J Therm Anal Calorim (2010) 100:233–238
DOI 10.1007/s10973-009-0437-1

Preparation, X-ray crystallography, and thermolysis of phenylenediammonium dibromide salts

Part LIX.

**Pratibha Srivastava · Inder Pal Singh Kapoor ·
Gurdip Singh · Roland Fröhlich**

Received: 22 June 2009 / Accepted: 18 August 2009 / Published online: 17 September 2009

Abstract Phenylenediammonium dibromide (PDADBr) salts have been prepared and characterized by X-ray crystallography. The thermal decomposition of PDADBr has been studied by thermogravimetry (TG) and differential thermal analysis (DTA). Kinetic parameters have been evaluated using model fitting and isoconversional methods. The thermolytic pathways have also been suggested which involve proton transfer as a primary step to regenerate parent amine and HBr. Interaction between amine and HBr at higher temperature yields gaseous products.

Keywords Phenylenediammonium dibromide · Crystal structure · Kinetics · Isoconversional method · Thermolysis · Proton transfer

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]. Erdey and co-authors [2–4] 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 °C and marked decomposition was observed above 250 °C.

Singh et al. reported a lot of work on the thermolysis of various ring substituted anilinium sulfates, nitrates, perchlorates, chlorides, bromides [5–10], dinitrates [11], diperchlorates [12], and dichlorides [13]. Proton transfer was suggested as a primary step in the thermal decomposition of these salts. These studies are very significant since alkyl and arylammonium halides are generally used as phase transfer catalyst and corrosion inhibitors [14]. Although several monobromides of ring substituted arylamines are known [6], studies on dibromide salts are not yet available in the literature. As a part of our ongoing research programs, the preparation, characterization, and thermolysis of phenylenediammonium dibromide (PDADBr) salts have been reported in this article.

Experimental

Materials

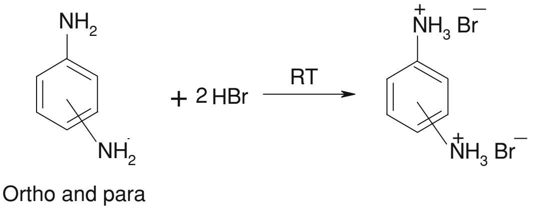
Following AR grade, commercially available chemicals were used as-received phenylene-1,2-diamine (s.d. fine); phenylene-1,4-diamine (s.d. fine); 70% HBr (E-Merck), silica gel TLC grade (Qualigens), iodine, and silver nitrate.

Preparation of the PDADBr salts

PDADBr salts (yield 90%) were prepared by reacting corresponding phenylene diamines with 20% HBr directly in 1:2 molar ratios at room temperature.

P. Srivastava · I. P. S. Kapoor · G. Singh (✉)
Department of Chemistry, DDU Gorakhpur University,
Gorakhpur 273009, India
e-mail: gsingh4us@yahoo.com

R. Fröhlich
Organisch-Chemisches Institut, Universität Münster,
48149 Münster, Germany



All these salts were washed with ethyl acetate, recrystallized from distilled water, and dried over fused $CaCl_2$ in a vacuum desiccator.

Crystallographic and thermal decomposition studies

Crystallographic study has been done using same techniques as reported earlier [13]. The non-isothermal analyses [e.g., thermogravimetry (TG) in N_2 and TG, differential thermal analysis (DTA) in air atmosphere] were undertaken at a heating rate of 10 °C min^{-1}. The non-isothermal TG curves on the salts (mass ~20 mg) were obtained on thermal analyzer (TA) Q 50 in N_2 atmosphere and indigenously fabricated TG apparatus [12] in static air (sample mass ~20 mg). DTA curves were taken under flowing air (at a rate of 60 mL min^{-1}) using Universal Thermal Analysis Instrument, Mumbai (sample mass ~20 mg). Isothermal TG on these salts (mass ~33 mg) was done in static air using the same apparatus [12] at appropriate temperatures.

Kinetic analysis of isothermal TG data

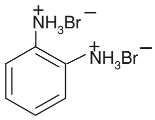
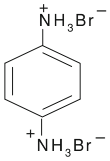
The kinetic analysis using isothermal TG data has been done as reported earlier [12].

Results and discussion

Results of X-ray crystallography, elemental analysis, gravimetric estimation, and thin-layer chromatography (Tables 1, 2, 3) clearly confirmed the formation of PDADBr salts. Crystal parameters (Table 2) show that P-1,2-DADBr have the crystal system triclinic with unit cell dimensions $a = 4.489(1)$ Å, $\alpha = 70.21(1)°$, $b = 6.111(1)$ Å, $\beta = 75.25(1)°$, $c = 8.731(1)$ Å, $\gamma = 78.98(1)°$, whereas P-1,4-DADBr have the crystal system orthorhombic with unit cell dimensions $a = 4.740(1)$ Å, $b = 7.541(1)$ Å, $c = 12.682(1)$ Å. Hydrogen atoms were placed on calculated positions and refined riding. Refinement with anisotropic thermal parameters for non-hydrogen atoms led to the R-values of 0.021 and 0.034, respectively. The molecular structure and atom labeling scheme for PDADBr salts are shown in Figs. 1 and 2. The details of bond lengths and angles are given in Table 3.

To detect the effect of atmospheric change on thermolysis of these salts, TG studies have been carried out in nitrogen and air atmospheres (Fig. 3). As can be seen from thermoanalytical data, the decomposition of both salts takes place in single step in nearly same range of temperature (190–350 °C). Presence of single endothermic peak (Fig. 4) in DTA thermogram suggests that similar trend was observed in DTA studies. During DTA runs under a flowing air atmosphere, we have observed white deposits near the lower and colder region of glass tube, covering the sample and thermocouples. The deposits gave the same R_f values as the parent compound on TLC analysis. This indicates that sublimation takes place during heating. However, sublimation is not the only process occurring during heating because some carbonaceous residues are left

Table 1 Physical and elemental parameters of PDADBr salts

Name of compound	Structural formula	Crystal color	pK_a	R_f[a]	Elemental analysis			
					C	H	N	Br
P-1,2-DADBr		Colorless crystal	9.48	0.87 (a:b:c)[b]	26.15 (26.67)	3.56 (3.70)	10.40 (10.37)	58.90 (59.26)
P-1,4-DADBr		Dirty yellow crystals	7.96	0.83 (a:b:c)[b]	25.95 (26.67)	3.76 (3.70)	10.75 (10.37)	59.90 (59.26)

[a] Retention factor

[b] Eluent-2:1:1(H_2O:n-BuOH:gl.AcOH)

Table 2 Crystal data and structure refinement for PDADBr salts

Salts designation	P-1,2-DADBr	P-1,4-DADBr
Empirical formula	$C_6 H_{10} Br_2 N_2$	$C_6 H_{10} Br_2 N_2$
Color	Colorless	Yellow
Formula weight	269.98	269.98
Temp/K	223(2)	198(2)
λ/Å	0.71073	0.71073
Crystal system	Triclinic, P-1 (No. 2)	Orthorhombic, Pmmn (No. 59)
Cell constants	$a = 4.489(1)$ Å, $\alpha = 70.21(1)°$	$a = 4.740(1)$ Å
	$b = 6.111(1)$ Å, $\beta = 75.25(1)°$	$b = 7.541(1)$ Å
	$c = 8.731(1)$ Å, $\gamma = 78.98(1)°$	$c = 12.682(1)$ Å
Volume/Å^3	216.48(6)	453.31(12)
Molecules per unit cell, Z	1	2
Calculated density/Mg/m^3	2.071	1.978
Absorption coefficient/mm^{-1}	9.291	8.874
F(000)	130	260
Crystal size/mm	0.45 × 0.45 × 0.20	0.30 × 0.30 × 0.25
θ Range for data collection/°	2.53–27.86	3.14–27.86
Limiting indices	$-5 \le h \le 5, -7 \le k \le 8, -8 \le l \le 11$	$-5 \le h \le 6, -7 \le k \le 9, -16 \le l \le 16$
Data/restraints/parameters	1015/0/48	645/0/35
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0341$, w$R_2 = 0.0882$	$R_1 = 0.0205$, w$R_2 = 0.0508$
R indices (all data)	$R_1 = 0.0358$, w$R_2 = 0.0896$	$R_1 = 0.0237$, w$R_2 = 0.0517$
Extinction coefficient	0.100(13)	0.028(2)
Largest diff. peak and hole/eÅ^{-3}	0.872 and −0.696	0.488 and −0.415
CCDC no.	636312	636313

Table 3 Bond lengths (Å) and angles (°) for PDADBr salts

P-1,2-DADBr	P-1,4-DADBr
Bond lengths	
N(1)–C(1) 1.462(4)	N(1)–C(1) 1.461(3)
C(1)–C(2) 1.382(5)	C(1)–C(1) 1.388(6)
C(1)–C(3) 1.387(4)	C(1)–C(2) 1.390(4)
C(2)–C(3) 1.389(5)	C(2)–C(3) 1.387(4)
C(3)–C(2) 1.389(5)	C(3)–C(3) 1.378(7)
Bond angles	
C(2)–C(1)–C(3) 122.0(3)	C(1)–C(1)–C(2) 119.82(17)
C(2)–C(1)–N(1) 119.5(3)	C(1)–C(1)–N(1) 122.75(15)
C(3)–C(1)–N(1) 118.5(3)	C(2)–C(1)–N(1) 117.4(3)
C(1)–C(2)–C(3) 118.8(3)	C(3)–C(2)–C(1) 120.0(3)
C(2)–C(3)–C(1) 119.1(3)	C(3)–C(3)–C(2) 120.14(18)

behind in the crucible. It seems that sublimation takes place initially and as the temperature rises, oxidative decomposition also takes place in the condensed state [13].

As suggested earlier [6], the thermal stability of PDADBr may depend upon the tendency of phenylenediammonium ion to release a proton to bromide ion. Low pK_a (higher acidity) of amine causes an easy removal of proton from $–NH_3^+$ which clearly indicates that thermal stability of bromide salts depend upon pK_a value of corresponding amine. Proton transfer via an activated complex is assumed as a primary rate determining step which leads to the formation of corresponding phenylenediamine and HBr, both in condensed as well as gaseous phase (Scheme 1).

The kinetics of thermal decomposition of PDADBr was evaluated using 14 mechanism-based kinetic models [12].

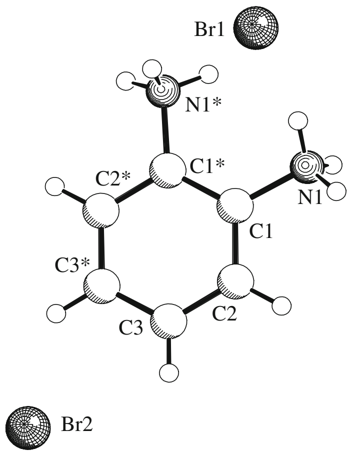


Fig. 1 Crystal structure of P-1,2-DADBr salt

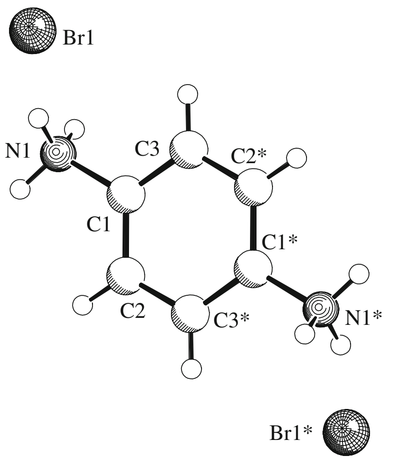


Fig. 2 Crystal structure of P-1,4-DADBr salt

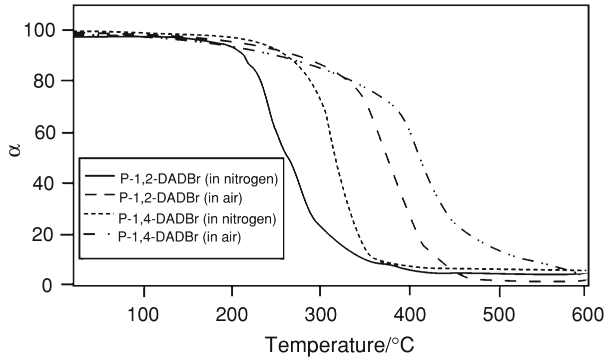


Fig. 3 Non-isothermal TG curves of PDADBr in nitrogen and air atmosphere

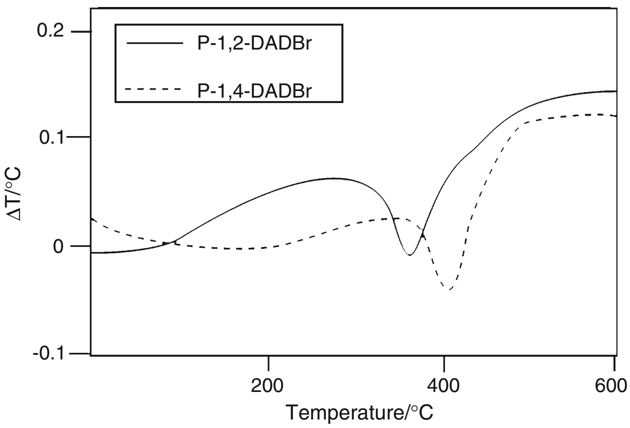
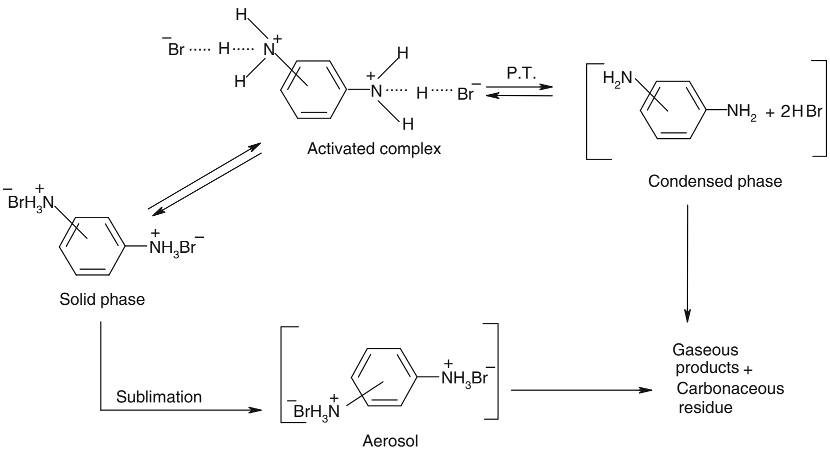


Fig. 4 DTA curves of PDADBr salts in flowing air

In the model fitting method, the kinetics is analyzed by choosing a "best fit" model based on the value of correlation coefficient r close to 1. Among various values of r calculated for different models, highest value of r for P-1,2-DADBr corresponds to model 1 and for P-1,4-DADBr corresponds to model 11. The corresponding value of E as reported in Table 4 for P-1,2-DADBr and P-1,4-DADBr is, respectively, 79.0 and 96.8 kJ mol^{-1}. The energy of activation for thermal decomposition of P-1,2-DADBr is less as compared to P-1,4-DADBr, may be due to the ortho effect which have already been reported for amine nitrates [11] and perchlorates [12] (Fig. 5).

Isoconversional method is known to evaluate the activation energy values at progressive degrees of conversion without modelistic assumptions. In our case, we have adopted the isoconversional method reported by Vyazovkin [15, 16]. This approach indicates that the decomposition of these salts is not simple as indicated by model fitting method. As can be seen from Fig. 6, initially E_a values for thermal decomposition of both salts are lower in alpha range 0.05–0.1, which increases to high values in the range of 0.1–0.3 and after this range E_a is nearly constant for both the salts.

Scheme 1 Thermolytic pathways of PDADBr



P.T.- Proton Transfer

Table 4 Arrhenius parameters for isothermal decomposition of PDADBr P-1,2-DADBr P-1,4-DADBr

S. no.	Reaction models	E /kJ mol^{-1}	r	E/kJ mol^{-1}	r
1	Power law	79.0	0.9762	97.2	0.9143
2	Power law	79.2	0.9760	97.3	0.9154
3	Power law	79.7	0.9755	97.4	0.9174
4	Power law	81.6	0.9733	97.5	0.9263
5	One-dimensional diffusion	82.2	0.9725	97.3	0.9293
6	Mampel (first order)	81.3	0.9737	97.2	0.9265
7	Avrami–Erofeev	79.5	0.9757	97.2	0.9176
8	Avrami–Erofeev	79.8	0.9754	97.3	0.9188
9	Avrami–Erofeev	80.3	0.9749	97.3	0.9210
10	Contracting sphere	81.2	0.9738	97.4	0.9252
11	Three-dimensional diffusion	82.4	0.9725	96.8	0.9321
12	Contracting cylinder	81.1	0.9739	97.4	0.9245
13	Prout–Tomkins	79.2	0.9761	97.1	0.9162
14	Ginstling–Brounshtein	82.4	0.9725	97.0	0.9312

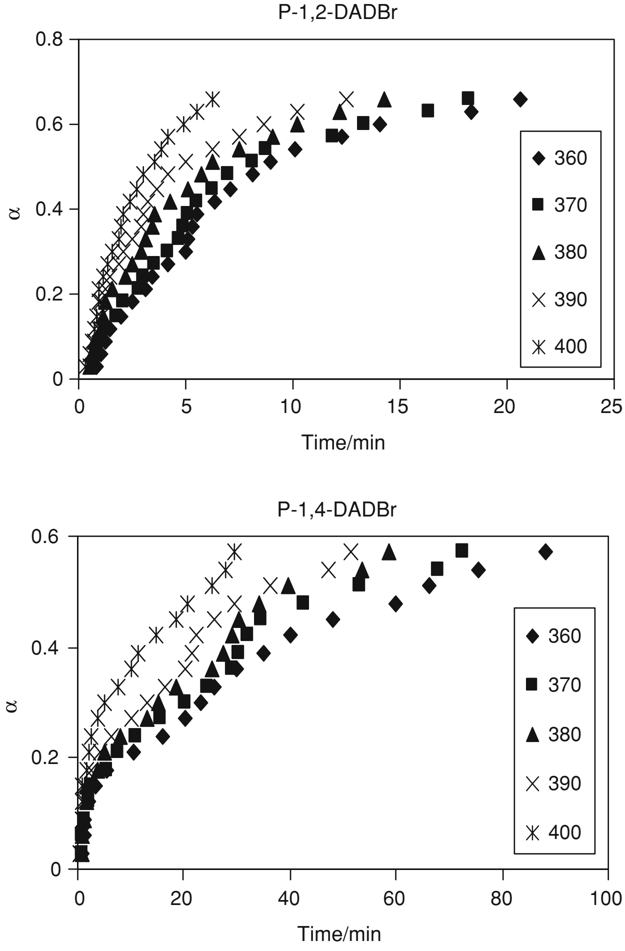


Fig. 5 Isothermal TG of PDADBr salts

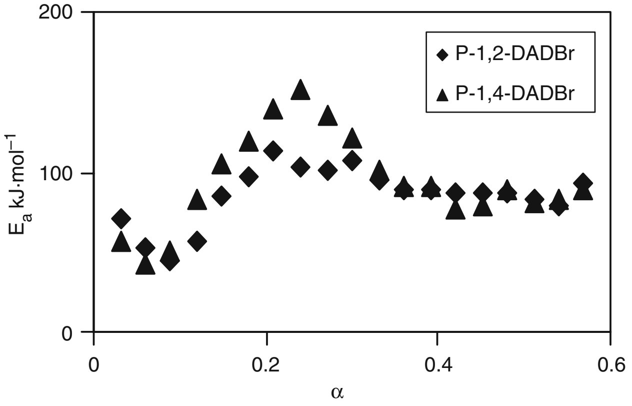


Fig. 6 Dependencies of activation energy on the extent of conversion

Conclusions

Thermal decomposition of PDADBr occurs principally by dissociation into HBr and the corresponding phenylenediamine. The regenerated parent compounds may then further go into vapor phase (dissociative sublimation) and/or undergo oxidative decomposition in the condensed phase. The results show that proton transfer reaction plays an important role in the thermal decomposition of these salts.

Acknowledgements Thanks are due to Head of Chemistry Department for providing laboratory facilities. Council of Science and Industrial Research (CSIR) is also thanked for financial assistance to Dr. Pratibha Srivastava (Research Associate) and Dr. Gurdip Singh (Emeritus Scientist).

References

1. Rodebush WR, Michaliks JC. The vapor pressure and vapor density of intensively dried ammonium chloride. J Am Chem Soc. 1929;51:748–59.
2. Mack JL, Wilmot GB. Vaporization of some amine-type per chlorates. J Phys Chem. 1967;71:2155–9.
3. Erdey L, Gal S. Thermoanalytical investigations of high temperature fusion reactions. Talanta. 1963;10:23–36.
4. Erdey L, Gal S, Liptay G. Thermoanalytical properties of analytical-grade reagents: ammonium salts. Talanta. 1964;11:913–40.
5. Kapoor IPS, Kapoor M, Singh G. Thermolysis of hydrogen sulphate nitrate and perchlorate salts of diphenyl amine. J Therm Anal Calorim. 2009. doi:10.1007/s10973-009-0230-1.
6. Singh G, Srivastava P, Srivastava J. Studies on (non) energetic compounds part: 38 kinetics of thermolysis of dichloroanilinium bromide salts. J Therm Anal Calorim. 2007;89:181–9.
7. Kapoor IPS, Srivastava P, Singh G, Froehlich R. Preparation, characterization and crystal structure of phenylene-1,3-diammonium sulfate. Indian J Chem A. 2006;45:1820–4.
8. Kapoor IPS, Srivastava P, Singh G. Sulfonation of arylamines Part 16. Preparation, characterization and kinetics of thermal decomposition of benzenediammonium sulfates. J Therm Anal Calorim. 2008;92(2):553–8.
9. Singh G, Felix SP, Soni P. Studies on energetic compounds part 28: thermolysis of HMX and its plastic bonded explosives. Thermochim Acta. 2003;399:153–65.

10. Singh G, Srivastava J. Studies on (non)energetic compounds part 44: kinetics of thermolysis of dichloroanilinium chloride salts. Indian J Chem Technol. 2004;11:834–42.
11. Kapoor IPS, Srivastava P, Singh G. Preparation, characterization and thermolysis of phenylenediammonium dinitrate salts. J Hazard Mater. 2008;150:687–94.
12. Kapoor IPS, Srivastava P, Singh G, Singh UP, Frohlich R. Preparation, crystal structure and thermolysis of phenylenediammonium diperchlorate salts. J Phys Chem. 2008;112:652–9.
13. Kapoor IPS, Srivastava P, Singh G, Frohlich R. Preparation, crystal structure and thermal decomposition of phenylenediammonium dichloride salts. Indian J Chem A. 2007;46:1277–82.
14. Bhalerao UT, Mathur SN, Rao SN. Trialkyl acyl ammonium halides—a new series of phase transfer catalysts. Synth Commun. 1992;22:1645–9.
15. Vyazovkin S. Kinetic concepts of thermally stimulated reactions in solids: a view from a historical perspective. Int Rev Phys Chem. 2000;19:45–60.
16. Vyazovkin S. Computational aspects of kinetic analysis: part C. The ICTAC kinetics project-the light at the end of the tunnel. Thermochim Acta. 2000;355:155–63.