*p*-toluene sulphonamide, i.e., chloramine-T (hereafter abbreviated as CT) is a well-known oxidimetric titrant¹⁻⁴. N,N-dichloro-*p*-toluene sulphonamide or dichloramine-T (hereafter abbreviated to DCT) has recently been introduced as an oxidimetric titrant in non-aqueous media^{5,6}. We have found that the bromine analogue of dichloramine-T, i.e., dibromamine-T (N,N-dibromo-*p*-toluene sulphonamide (hereafter abbreviated to DBT) may also be conveniently used as an oxidimetric titrant in non-aqueous media⁷. In order to establish optimum drying temperatures for these three oxidants, preliminary thermogravimetric runs were made. Since these gave interesting results and a reference to literature showed that no work has so far been done on the thermal decomposition of these compounds, simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) studies were carried out. The TG curves were also subjected to a mathematical analysis and the kinetic parameters for the thermal decomposition were evaluated. Similar studies were also carried out on *p*-toluene sulphonamide (PTSA) itself and on two of its N-metal derivatives, i.e., the Ag and the Hg derivatives (Ag-PTSA and Hg-PTSA). The results of these studies are reported in this communication.

EXPERIMENTAL

Preparation of the samples

PTSA (BDH, LR) was used as such. Chloramine-T (BDH) was recrystallised

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from distilled water and dried in a vacuum desiccator. Dichloramine-T was prepared as recommended by Nair and Jacob⁵. Dibromamine-T was prepared by adding liquid bromine slowly, with constant stirring, to a 5% aqueous solution of chloramine-T. The pale yellow precipitate obtained was thoroughly washed with water and filtered under suction. It was dried by sucking dry air through it while on the filter for 3 h and keeping it in a vacuum desiccator for 24 h. The purity was checked by elemental analysis for N, S and Br (found: N = 4.28%, S = 9.59%, Br = 48.52%; required: N = 4.26%, S = 9.73%, Br = 48.56%).

The Ag and Hg derivatives of PTSA were prepared by the methods reported in the literature⁸. The purities were checked by elemental analysis for the metal, N and S (Ag-NHSO₂C₆H₄CH₃: found: Ag = 39.07%, N = 5.06%, S = 11.43%; required: Ag = 38.81%, N = 5.04%, S = 11.50%; Hg(NHSO₂C₆H₄CH₃)₂: found: Hg = 36.82%, N = 5.18%, S = 11.69%; required: Hg = 37.08%, N = 5.18%, S = 11.83%).

Apparatus

The apparatus used and experimental conditions employed were the same as those described earlier⁹.

TREATMENT OF DATA

The instrumental TG traces were redrawn as the mass vs. temperature (TG) curves and also as the rate of loss of mass vs. temperature (DTG) curves. The curves were drawn using standard curve sets. The instrumental DTA curves were used as such. The peak temperatures as well as the peak widths in the DTG and DTA curves were noted and compared.

Determination of the order of reaction

The order of reaction n was first determined using the equation suggested by Horowitz and Metzger, i.e.,

$$C_s = n^{(1/1-n)} \quad (1)$$

where n is the order of the reaction, C_s is the weight fraction present at the temperature T_s corresponding to the DTG peak. A 'master curve' was constructed as described earlier⁹ and from the determined value of C_s , n was found out.

Evaluation of kinetic parameters

The Coats-Redfern equation was used in one of the following forms¹⁰, depending on the value of n .

$n \neq 1$:

$$\log \left[\frac{1 - C^{(1-n)}}{(1-n) T^2} \right] = \log \frac{Z R}{\phi E^*} - \frac{E^*}{2.303 RT} \quad (2)$$

$n = 1$:

$$\log \left[\frac{\ln C^{-1}}{T^2} \right] = \log \frac{Z R}{\phi E^*} - \frac{E^*}{2.303 RT} \quad (3)$$

where $C = (W_x - W)/W_x$, Z is the pre-exponential factor, ϕ is the heating rate, E^* the energy of activation, R the gas constant, T the absolute temperature and n the order of the reaction. Plotting the left-hand side expressions of eqns (2) and (3) against $1/T$, straight line graphs were obtained. The slope of this line gives $-E^*/2.303 R$ and the intercept gives $\log Z/\phi \cdot R/E^*$. Thus, E^* was calculated from the slope and knowing E^* , Z was calculated. From the relation,

$$Z = \frac{kT_s}{h} e^{\Delta S^*/R} \quad (4)$$

the entropy of activation ΔS^* was calculated⁹. All the linear plots were drawn by the method of least squares and the corresponding correlation coefficients were also calculated.

RESULTS AND DISCUSSION

The peak temperatures and peak widths in DTG and DTA as well as the plateaus in TG are tabulated in Table 1. The kinetic parameters are given in Table 2. All temperatures are given in °C. Typical TG, DTG and DTA traces are given in Figs. 1-6.

Thermal behaviour

It has been mentioned that, while discussing thermoanalytical data, more significance is to be attached to the temperature ranges (or to the temperature of initiation, T_i and the final temperature, T_f) rather than, to the peak temperatures, T_s , because the latter are dependent on variables such as sample mass, surface area and heating rate^{11,12}. However, since we have carried out simultaneous TG and DTA, we believe that it would be instructive to compare DTG and DTA peaks obtained under *identical* conditions.

PTSA shows a stability plateau in TG up to 220°C and shows only two peaks at 328 and 443°C in DTG. These correspond closely with two exothermic DTA peaks at 326 and 435°C. An additional feature of the DTA curve is the existence of an endothermic peak at 170°C; here no corresponding DTG peak is found. This endothermic peak must therefore represent a phase change, probably melting.

The DTG curve for CT shows four peaks at 122, 201, 274 and 580°C; the DTA peaks are at 140, 207, and 620°C. There is satisfactory correspondence between DTG and DTA as far as the first two peaks are concerned. The first peak represents dehydration temperature, at which the trihydrate passes over to the anhydrous salt. The corresponding DTA peak is endothermic as expected. The most important decomposition peak is the second one. This occurs at 201°C in DTG and at 207°C in

TABLE I

PLATEAUS, PEAKS AND PEAK WIDTHS IN TG, DTG AND DTA CURVES

Abbreviations: exo = exothermic; endo = endothermic; w = weak; m = medium; s = strong; vs = very strong; sh = shoulder; br = broad.

<i>Compound</i>	<i>Plateaus in TG (°C)</i>	<i>Peaks in DTG (°C)</i>	<i>Peak widths in DTG (°C)</i>	<i>Peaks in DTA (°C)</i>	<i>Peak widths in DTA (°C)</i>
1 <i>p</i> -Toluene sulphonamide	upto 220 380-390 after 480	328 vs 443 m	210-380 390-490	170 endo m 326 exo m 435 exo s	150-175 306-336 367-500
2 Chloramine-T	upto 90 130-190 after 730	122 w 201 vs 274 w 580 w	90-140 180-220 230-300	140 endo w 207 exo vs 620 exo w (br)	100-147 200-210 500-640
3 Dichloramine-T	upto 190 after 550	225 s 281 m 332 w 460 m 501 m	200-240 240-300 300-360 440-480 480-540	120 endo w 228 exo s 276 exo w 518 exo m (br)	110-126 190-240 260-290 420-550
4 Dibromamine-T	upto 140 180-240 after 580	172 s 318 m 450 m 490 w 530 s	130-190 270-370 430-470 470-510 510-570	98 endo w 133 exo m 220 exo m 460 exo m 508 exo m	80-100 100-160 160-260 360-500 500-560
5 Ag-NHSO ₂ C ₆ H ₄ CH ₃	upto 260 after 560	331 vs 490 s	230-350 430-530	294 exo m 321 exo w 497 exo vs 542 exo m	280-300 305-340 400-520 520-580
6 Hg(NHSO ₂ C ₆ H ₄ CH ₃) ₂	upto 230 after 530	329 vs 380 w 420 w 487 w (sh)	220-360 360-400 400-440 440-520	254 endo m 331 exo m 397 exo m 460 exo s 478 exo s	230-270 300-370 380-400 400-465 465-530

DTA. The DTA peak here is exothermic. The final residue left after heating upto 750°C was analysed and found to be NaCl. The weight loss expected for this decomposition is 80.83%, in good agreement with the observed weight loss of 80.68%. The higher temperature peaks in DTG and DTA are smaller and may represent oxidative processes involving combustion of the carbonaceous residues.

DCT appears to be stable upto 190°C. The strong DTG peak at 225°C is closely paralalled by a strong exothermic DTA peak at 228°C. This should denote the main decomposition stage because the remaining peaks are weak. It is interesting to note that this strong decomposition peak of DCT lies at a temperature quite near the strong decomposition peak of CT. The weak endothermic DTA peak at 120°C may

TABLE 2
KINETIC PARAMETERS FOR THE DECOMPOSITION STAGES

Compound	Decomposition stage	DTG peak temperature ^a (°C)	Order of reaction, n	Energy of activation, E* (kJ mol ⁻¹)	Pre-exponential factor, Z (cm ³ (g ⁿ⁻¹)mol ⁽¹⁻ⁿ⁾ sec ⁻¹)	Entropy of activation, ΔS* (J K ⁻¹ mol ⁻¹)	Enthalpy terms (kJ mol ⁻¹)	Correlation coefficient, r
1 <i>p</i> -Toluene sulphonamide	First	328 vs	1	127.3	1.217 × 10 ¹⁵	38.07	22.88	0.9993
	Second	443 m	1	250.8	1.209 × 10 ²²	170.6	122.1	0.9979
2 Chloramine-T	First	122 w	1	136.7	3.712 × 10 ²¹	165.7	65.45	0.9945
	Second	201 vs	2	513.2	2.477 × 10 ⁶⁰	907.8	430.3	0.9988
	Third	274 w	2	221.0	3.347 × 10 ²⁴	219.6	120.1	0.9995
3 Dichloramine-T	First	225 s	1	164.0	7.461 × 10 ²⁰	150.4	74.90	0.9874
	Second	281 m	½	552.7	6.615 × 10 ⁵⁶	837.9	464.2	0.9709
4 Dibromamine-T	First	172 s	1	301.3	3.405 × 10 ⁵⁹	515.7	229.5	0.9945
	Second	318 m	3/2	132.9	1.569 × 10 ¹⁵	40.23	23.78	0.9792
5 Ag-NHSO ₂ C ₆ H ₄ CH ₃	First	331 vs	2/3	157.4	2.985 × 10 ¹⁷	83.77	50.60	0.9949
	Second	490 s	2	413.4	6.782 × 10 ³¹	356.7	272.2	0.9915
6 Hg(NHSO ₂ C ₆ H ₄ CH ₃) ₂	First	329 vs	1	131.0	5.755 × 10 ²²	185.0	111.4	0.9840

^a Included to facilitate the identification of the stage.

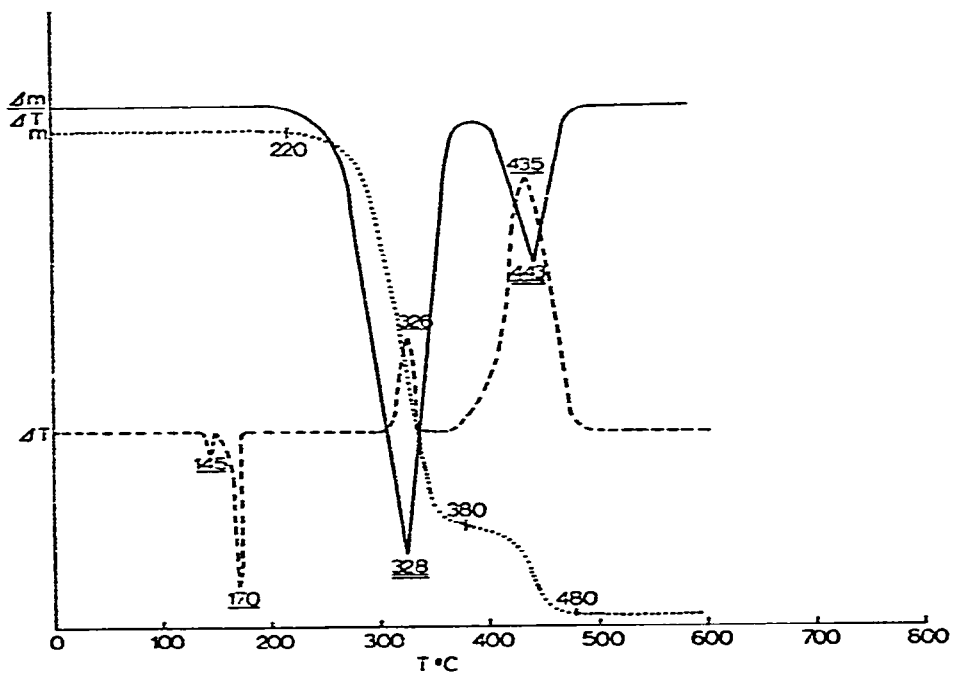


Fig. 1. Thermal decomposition of *p*-toluene sulphonamide., TG curve; —, DTG curve; ---, DTA curve.

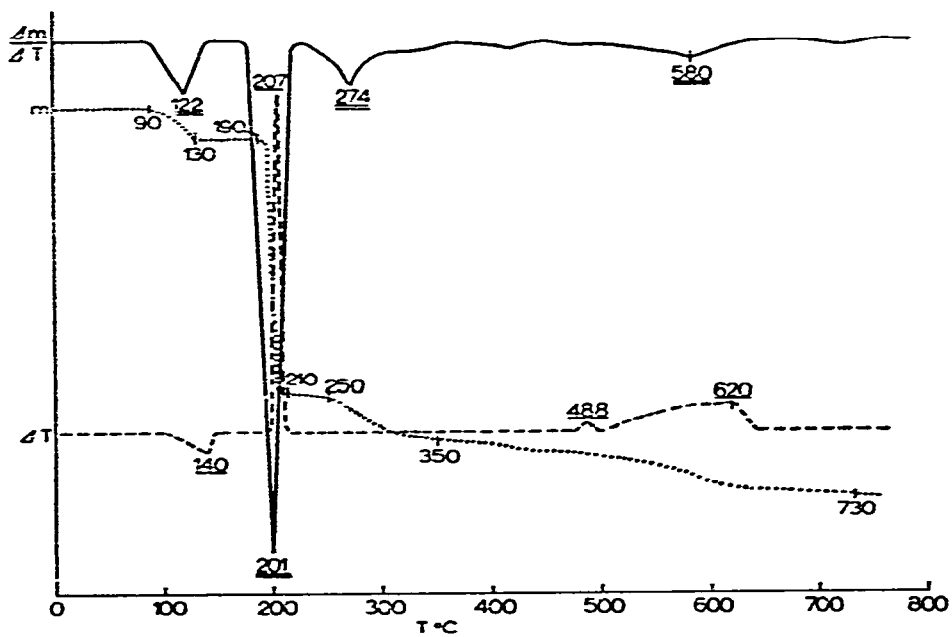


Fig. 2. Thermal decomposition of chloramine-T.

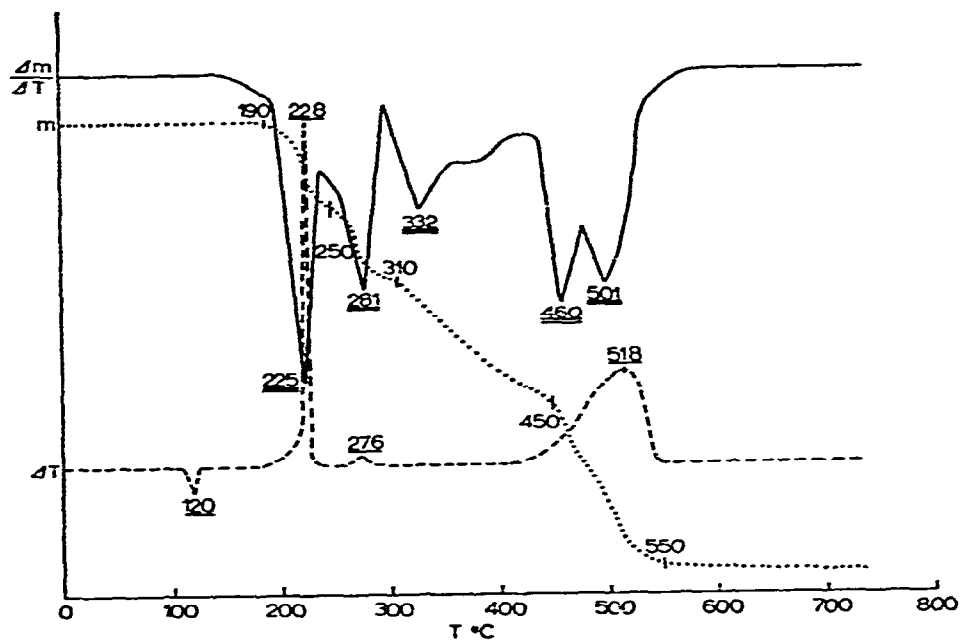


Fig. 3. Thermal decomposition of dichloramine-T.

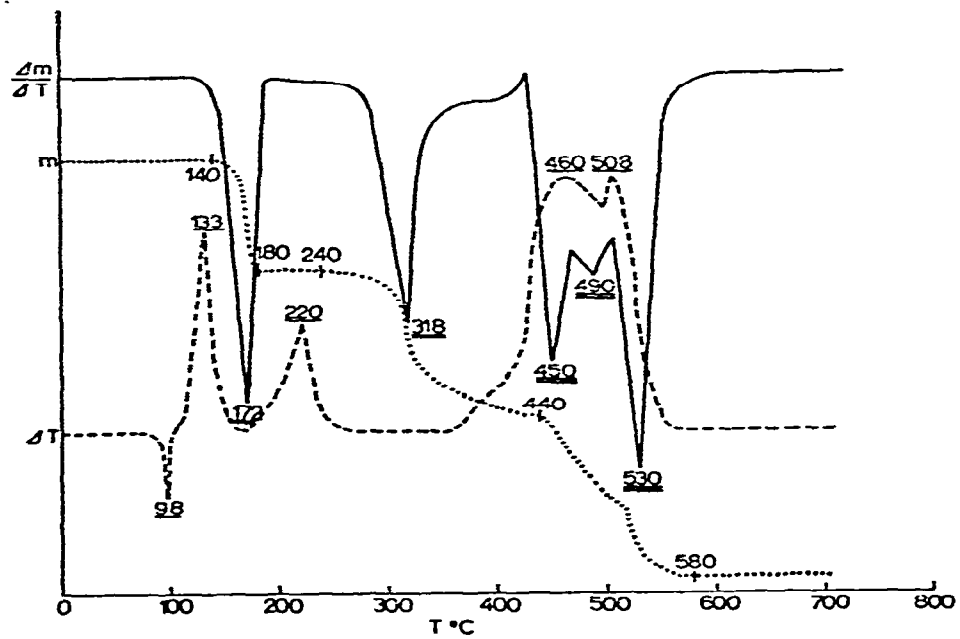


Fig. 4. Thermal decomposition of dibromamine-T.

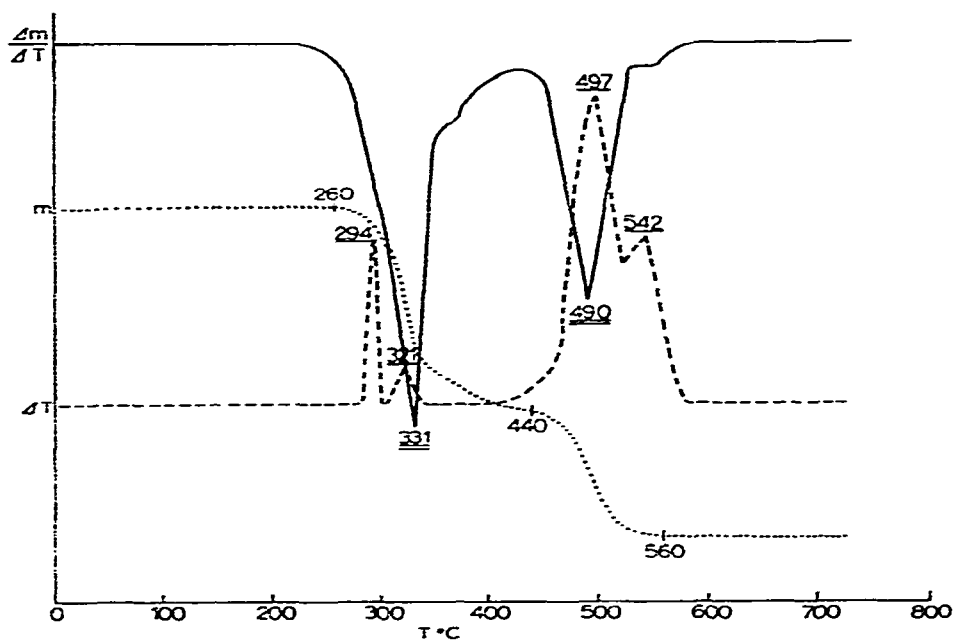


Fig. 5. Thermal decomposition of $\text{Ag-NHSO}_2\text{C}_6\text{H}_4\text{CH}_3$.

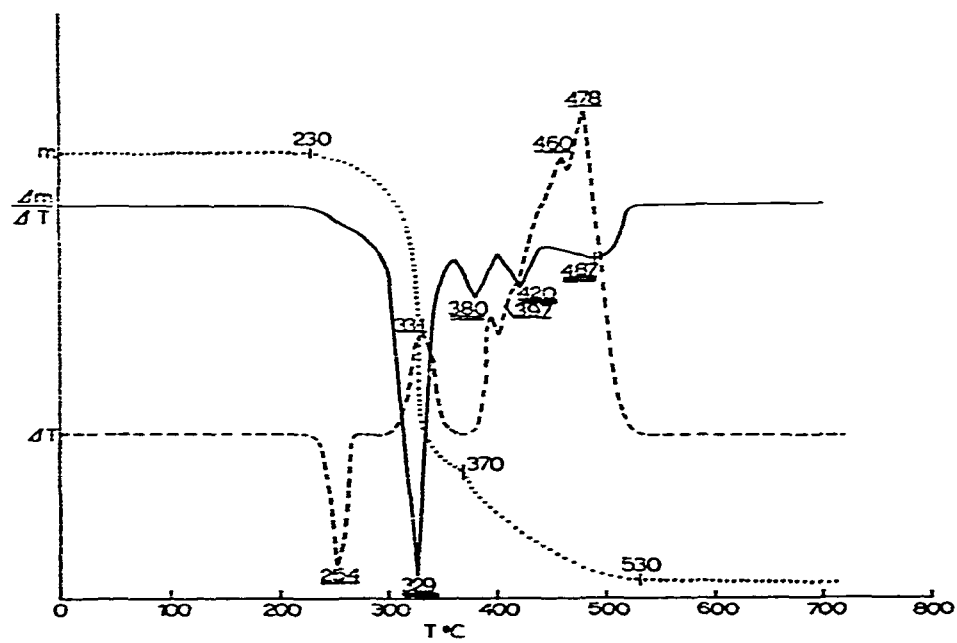


Fig. 6. Thermal decomposition of $\text{Hg}(\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3)_2$.

be attributed to phase changes, probably melting, since there is no parallel peak in DTG. The remaining medium and weak peaks correspond fairly well in DTG and DTA as may be seen from Table 1.

DBT is stable upto 140°C. The weak endothermic peak at 98°C, which has no parallel in DTG, may represent melting. The strong DTG peak at 172°C has no straight parallel in DTA; but there are two DTA peaks, both exothermic at 133 and 220°C. It is possible that the DTG peak at 172°C is an overlap peak of two DTG peaks, corresponding to the above-mentioned DTA peaks. Similar overlaps have been observed¹³ earlier. There is good correspondence between the remaining medium and weak peaks as may be seen from Table 1.

Ag-PTSA is stable upto 260°C, whereas the Hg derivative is stable upto 230°C. The endothermic DTA peak at 254°C for the Hg salt represents melting. An independent experiment to determine the melting points confirmed that the Hg salt melts before decomposing at $\approx 260^\circ\text{C}$, whereas the Ag salt decomposes without melting. The main decomposition temperature of the silver derivative is 331°C in DTG; corresponding to this DTG peak, there are two closely spaced DTA peaks, both exothermic, at 294 and 321°C. The main decomposition peak for the mercury derivative occurs at 329°C (DTG) and 331°C (DTA). The Ag salt shows only one other DTG peak at 490°C (corresponding DTA peak at 497°C), while the Hg salt shows three DTG peaks which have parallels in DTA. The final residue on heating the Ag salt upto 800°C is metallic silver (loss of mass expected theoretically = 61.2%; loss of mass observed = 60.7%) whereas, for the Hg salt, as expected, no residue is left on heating to 800°C.

Decomposition kinetics

The kinetic parameters have been calculated for all the non-overlapping and clear-cut decomposition stages. It may be seen from Table 2 that the order of the first stage decomposition in all the compounds studied except the Ag salt is unity. This stands to reason, because among these six compounds studied, four (DCT, DBT, PTSA and Hg-PTSA) decompose after melting, and hence first-order kinetics are to be expected for decomposition in the liquid state. For CT, the first-stage decomposition represents dehydration. The subsequent decomposition stages sometimes have fractional orders which are not uncommon for solid-state decomposition¹⁴.

The energies of activation all have the same order of magnitude (a few hundreds of kJ mol^{-1}). The satisfactory values of the correlation coefficients indicate good agreement with the experimental data.

Correlations of the energy of activation with the energies of the bonds expected to be broken have been made. It has been remarked that although the energy terms may not always be interpretable in a chemical context, such a view may become tenable while comparing the energy terms of a series of similar compounds¹⁴.

It is therefore of interest to make some similar qualitative correlations in the present case. The high value of E^* for the main decomposition stage of CT may tentatively be attributed to the fact that it is an ionic compound. The bonds expected

to be broken during thermal decomposition of the compounds under the present study and their bond energies¹⁵ in kJ mol^{-1} are: N-Cl = 201, N-S = 230, N-Br = 242, C-S = 259, C-C = 347, N-H = 389 and C-H = 414. While no definite correlations are possible, it is nevertheless interesting to note that the determined values of E^* for the various decomposition stages have the same order of magnitude as the bond energies listed above.

It has been stated that the peak temperatures T_p may be identified as thermodynamic decomposition temperatures¹⁶. On this basis, considering that the free energy change ΔG at this equilibrium temperature can be equated to zero, the Gibbs-Helmholtz equation becomes

$$\Delta H = T_p \Delta S \quad (5)$$

Enthalpy terms have been calculated from eqn (5) and are listed in Table 2 and it may be seen that these have the expected orders of magnitude.

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