Thermochimica Acta, 225 (1993) 43–51
Elsevier Science Publishers B.V., Amsterdam

The thermal investigation of some normal propylammonium salts in the solid state

Samiran Mitra [a,*,1] and Heigrujam Phalguni Singh [b]

[a] *Department of Chemistry, Jadavpur University, Calcutta-700 032 (India)*
[b] *Department of Chemistry, Manipur University, Imphal-795 003 (India)*

(Received 8 January 1993; accepted 24 February 1993)

Abstract

Normal propylammonium salts of general formula $(C_3H_7)_nNH_{4-n}X$, where X is Cl, Br or HSO_4 and n is 1–3, have been synthesised. The purity of the salts was checked by elemental analyses and none of the salts was found to contain free acid or base. Some of the salts are very hygroscopic; they undergo dehydration before decomposition, showing identical endothermic DTA peak(s). The anhydrous salts undergo thermal decomposition leading to total volatilisation. Some of the salts also show phase transition. In some cases, DTA phase transition peaks escape detection because they overlap with DTA dehydration peaks. The activation energy E_a^*, enthalpy change ΔH and entropy change ΔS were evaluated for the dehydration and decomposition reactions of the salts, using some standard methods. A linear correlation between the values of E_a^* and ΔS for the decomposition reaction of the salts was observed. The order of stability of the salts with respect to E_a^* and the number of propyl groups is also given.

INTRODUCTION

Alkylammonium salts are the very simple salt-like derivatives of amines. Although a number of properties of these compounds have been reported, a literature survey shows that the thermodynamics and kinetics of their decomposition processes have been studied in less detail [1–5]. In this study, the thermal investigations of the substituted *n*-propylammonium salts of chloride, bromide and bisulphate have been studied by TG and DTA, and the activation energy E_a^*, enthalpy change ΔH and entropy change ΔS parameters are evaluated. Such data are of interest in examining the trends and variations of thermodynamic parameters with respect to reaction path. Some useful conclusions related to the activation energy E_a^* and the number of alkyl groups n present in the salts have been drawn, and

* Corresponding author.
[1] Former address: Department of Chemistry, Manipur University, Imphal-795 003, India.

a correlation between $E_a^\star$ and ΔS for the decomposition reactions of the salts has been observed.

EXPERIMENTAL

Materials and methods

Acids of AnalaR grade were used as received. Analar grade *n*-propylamine, *n*-dipropylamine and *n*-tripropylamine (Merck, Germany) were used as received. Ethanol was dried by a standard procedure [6].

Preparation of the salts

n-Propylammonium salts of general formulae $(C_3H_7)_nNH_{4-n}X$ where X is Cl, Br or HSO_4 and $n = 1–3$, were synthesised by neutralising the amine with the corresponding acid. The resulting white precipitates were filtered, recrystallised, dried and stored in a desiccator over P_4O_{10}. Carbon, hydrogen and nitrogen were determined using a Carlo Erba 1106 elemental analyser; results are given in Table 1. The thermal investigation (TG and DTA) was carried out on a Shimadzu DT-30 thermal analyser in dynamic nitrogen at a heating rate of 10°C Min^{-1}. α-Al_2O_3 was used as a reference standard. The activation energy $E_a^\star$ for the dehydration and decomposition reactions of the salts were calculated from the TG curves using the equation of Horowitz and Metzger [7], and from the DTA curves using that of Borchardt and Daniels [8]. The enthalpy change ΔH was evaluated from the DTA curves using the relation $\Delta H = KA$ [8], where K is the heat transfer coefficient (the calibration or cell constant); the cell used was a platinum crucible and its constant K was evaluated from the data obtained

TABLE 1

Analytical data (calculated values in parentheses) of normal mono, di- and tripropylammonium salts

No.	Salts	Colour	Analytical (%)		
			C	H	N
1	$C_3H_7NH_3Cl \cdot H_2O$	White	31.25 (31.71)	10.42 (10.57)	12.10 (12.33)
2	$C_3H_7NH_3Br \cdot H_2O$	White	22.71 (22.78)	7.24 (7.59)	8.52 (8.56)
3	$C_3H_7NH_3HSO_4 \cdot 2H_2O$	White	20.51 (20.57)	7.32 (7.43)	8.22 (8.00)
4	$(C_3H_7)_2NH_2Cl$	White	51.63 (52.36)	11.59 (11.64)	9.97 (10.18)
5	$(C_3H_7)_2NH_2Br$	White	39.50 (39.56)	8.72 (8.79)	7.60 (7.62)
6	$(C_3H_7)_2NH_2HSO_4 \cdot 2H_2O$	White	30.11 (30.64)	8.61 (8.94)	5.49 (5.96)
7	$(C_3H_7)_3NHCl \cdot 2H_2O$	White	50.01 (50.12)	12.10 (12.06)	6.43 (6.50)
8	$(C_3H_7)_3NHBr$	White	48.03 (48.21)	9.58 (9.82)	6.04 (6.25)
9	$(C_3H_7)_3NHHSO_4 \cdot 2H_2O$	White	38.90 (38.99)	9.61 (9.75)	5.00 (5.05)

using indium metal as a calibrant. The parameter A represents the total area under a particular DTA peak, measured using a compensating planimeter (Fuji Corona 027).

The entropy change ΔS was calculated using the relation $\Delta S = \Delta H/T_m$, where T_m is the DTA peak temperature in kelvin.

RESULTS AND DISCUSSION

$C_3H_7NH_3Cl \cdot H_2O$ (1), $(C_3H_7)_2NH_2Cl$ (4) and $(C_3H_7)_3NHCl \cdot 2H_2O$ (7)

The chloride salts of normal mono-, di- and tripropylamine are white crystalline solids. The salts (1) and (7) have water of crystallisation, which was confirmed by IR spectral data and the mass loss on the TG curves. The absorbed moisture is not responsible for the hygroscopic nature of the salts, because the dehydration takes place in the ranges 45–120 and 55–130°C for salts (1) and (7), respectively. Salt (1) has a melting point at 120°C, which overlaps with the dehydration peak; this was confirmed visually in a melting point bath. Just after dehydration and before decomposition, the DTA curve shows a sharp peak at 150°C (Fig. 1) which may be due to some phase transition. After the phase transition, there is total volatilisation in the range 153–284°C showing a single endothermic peak at 270°C (Fig. 1). The activation energy evaluated from the TG and DTA curves is 119 and 132 kJ mol^{-1}, respectively. The enthalpy and entropy changes were also evaluated and the values are 52 kJ mol^{-1} and 96 J K mol^{-1}, respectively.

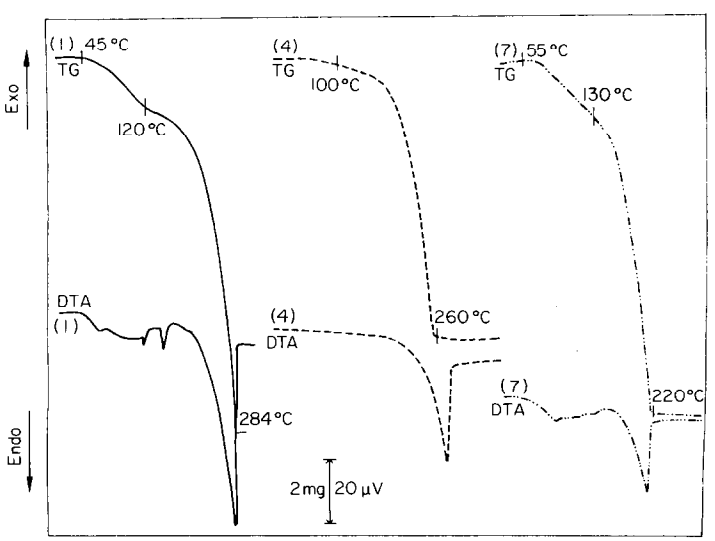

Fig. 1. Thermal curves of: $C_3H_7NH_3Cl \cdot H_2O$ (1) (——), sample mass 10.2 mg; $(C_3H_7)_2NH_2Cl$ (4) (– – –), sample mass 8.6 mg; and $(C_3H_7)_3NHCl \cdot 2H_2O$ (7) (– · · –), sample mass 10.8 mg.

Salt (4) has no water of crystallisation and does not show any endothermic melting peak before decomposition. It decomposes completely between 100 and 260°C, and the corresponding DTA peak appears at 260°C. The activation energy values obtained from the TG and DTA curves are 79 and 156 kJ mol^{-1}, respectively. The enthalpy and entropy changes for the corresponding step are 51 kJ mol^{-1} and 90 J K^{-1} mol^{-1} respectively.

Salt (7) contains two molecules of water of crystallisation and, on heating, it loses the water molecules between 55 and 130°C. The melting point which is confirmed visually at 130°C, may overlap with the dehydration peak. The anhydrous salt undergoes total volatilisation between 130 and 220°C. The corresponding DTA peak is endothermic and appears at 215°C. The activation energy values for the decomposition have been obtained from the TG and DTA curves as 88 and 99 kJ mol^{-1}, respectively. The enthalpy and entropy changes for the corresponding step have also been evaluated and are given in Table 2.

$(C_3H_7)NH_3Br \cdot H_2O$ (2), $(C_3H_7)_2NH_2Br$ (5) and $(C_3H_7)_3NHBr$ (8)

All these salts are white. Salt (2) contains one molecule of water of crystallisation, confirmed by IR spectral data and the mass loss in the TG curve in the temperature range 40–170°C. The DTA peak for the dehydration is endothermic and shows multiple peaks. Just after dehydration it shows a sharp endothermic peak at 172°C which may be due to some phase transition as no mass loss is found in the TG curve in this region. On further heating, it undergoes total volatilisation in the temperature range 175–318°C. The corresponding DTA peak is endothermic, at 310°C. The peak for melting merges with the decomposition peak and is apparent at 204°C. The activation energy for decomposition was evaluated and the values are 114 and 131 kJ mol^{-1} from the TG and DTA curves, respectively. The ΔH and ΔS values for this step are 49 kJ mol^{-1} and 84 J K^{-1} mol^{-1} respectively.

The salt $(C_3H_7)_2NH_2Br$ (5) has no water of crystallisation. Before decomposition begins, the salt melts and a sharp endothermic peak appears at 250°C. This peak is due to melting, as confirmed visually. It then instantaneously undergoes decomposition in two steps in the ranges 250–288 and 288–325°C. This is confirmed in the TG curve (Fig. 2). But the corresponding DTA curve shows only one peak at 310°C. The activation energy was evaluated from the TG and DTA curves and the values are given in Table 2. The overall ΔH and ΔS values were also determined as 58 kJ mol^{-1} and 99 J K^{-1} mol^{-1}, respectively.

The salt $(C_3H_7)_3NHBr$ (8) is a white crystalline solid with no water of crystallisation. On heating, the salt undergoes total volatilisation in a single step between 85 and 298°C, as observed in the TG curve. The DTA curve shows two peaks, one relatively small at 180°C, and the other relatively

TABLE 2

Thermal parameters of normal mono-, di- and tripropylammonium salts

No.	Compounds	Dehydration/ decomposition	Temperature of DTA peak/°C		Tempera- ture range/°C	DTA peak tempera- ture/ °C	E_a^*/(kJ mol^{-1})		ΔH/(kJ mol^{-1})	ΔS/(J K^{-1} mol^{-1})
			Phase transition	Melting			TG	DTA		
1	$C_3H_7NH_3Cl \cdot H_2O$	Dehydration	150	120	45–120	45	–	–	–	–
	$C_3H_7NH_3Cl$	Decomposition	–	–	153–284	270	119	132	52	96
2	$C_3H_7NH_3Br \cdot H_2O$	Dehydration	172	–	40–170	50, 110	–	–	–	–
	$C_3H_7NH_3Br$	Decomposition	–	204	175–318	310	114	131	49	84
3	$C_3H_7NH_3HSO_4 \cdot 2H_2O$	Dehydration	–	90	28–120	60	–	–	–	–
	$C_3H_7NH_3HSO_4$	Decomposition	–	–	160–270	225	73	–	–	–
				–	270–319	295	180	194	55	108
4	$(C_3H_7)_2NH_2Cl$	Decomposition	–	–	100–260	260	79	156	51	90
5	$(C_3H_7)_2NH_2Br$	Decomposition	–	250	250–288		125			
					288–325	310	250	–	58	99
6	$(C_3H_7)_2NH_2 \cdot HSO_4 \cdot 2H_2O$	Dehydration			30–110	60	–	193	59	102
					110–260	135	36	–	–	–
	$(C_3H_7)_2NH_2HSO_4$	Decomposition			260–325	304	332	–	–	–
7	$(C_3H_7)_3NHCl \cdot 2H_2O$	Dehydration	–	–	50–130	60, 130	–	–	–	–
	$(C_3H_7)_3NHCl$	Decomposition	–	–	130–220	215	88	99	52	107
8	$(C_3H_7)_3NHBr$	Decomposition	–	180	85–298	285	109	113	68	122
9	$(C_3H_7)_3NHHSO_4 \cdot 2H_2O$	Dehydration and decomposition	–	–	28–201	95, 175	78	110	78	174

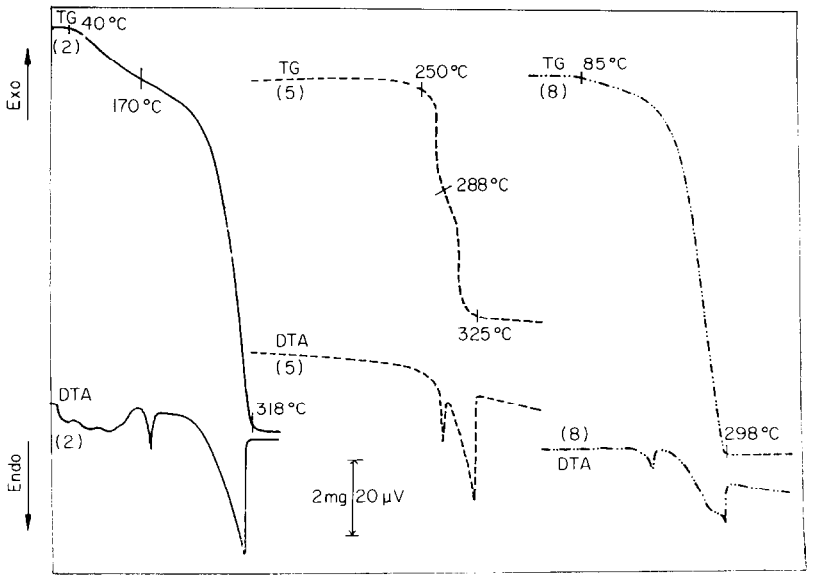

Fig. 2. Thermal curves of: $C_3H_7NH_3Br \cdot H_2O$ (2) (——), sample mass 9.2 mg; $(C_3H_7)_2NH_2Br$ (5) (– – –), sample mass 6.4 mg; and $(C_3H_7)_3NHBr$ (8) (– · · –), sample mass 10.1 mg.

large at 285°C. The first peak corresponds to melting and the second peak represents the decomposition of the salt. The activation energy values determined from the TG and DTA curves are 109 and 113 kJ mol^{-1}, respectively. The values of ΔH and ΔS are also given in Table 2 for the first and second steps of decomposition.

$(C_3H_7)NH_3HSO_4 \cdot 2H_2O$ (3), $(C_3H_7)_2NH_2HSO_4 \cdot 2H_2O$ (6) and $(C_3H_7)_3NHHSO_4 \cdot 2H_2O$ (9)

The salts (3), (6) and (9) are white crystalline solids, and each contains two molecules of water of crystallisation; this was confirmed by IR spectral data and from the mass losses on the TG curves.

On heating, the salt $(C_3H_7)NH_3HSO_4 \cdot 2H_2O$ (3) loses two molecules of water of crystallisation between 28 and 120°C. The corresponding DTA curve shows an endothermic peak at 60°C (Fig. 3). The melting point of the salt was determined in a melting point bath as 90°C. The decomposition follows the dehydration and occurs in two steps in the ranges 160–270°C and 270–319°C. The same kind of decomposition is reflected in the DTA curve, with the corresponding peaks appearing at 225 and 295°C. The values of E_a^*, ΔH and ΔS for the dehydration and decomposition steps were calculated and are presented in Table 2.

The salt $(C_3H_7)_2NH_2HSO_4 \cdot 2H_2O$ (6) loses two molecules of water in the range 30–110°C on heating, and the corresponding DTA peak appears at

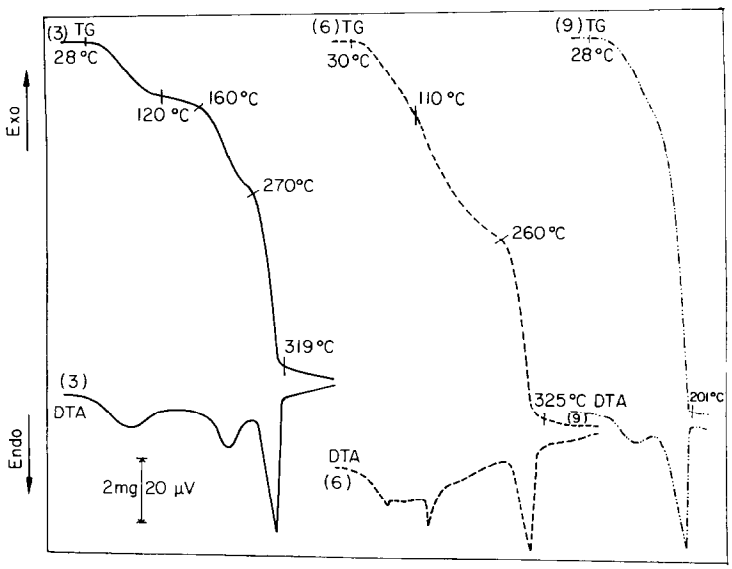

Fig. 3. Thermal curves of: $C_3H_7NH_3HSO_4 \cdot 2H_2O$ (3) (——), sample mass 8.2 mg; $(C_3H_7)_2NH_2HSO_4 \cdot 2H_2O$ (6) (– – –), sample mass 9.8 mg; and $(C_3H_7)_3$ $NHHSO_4 \cdot 2H_2O$ (9) (– · · –), sample mass 11.4 mg.

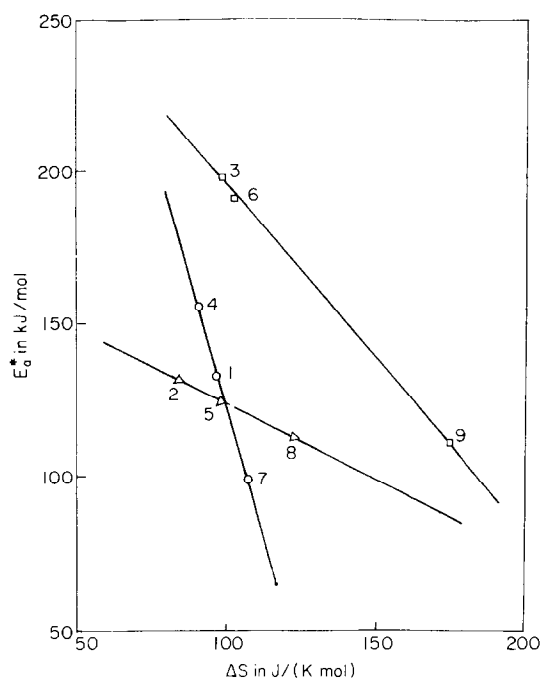

Fig. 4. Plots of the values of $E_a^{\ddagger}$ versus ΔS for the decomposition of: ○, $C_3H_7NH_3Cl$ (1), $(C_3H_7)_2NH_2Cl$ (4) and $(C_3H_7)_3NHCl$ (7); △, $C_3H_7NH_3Br$ (2), $(C_3H_7)_2NH_2Br$ (5) and $(C_3H_7)_3NHBr$ (8); and □, $C_3H_7NH_3HSO_4$ (3), $(C_3H_7)_2NH_2HSO_4$ (6) and $(C_3H_7)_3NHHSO_4$ (9).

60°C (Fig. 3). The anhydrous salt then undergoes complete volatilisation in two steps in the ranges 110–260 and 260–325°C. The peaks for dehydration and the first decomposition step are partially overlapping. The DTA peaks for the first and second steps of decomposition appear at 135 and 304°C, respectively.

The activation energies were evaluated from the TG and DTA curves for the first and second steps of decomposition and are given in Table 2, together with the values of ΔH and ΔS for the same steps.

On heating, the salt $(C_3H_7)_3NHHSO_4 \cdot 2H_2O$ (9) loses two molecules of water. The DTA curve shows one endothermic peak at 95°C but the thermogravimetric curve shows that the dehydration and decomposition occurs in a single step in the range 28–201°C and the DTA peak appears at 175°C. The activation energy, and the enthalpy and entropy changes have been calculated and are shown in Table 2.

Plots of the values of E_a^* versus ΔS (Fig. 4) show a linear relationship for the decomposition of the salts. This indicates that a system with a higher entropy change will require less energy for its decomposition [9].

When the values of E_a^* are plotted against the number of propyl groups n, the stability of the salts follows the trend $(C_3H_7)_3NHX < (C_3H_7)NH_3X < (C_3H_7)_2NH_2X$ where X is Cl, Br or HSO_4 (Fig. 5). It may be

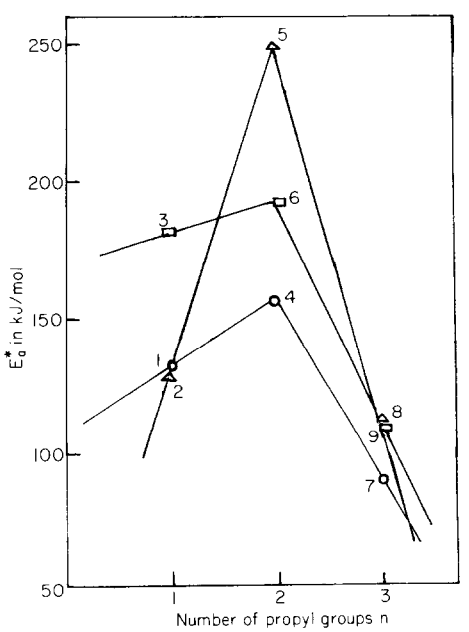

Fig. 5. Plots of the values of E_a^* versus number of propyl groups (n) for the thermal decomposition of: ○, $C_3H_7NH_3Cl$ (1), $(C_3H_7)_2NH_2Cl$ (4) and $(C_3H_7)_3NHCl$ (7); △, $C_3H_7NH_3Br$ (2), $(C_3H_7)_2NH_2Br$ (5) and $(C_3H_7)_3NHBr$ (8); and □, $C_3H_7NH_3HSO_4$ (3), $(C_3H_7)_2NH_2HSO_4$ (6) and $(C_3H_7)_3NHHSO_4$ (9).

suggested that dipropylammonium salts are the most stable among the three, where as tripropylammonium salts are less stable than the monopropylammonium salts, due to the crowdedness of the propyl groups which introduces steric factors [10].

ACKNOWLEDGEMENTS

The authors thank the Department of Chemistry, Manipur University, Imphal 795003, India for providing the laboratory facilities and C.D.R.I., Lucknow, India for elemental analyses.

REFERENCES

1 J. Blazejowaki, Thermochim. Acta, 68 (1983) 233.
2 J. Blazejowaki and E. Kowalewaka, Thermochim. Acta, 92 (1985) 811.
3 H. Ishida, R. Ikeda and D. Nakamura, J. Phys. Chem., 86 (1982) 1003.
4 G. Singh and I.P.S. Kapoor, J. Chem. Soc. Perkin Trans., (1980) 11.
5 S.R. Jain, M.V. Rao and V.R.P. Verneker, Proc. Indian Acad. Sci., Sect. A, 87 (1978) 31.
6 A Text Book of Practical Organic Chemistry, ELBS and Longmans, London, 4th edn., 1980, p. 272.
7 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
8 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
9 S. Mitra and L.K. Singh, J. Chem. Soc. Dalton Trans., (1987) 2089.
10 I.L. Finar, Organic Chemistry, Vol. 1, ELBS and Longmans, London, 6th edn., 1982, pp. 373, 374.