

Thermal investigation of some ethylammonium salts in the solid state.

Part I

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(Received 19 July 1991)

Abstract

Ethylammonium salts of general formula $(C_2H_5)_nNH_{4-n}X$ (where X represents Cl, Br or HSO_4 and $n = 1-3$) have been synthesised. The purity of the salts was checked by elemental analyses. None of the salts was found to contain free acid or base. The anhydrous white crystalline salts are stable up to their melting points and undergo thermal decomposition leading to total volatilisation. The activation energy (E_a^*), enthalpy change (ΔH) and entropy change (ΔS) were calculated for each step of the decomposition reaction of the salts by using some standard methods. In some cases phase transitions were also noticed. A linear correlation between E_a^* and ΔS was noted for the decomposition reaction of the salts. The stability order of the salts with respect to E_a^* followed the trend $C_2H_5NH_3X < (C_2H_5)_3NHX < (C_2H_5)_2NH_2X$. The probable mechanistic paths of the decomposition reactions are proposed.

INTRODUCTION

Alkylammonium salts are the simplest salt-like derivatives of amines. Although a number of properties of these compounds are known, a literature survey showed that the thermodynamics and kinetics of the processes have been studied in less detail [1–5]. The thermodynamic and kinetic parameters for the substituted ethylammonium salts of chloride, bromide and bisulphate have been studied using TG and DTA. Such data are of interest in the examination of the trends and variations of the thermodynamic parameters such as activation energy (E_a^*), enthalpy change (ΔH) and entropy change (ΔS). Attempts have also been made to correlate E_a^* with the number of alkyl groups (n) present in the salts, and a correlation between E_a^* and ΔS for the decomposition reactions of the salts has been found.

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EXPERIMENTAL

Materials and methods

Acids of AnalaR grade were used as received. AnalaR grade ethylamine (Fluka, AG, Switzerland), diethylamine (SD's Lab., Bombay, India) and triethylamine (Ferah, Berlin, Germany) were used. Ethanol was dried using the standard procedure [6].

Preparation of the salts

Ethylammonium salts of general formula $(C_2H_5)_nNH_{4-n}X$ where $X = Cl, Br$ or HSO_4 and $n = 1-3$, were synthesised by neutralising the ethyl-, diethyl- or triethylamine with the corresponding acids. The resulting white precipitates were filtered, recrystallised, dried and stored in a vacuum desiccator over phosphorus pentoxide. Carbon, hydrogen and nitrogen were estimated using a Carlo Erba 1106 elemental analyser. The results of the elemental analyses are given in Table 1. Thermal investigations (TG and DTA) were carried out on a Shimadzu DT-30 thermal analyser in dynamic nitrogen at a heating rate of $10^\circ C \text{ min}^{-1}$; $\alpha-Al_2O_3$ was used as a standard reference substance. The activation energy (E_a^*) for the decomposition reactions of the salts was 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 $\Delta H = KA$, where K is the heat transfer coefficient [8] (calibration or cell constant). The cell used was a platinum crucible and its constant K was evaluated from the data obtained using indium metal as a calibrant and the total area A under the particular DTA

TABLE 1

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

No.	Salts	Colour	Analysis (%)		
			C	H	N
1	$C_2H_5NH_3Cl$	White	29.49 (29.45)	9.82 (9.82)	17.20 (17.18)
2	$C_2H_5NH_3Br$	White	19.08 (19.05)	6.38 (6.35)	11.17 (11.11)
3	$C_2H_5NH_3HSO_4$	White	16.81 (16.78)	6.25 (6.29)	9.97 (9.79)
4	$(C_2H_5)_2NH_2Cl$	White	43.81 (43.83)	10.99 (10.96)	12.81 (12.79)
5	$(C_2H_5)_2NH_2Br$	White	31.20 (31.17)	7.82 (7.79)	9.13 (9.09)
6	$(C_2H_5)_2NH_2HSO_4$	White	28.12 (28.07)	7.76 (7.60)	8.25 (8.19)
7	$(C_2H_5)_3NHCl$	White	52.41 (52.36)	11.71 (11.63)	10.16 (10.18)
8	$(C_2H_5)_3NHBr$	White	39.41 (39.56)	8.73 (8.79)	7.75 (7.69)
9	$(C_2H_5)_3NHHSO_4$	White	36.21 (36.18)	8.59 (8.54)	7.08 (7.04)

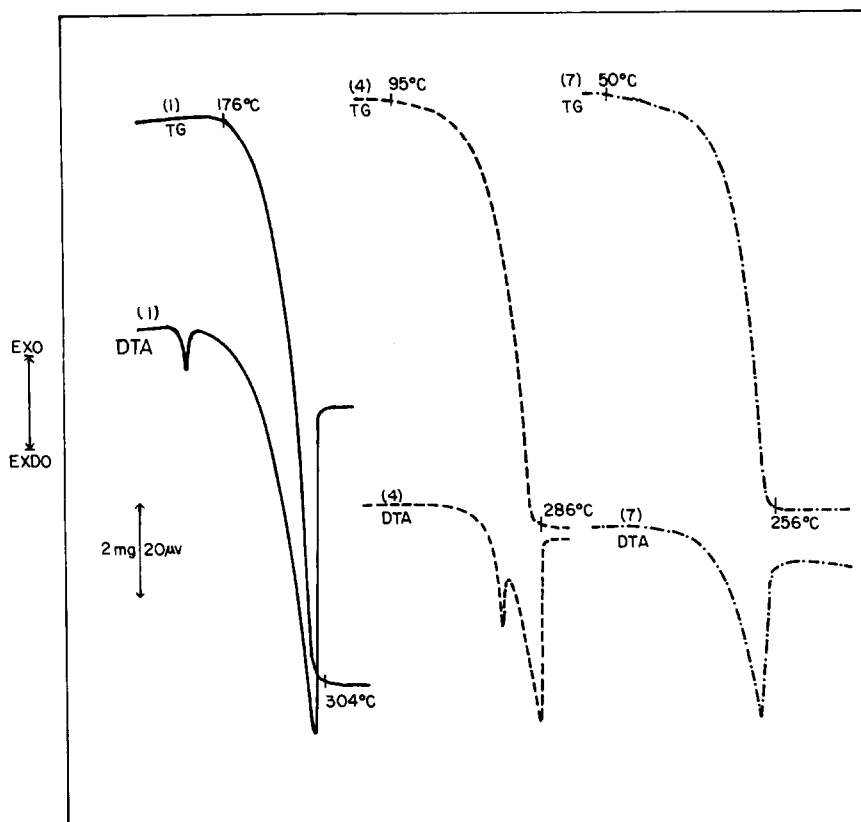


Fig. 1. Thermal curves of $C_2H_5NH_3Cl$ (1) (—), sample mass 11.8 mg; $(C_2H_5)_2NH_2Cl$ (4) (-----), sample mass 8.2 mg; and $(C_2H_5)_3NHCl$ (7) (-.-.-), sample mass 8.3 mg.

peak was measured using a compensating planimeter with an optical tracer (Fuji Corona 027).

The entropy change (ΔS) was calculated using the relation [9] $\Delta S = \Delta H/T_m$, where T_m is the DTA peak temperature (K).

RESULTS AND DISCUSSION

$C_2H_5NH_3Cl$ (1), $(C_2H_5)_2NH_2Cl$ (4) and $(C_2H_5)_3NHCl$ (7)

The chloride salts of mono-, di- and triethylamine are white crystalline solids. When the salts are heated under non-isothermal conditions, the endothermic DTA peaks for the melting of salts 1 and 4 appear at 109 and 220°C (Fig. 1 and Table 2). For salt 7, no separate endothermic peak for melting is observed because it merges with the decomposition peak. The decomposition temperature ranges of salts 1, 4 and 7 lie between 176 and 304, 95 and 286 and 50 and 256°C respectively (Fig. 1 and Table 2) and the corresponding DTA peaks appear at 278, 266 and 232°C respectively. The

TABLE 2
Thermal parameters of mono-, di- and triethylammonium salts

No.	Compounds (undergoing complete decomposition)	Phase transition (°C)	Melting point (°C)	Temperature range (°C)	DTA peak temp. (endo) (°C)	E_a^* (kJ mol ⁻¹) TG DTA	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
1	C ₂ H ₅ NH ₃ Cl	-	109	176-304	278	100 115	68	131
2	C ₂ H ₅ NH ₃ Br	89	150	164-374	317	110 113	148	115
3	C ₂ H ₅ NH ₃ HSO ₄	-	205	266-341	292	170 214	28	53
4	(C ₂ H ₅) ₂ NH ₂ Cl	-	220	95-286	266	144 148	34	69
5	(C ₂ H ₅) ₂ NH ₂ Br	-	218	138-335	309	163 131	54	99
6	(C ₂ H ₅) ₂ NH ₂ HSO ₄	-	141	276-331	301	225 188	100	185
7	(C ₂ H ₅) ₃ NHCl	-	244	50-256	232	110 109	81	143
8	(C ₂ H ₅) ₃ NHBr	-	239	121-320	298	121 173	32	61
9	(C ₂ H ₅) ₃ NHHSO ₄	-	217	128-275	265	200 205	58	116

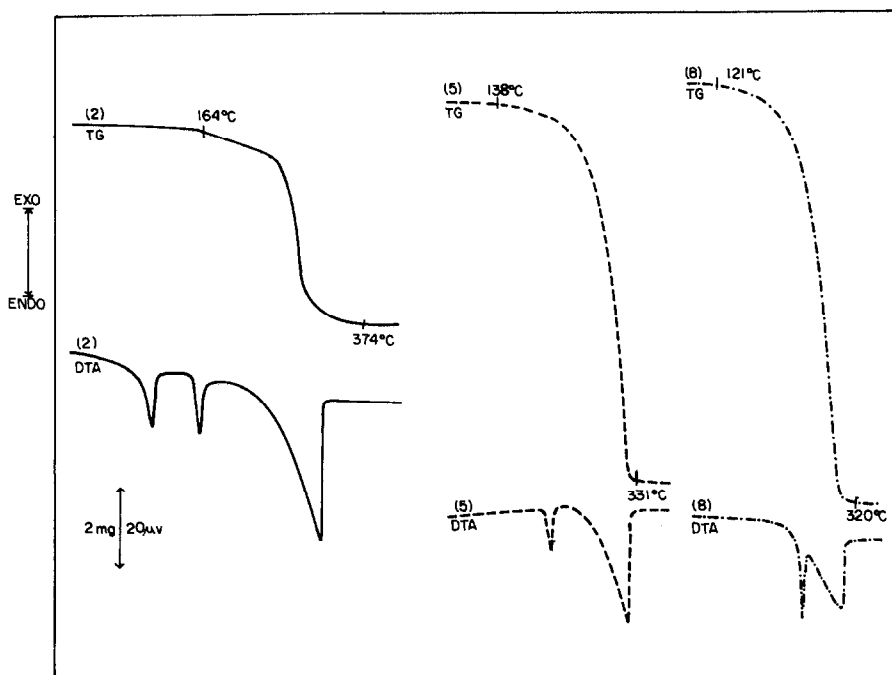


Fig. 2. Thermal curves of $C_2H_5NH_3Br$ (2) (—), sample mass 4.8 mg; $(C_2H_5)_2NH_2Br$ (5) (- - - - -), sample mass 7.8 mg; and $(C_2H_5)_3NHBr$ (8) (· · · · ·), sample mass 9.6 mg.

values of activation energy (E_a^*), enthalpy change (ΔH) and entropy change (ΔS) for the decomposition processes are evaluated and given in Table 2. The probable mechanistic paths of decomposition are shown in the Scheme.

$C_2H_5NH_3Br$ (2), $(C_2H_5)_2NH_2Br$ (5) and $(C_2H_5)_3NHBr$ (8)

All three salts, 2, 5 and 8, were isolated as white crystalline solids. The DTA curve of salt 2 has one endothermic peak at $89^\circ C$ (Fig. 2). This peak corresponds to phase transition [10]. After the phase transition, the thermal curve shows another endothermic DTA peak at $150^\circ C$ which corresponds to its melting point. Salts 5 and 8 also show very sharp endothermic peaks of melting at 218 and $239^\circ C$ respectively in the corresponding DTA curves. After melting, salts 2, 5 and 8 undergo complete volatilisation between 164 and $374^\circ C$, 138 and $335^\circ C$ and 121 and $320^\circ C$ respectively (Fig. 2 and Table 2). The corresponding DTA curves show endotherms and peaks appear at 317, 309 and $298^\circ C$ (Fig. 2 and Table 2). The values of ΔH for the phase transition of salt 2 is 12 kJ mol^{-1} . The activation energy (E_a^*), enthalpy change (ΔH) and entropy change (ΔS) for the decomposition of salts 2, 5 and 8 were calculated and are shown in Table 2. The probable mechanistic paths of the decompositions are shown below in the Scheme.

$C_2H_5NH_3HSO_4$ (3), $(C_2H_5)_2NH_2HSO_4$ (6) and $(C_2H_5)_3NHHSO_4$ (9)

Salts 3, 6 and 9 also formed white crystalline solids. The temperature ranges of decomposition are 266–341, 276–331 and 128–275°C for the salts 3, 6 and 9 respectively (Fig. 3 and Table 2). The corresponding DTA curves of salts 3, 6 and 9 show endotherms at 292, 301 and 265°C respectively, and sharp melting peaks at 205, 141 and 217°C respectively (Fig. 3 and Table 2). The values of activation energy (E_a^*), enthalpy change (ΔH) and entropy change (ΔS) for the decomposition of the salts are also listed in Table 2.

A linear correlation is observed when the values of E_a^* are plotted against ΔS for the decomposition reactions of the mono-, di- and triethylammonium salts (Fig. 4). This shows that a system having a higher entropy change will require less activation energy for its thermal decomposition [9].

Furthermore, when the values of E_a^* are plotted against the number of ethyl groups (n), the stability trend of the salts follows the order $C_2H_5NH_3X < (C_2H_5)_3NHX < (C_2H_5)_2NH_2X$ where $X = Cl, Br$ or HSO_4 (Fig. 5). It can be suggested that diethylammonium salts are the most stable

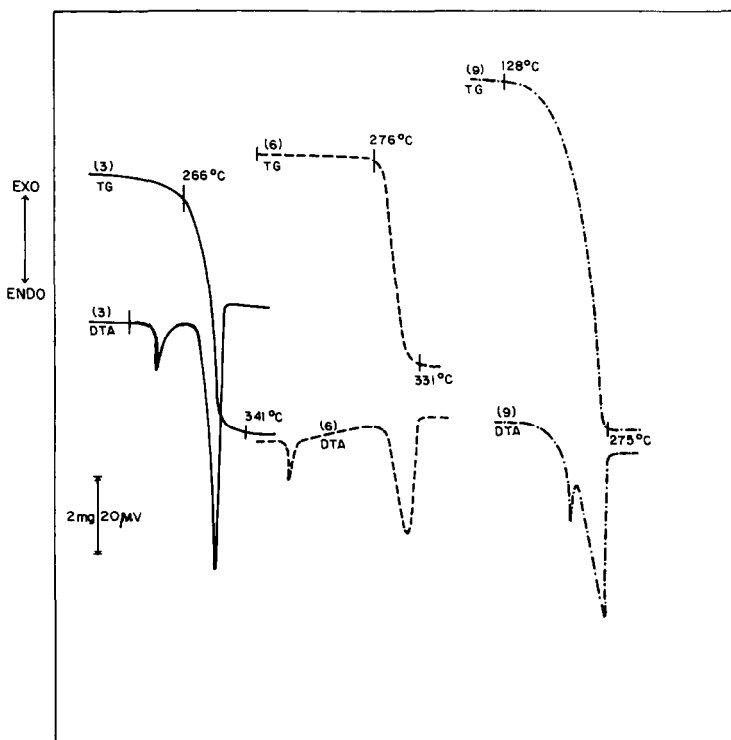


Fig. 3. Thermal curves of $C_2H_5NH_3HSO_4$ (3) (—), sample mass 7.7 mg; $(C_2H_5)_2NH_2HSO_4$ (6) (-----), sample mass 5.2 mg; and $(C_2H_5)_3NHHSO_4$ (9) (-·-·-), sample mass 8.4 mg.

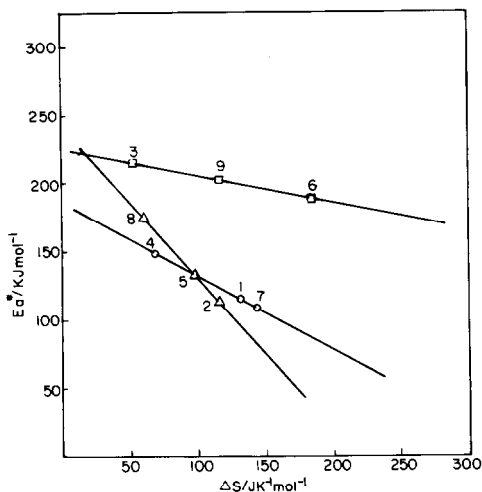


Fig. 4. Plots of the values of E_a^* versus ΔS for the thermal decomposition of $C_2H_5NH_3Cl$ (1), $(C_2H_5)_2NH_2Cl$ (4) and $(C_2H_5)_3NHCl$ (7), \circ ; $C_2H_5NH_3Br$ (2), $(C_2H_5)_2NH_2Br$ (5) and $(C_2H_5)_3NHBr$ (8), Δ ; and $C_2H_5NH_3HSO_4$ (3), $(C_2H_5)_2NH_2HSO_4$ (6) and $(C_2H_5)_3NHHSO_4$ (9) \square .

among the three ethylammonium salts, whereas monoethylammonium salts are less stable than the triethylammonium salts due to steric factors [11] resulting from the crowdedness of the ethyl groups.

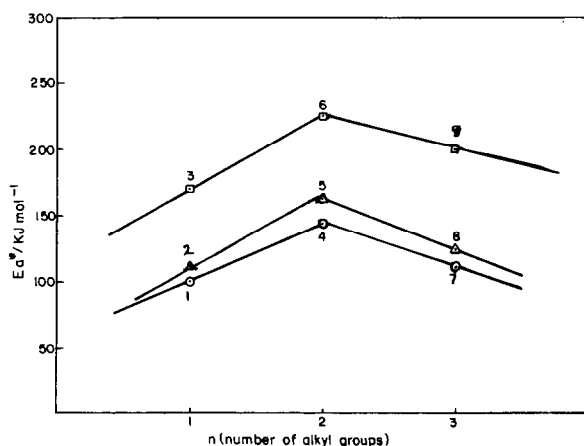
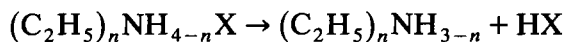


Fig. 5. Plots of the values of E_a^* versus number of ethyl groups (n) for the thermal decomposition of $C_2H_5NH_3Cl$ (1), $(C_2H_5)_2NH_2Cl$ (4) and $(C_2H_5)_3NHCl$ (7), \circ ; $C_2H_5NH_3Br$ (2), $(C_2H_5)_2NH_2Br$ (5) and $(C_2H_5)_3NHBr$ (8), Δ ; and $C_2H_5NH_3HSO_4$ (3), $(C_2H_5)_2NH_2HSO_4$ (6) and $(C_2H_5)_3NHHSO_4$ (9) \square .

Scheme

The probable mechanistic path of the volatilisation [1] may be represented as



where X = Cl, Br or HSO₄.

ACKNOWLEDGEMENT

The authors express their thanks to the Central Drug Research Institute, Lucknow, India for elemental analyses.

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