Journal of Thermal Analysis and Calorimetry, Vol. 62 (2000) 305–315

STUDIES ON ENERGETIC (NON) COMPOUNDS
Part 21: Preparation and thermal decomposition of ring substituted dimethyl anilinium bromides

G. Singh, I. P. Singh Kapoor and J. Kaur

Chemistry Department, D.D.U. Gorakhpur University, Gorakhpur, 273 009, India

(Received December 5, 1999)

Abstract

Six isomeric dimethyl anilinium bromides (DMABr) have been prepared and characterized by elemental and spectroscopic studies. Thermal decomposition of these salts has been studied by TG and simultaneous TG-DTA techniques. Kinetic parameters have been evaluated from isothermal TG data using contracting area and contracting cube equations. The decomposition pathways have also been suggested which involves simultaneous sublimation (at lower temperature) and dissociative vaporization/decomposition (at higher temperature).

Keywords: DTA, ring-substituted dimethyl anilinium bromides, TG

Introduction

The proton transfer mechanism has been postulated to play an important role in the thermal decomposition of almost all the ammonium salts. It is also known that sublimation/vaporization is involved during the decomposition of ammonium halides [1]. and Boryta [2] have measured the sublimation temperature of ammonium halides which is in the order $NH_4I>NH_4Br>NH_4Cl$. It has also been suggested by Mack and Wilmot [3] that a linear relationship does exist between the relative vaporization temperatures of amine salts of $HClO_4$ and pK_a values of their corresponding amines in aqueous solution. Erdey and coworkers [4–6] have investigated the thermal decomposition of various ammonium salts and results have been explained based on acid base theory. NH_4Br showed phase change at 150 and marked decomposition was observed above 250°C.

We have carried out a lot of work in the preparation and thermolysis of aryl ammonium sulphates (RSAS) [7–12], nitrates (RSAN) [13, 14] and perchlorates (RSAP) [15–17]. These salts have been found to dissociate to parent aryl amine and acid molecules [H_2SO_4, HNO_3, $HClO_4$] respectively and proton transfer processes seems to be the primary rate controlling step. Studies have also been undertaken recently on the thermolysis of ring substituted aryl ammonium chlorides (RSACl) [18] and dimethyl anilinium chlorides (DMACl) [19]. It has been observed that simultaneous sublimation/decomposi-

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

tion processes are involved during the thermolysis of RSACl and DMACl. As a program of our ongoing researches, we have prepared and characterized a large number of ring substituted dimethyl anilinium bromides (DMABr). The thermal decomposition of these salts has been undertaken by thermoanalytical techniques in order to understand their mechanism of decomposition. These studies are not yet reported in literature.

Experimental

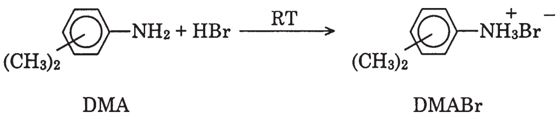
Materials

The following LR grade arylamines obtained from different sources given in parentheses were purified by usual methods.

2,3-Dimethyl aniline (Lancester), 2,4-dimethyl aniline (Merck), 2,5-dimethyl aniline (Merck), 2,6-dimethyl aniline (Lancester), 3,4-dimethyl aniline (Merck), 3,5-dimethyl aniline (Lancester). Hydrobromic acid (CDH), silica gel (Qualigens), silver nitrate (Qualigens) used as received.

Preparation and characterization of DMABr

The bromide salts of dimethyl anilines were prepared by reacting 49% aqueous solution of hydrobromic acid with dimethyl anilines (DMA) in 1:1 molar ratio at room temperature and reaction can be represented as follows:
where $(CH_3)_2$=2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-.



Instant precipitates were obtained in all the cases except 2,4-dimethyl anilinium bromide which precipitated out under ice cold condition. These salts were washed with petroleum spirit twice, recrystallized from aqueous solution and vacuum dried.

Purity was checked by TLC and these salts were characterized by elemental, gravimetric and spectroscopic analyses. Their structures and physical parameters are presented in Table 1.

Elemental and spectroscopic analyses

The C, H, N analysis was done with Heraeus Carlo Erba 1108 instrument and percentage of each element is given in Table 1. IR was taken in Perkin Elmer 983 with DS System using KBr pellets and ^{1}H NMR spectra were recorded using DMSO-d_6 on Em 390 (Varian) and data are summarized in Table 2.

Table 1 Structure, physical parameters, TLC, elemental and gravimetric analyses of DMABr

No.	Compound	Yield/%	*m.p.*[a]/°C	Crystal colour	R_f	Elemental composition (calculated value)/%			
						C(47.52)	H(5.94)	N(6.93)	Br(39.60)
1	2,3-DMABr	74	175	white	0.52	47.71	5.91	6.91	38.42
2	2,4-DMABr	70	160	white	0.61	47.51	6.06	6.35	39.24
3	2,5-DMABr	66	210	white	0.61	47.37	6.37	6.73	39.56
4	2,6-DMABr	78	210	brown	0.48	46.59	5.90	6.96	39.20
5	3,4-DMABr	72	220	yellow white	0.56	47.06	6.00	6.43	39.42
6	3,5-DMABr	72	230	light brick colour	0.42	47.63	5.46	6.00	39.72

[a] – undergo sublimation; locating reagents – iodine, eluents – hexane:ethyl acetate:alcohol (2:1:1)

Table 2 IR and ^{1}H NMR spectral data on DMABr

Assignments	Absorption frequencies (cm^{-1}) on DMABr					
	2,3–	2,4–	2,5–	2,6–	3,4–	3,5–
Primary amine salts (arom.)	3493	3091	3406	3503	3437	3498
Disubstituted	1931	1946	2128	1959	1982	1966
ν(C–N)	1192	1308	1237	1265	1226	1190
ν(C=C)	1691	1620	1622	1631	1496	1623
ν(C–C)	1129	1092	1122	1155	1020	1100
ν(C–H)	2854	3091	3064	3040	3102	3173
ν(C–H) in CH_3	3037	3091	2930	3040	2966	2937
ν(N–H)	1619	1620	1622	1631	1563	1578
δ(N–H)	892	893	879	890	867	875
ν(1,2,3–sub.)	892, 1401, 1588	–	–	–	–	–
ν(1,2,4–sub.)		893, 1450, 1550	–	–	–	–
ν(1,2,5–sub.)			852, 1497, 1550	–	–	–
ν(1,2,6–sub.)				892, 1470, 1586	–	–
ν(1,3,4–sub.)					867, 1445, 1563	–
ν(1,3,5–sub.)						845, 875, 1466, 1578
^{1}H NMR chemical shift (δ ppm)	6–8 (m, 3H, Ar) 2–2.7 (s, CH_3)	6.5–8 (m, 3H, Ar) 2–2.8(s, CH_3)	6.4–8 (m, 3H, Ar) 2.4–2.8(m, CH_3)	6.4–7.6 (m, 3H, Ar) 2.4–2.7(s, CH_3)	6.6–8(m, 3H, Ar) 2.2–2.6(s, CH_3)	6–8(m, 3H, Ar) 2.4–3(s, CH_3)

Table 3 Kinetics parameters and correlation coefficients (r) for isothermal decomposition of DMABr

Compd. No.	Contracting area (n=2)							Contracting cube (n=3)						
	Rate constant ($k\cdot 10^{-3}$/min^{-1}) at T/K					r	E_a/kJ mol^{-1}	Rate constant ($k\cdot 10^{-3}$/min^{-1}) at T/K					r	E_a/kJ mol^{-1}
	413	423	433	443	453			413	423	433	443	453		
1	10.1	15.1	24.2	75.1	85.1	1.0000	76.6	8.0	16.2	20.2	51.2	80.1	0.9856	95.7
2	8.0	11.1	17.0	33.1	66.2	0.9793	95.9	6.1	25.0	16.1	30.2	60.0	0.9876	86.5
3	11.0	26.1	60.1	80.0	150.2	0.9889	95.7	9.2	25.0	40.1	71.2	16.3	0.9890	114.8
4	40.1	70.2	13.3	21.2	120.2	0.9490	95.7	3.2	5.7	12.1	10.1	100.1	0.9350	114.8
5	8.2	13.1	20.3	35.2	60.2	0.9933	87.2	6.1	8.0	14.0	22.1	36.2	0.9900	78.6
6	10.1	21.2	32.5	34.2	120.8	0.9895	76.6	14.2	20.1	24.1	35.1	71.4	0.9608	63.2

Gravimetric analysis

200 mg of each salt was dissolved in 150 ml of distilled water and 0.5 ml conc. HNO_3 was added. Thereafter $AgNO_3$ was added till precipitation was complete.

The precipitates were filtered off in sintered crucible, washed with ice cold water and dried in hot air oven. Percentage of bromide is given in Table 1.

Thermal decomposition of DMABr

Thermal decomposition of DMABr was investigated as follows:

Non–isothermal TG

TG studies on DMABr (mass 30 mg, 200–400 mesh) were undertaken in static air at a heating rate of 5C min^{-1} using indigeneously fabricated TG apparatus [20] fitted with temperature indicator with controller (model CT–808T century) and bucket type platinum crucible (*h*=10 mm, dia=10 mm) was used as sample holder. The decomposition (α) *vs*. temperature plots are given in Fig. 1. The temperature for complete decomposition (T_f) for these salts have been noted from Fig. 1 and data are reported in Table 3.

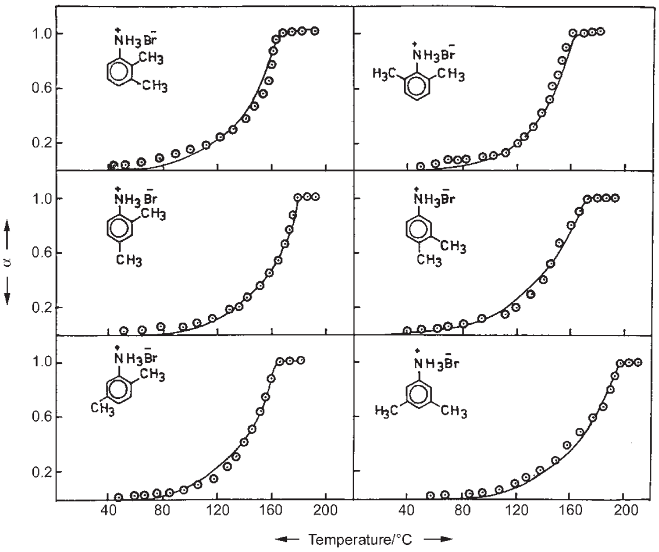


Fig. 1 Non-isothermal TG curves of DMABr

Isothermal TG

TG on DMABr samples (30 mg, 200–400 mesh) was carried out in static air at temperatures 140, 150, 160, 170 and180°C and α *vs*. time (t) plots are reported in Fig. 2.

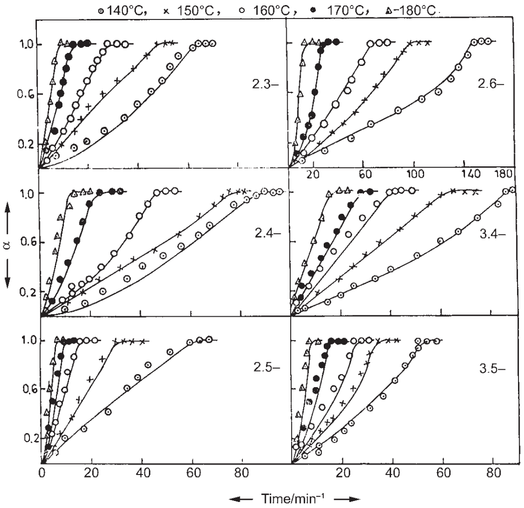


Fig. 2 Isothermal TG curves of DMABr

The kinetics of thermal decomposition have been evaluated from isothermal TG data which were fitted in nine mechanism based kinetic models [21, 22]. Contracting area and contracting cube equations (Eqs 1 and 2) have been found to give best fits.

$$1-(1-\alpha)^{1/2}=kt \tag{1}$$

$$1-(1-\alpha)^{1/3}=kt \tag{2}$$

The correlation coefficient values (r) were also evaluated using the relation

$$\text{Correlation coefficient: } r=\frac{\sum xy}{\sqrt{(\sum x^2)(\sum y^2)}}$$

where x and y are values at abscissa and ordinates respectively. The calculated values for rate constant (k) and estimated values of E_a are reported in Table 3.

Simultaneous TG–DTA

The samples of DMABr [~4 mg, 200–400 mesh] were run in N_2 atmosphere on DTA 1700/TG S2/TA DS 3600 (Perkin Elmer) apparatus and TG curves are given in Fig. 3. The TG and DTA profile data for all the bromide salts were noted from Fig. 3 and results are summarised in Table 4.

Discussion

Elemental, gravimetric, IR and ^{1}H NMR data reported in Tables 1 and 2 clearly confirms the formation of DMABr. TG (non-isothermal) and simultaneous TG-DTA plots (Figs 1 and 3) show that all the compounds undergo approximately 100% mass

Table 4 TG and DTA profile data of DMABr

Compd. No.	Temperatures of data peaks/°C				TG in N_2 atomosphere/°C				TG in static air T_f/°C
	Endotherm I		Endotherm II						
	T_{peak}	T_{endset}	T_{peak}	T_{endset}	T_{onset}	$T_{\text{inflection}}$	T_{endset}	Residue/%	
1	208	214	249	257	222	249	251	2.82	175
2	163	177	243	252	220	243	245	6.27	180
3	–	–	213	233	193	224	226	10.76	165
4	–	–	224	239	196	221	229	7.22	160
5	–	–	242	250	222	241	243	9.77	175
6	126	136	248	264	217	249	258	2.75	190

T_f – temperature at complete decomposition

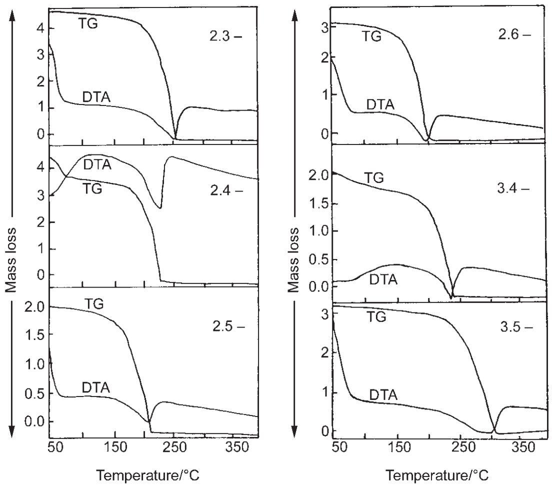
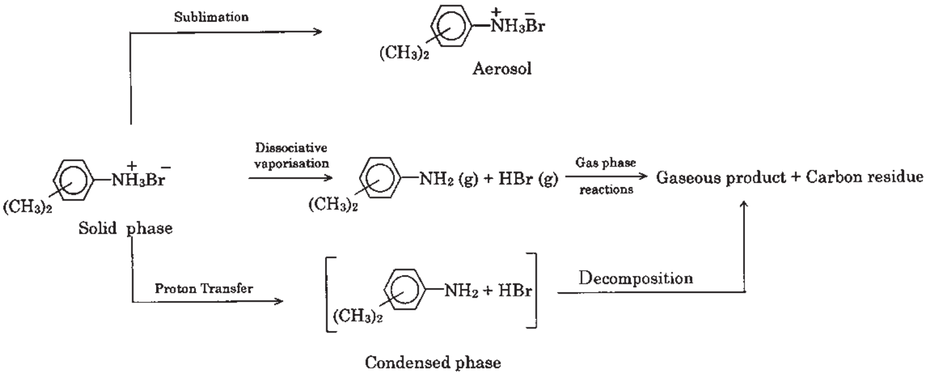


Fig. 3 Simultaneous TG-DTA of DMABr

loss in static air and very small amount of residue was obtained when TG was taken in N_2 atmosphere (Table 4). Lower T_f (final decomposition temperature) temperature were also observed when TG was taken in static air as compared to N_2 atmosphere (endset temperature) which may be due to the oxidising behaviour of the surrounding atmosphere (air). Two endotherms I and II were observed for 2,3-, 2,4-, 3,5-DMABr while single endotherm was obtained for 2,5-, 2,6-, 3,4-DMABr. The endotherm I may be due to phase transition and II endotherm may involve (i) sublimation (ii) dissociative vaporisation and (iii) decomposition processes. It seems that a part of the sample sublimes at lower temperatures followed by dissociative vaporisation and decomposition at higher temperatures [23, 24]. Thus the thermal decomposition pathway for DMABr can be suggested (Scheme 1).



Scheme 1 Schematic decomposition pathway of DMABr

DMABr salts seem to undergo mass loss due to evolution of aerosol (sublimation), Hbr (*g*), parent aryl amine (*g*) and other gaseous products. The samples were heated in long test tube and deposited residue on the cold part of test tube was collected and confirmed as DMABr and parent amine (TLC method). The evolved vapours were dissolved in distilled water and bromide was confirmed by chemical methods and parent amines by (TLC). It seems that simultaneous sublimation/dissociative vaporization/decomposition processes are involved in all the cases at higher temperatures (193–258°C). However, it is very difficult to isolate sublimation from dissociative vaporization.

Examination of Table 3 shows that kinetic parameters determined using CA and CC equations are almost independent of the reaction models. This clearly indicates that the increase in acidity of DMA causes a decrease in rate of decomposition and E_a showed the opposite trend. It is evident that there exists a correlation between proton transfer equilibria and relative stabilities of DMABr. The observed stability order is 3,5->3,4->2,4->2,3->2,5->2,6-DMABr.

Conclusions

The thermal decomposition of DMABr occurs principally by dissociation into HBr and the corresponding dimethyl aniline. The results show that proton transfer reaction plays an important role in the thermal decomposition of these salts.

* * *

Thanks are due to DST, New Delhi for financial assistance, RSIC, Nagpur for simultaneous TG-DTA, RSIC, Shillong for microanalysis & spectral data and Head, Chemistry Department, D.D.U. Gorakhpur University for laboratory and library facilities.

References

1 W. R. Rodebush and J. C. Michaleks, J. Am. Chem. Soc., 51 (1929) 748.
2 M. M. Markowitz and D. A. Boryta, J. Phys. Chem., 66 (1962) 1477.
3 J. L. Mack and G. B. Wilmot, J. Phys. Chem., 71 (1967) 2155.
4 L. Erdey, Periodica Polytech., 1 (1957) 91.
5 L. Erdey and S. Gál, Talanta, 10 (1963) 23.
6 L. Erdey, S. Gál and G. Liptay, Talanta, 11 (1964) 913.
7 G. Singh and I. P. S. Kapoor, J. Chem. Soc., Perkin Trans II, (1989) 2155.
8 G. Singh, I. P. S. Kapoor and M. Jain, J. Chem. Soc., Perkin Trans II, (1993) 1521.
9 G. Singh, I. P. S. Kapoor and M. Jain, Indian J. Chem., 35 B (1996) 369.
10 G. Singh, I. P. S. Kapoor and M. Jain, Thermochim. Acta, 292 (1997) 135.
11 G. Singh, I. P. S. Kapoor and J. Singh, Indian J. Chem., 36 B (1997) 590.
12 G. Singh, I. P. S. Kapoor and J. Singh, Indian J. Eng. Mat. Sci., 5 (1998) 334.
13 G. Singh and I. P. S. Kapoor, Combust and Flame, 92 (1993) 283.
14 G. Singh, I. P. S. Kapoor, S. M. Mannan and J. P. Agrawal, Combust and Flame, 97 (1994) 355.
15 G. Singh and I. P. S. Kapoor, J. Phys. Chem., 96 (1992) 1215.

16 G. Singh, I. P. S. Kapoor and S. M. Mannan, J. Energ. Mat., 13 (1995) 141.
17 G. Singh, I. P. S. Kapoor and S. M. Mannan, J. Thermal Anal., 46 (1996) 1751.
18 G. Singh, I. P. S. Kapoor and J. Kaur, Indian J. Chem., 38 B (1999) 56.
19 G. Singh, I. P. S. Kapoor and J. Kaur, Thermochim. Acta, 35 (1999) 45.
20 G. Singh and R. R. Singh, Res. Ind., 23 (1978) 92.
21 V. Satava, Thermochim. Acta, 2 (1971) 423.
22 C. M. Wyandt and D. R. Flanagan, Thermochim. Acta, 196 (1992) 379.
23 G. A. Heath and J. R. Majer, Trans. Faraday Soc., 60 (1964) 178.
24 M. H. Cassel and I. Libman, J. Chem. Phys., 34 (1961) 343.