ANALYTICAL PYROLYSIS OF ALKYLAMMONIUM TETRAPHENYLBORATES

M. N. Akhtar* and S. U. Sheikh

Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

Abstract

Various alkylammonium, dialkylammonium, trialkylammonium and tetraalkylammonium tetraphenylborates were prepared. The thermal decomposition curves of RNH_3BPh_4, $R_2NH_2BPh_4$, R_3NHBPh_4 and R_4NBPh_4 (where R = Me, Et, n-Bu) in nitrogen atmosphere indicate that the elimination of volatile matter leads to the formation of both 1:1 complex of trialkylamino triphenylborane and dialkylamino diphenylborene. Further elimination of volatile matter leads to the formation of borazine at 600–680°C. When borazine is further heated at 980–1090°C an exothermic change indicates the polycyclic condensation of the borazine leading to the formation of boron nitride. The volatile matter evolved in these reactions was measured quantitatively and reaction mechanisms were suggested.

Keywords: alkylammonium tetraphenylborates, pyrolysis, reaction mechanism

Introduction

During the least two decades, there has been considerable interest in the study of primary alkylammonium haloborates leading to the formation of polyborazynes $(RNBX)_n$ [1–4]. The major tendency of reactions between boron nitrogen compounds is to generate small rings (n = 3, 4). It was thought that it would be interesting to confine polymerization to linear structural compounds to inhibit the formation of ring type structures. In an attempt to prepare linear polymers, a number of tetraalkylammonium haloborates were obtained and py-

---

*   For correspondence P.O. Box# 967 King Fahad University of Petroleum & Minerals, Dhahran 31261, Kingdom of Saudi Arabia.

rolysis studies of these compounds using thermoanalytical [5] and macroscopic bench pyrolysis techniques have yielded interesting results. In part one [6] of this work we have studied the mechanism of the formation of linear boron nitrogen polymers of the type (i), (ii) and (iii) during thermal decomposition of alkylammonium tetraphenylborates in normal atmosphere.

The present work is part of the extensive research aimed at studying the mechanism of the formation of intermediates during the formation of boron nitride.

Experimental

Thermal analysis was carried out using a Netzsch simultaneous thermal analyser STA 429, which measures TG and DTA simultaneously on the same sample.

In all runs, the samples (30–50 mg) were placed in small platinum crucibles. The crucibles were then mounted on a palladium-ruthenium platform on twin ceramic stems in such a way that the beads of two Pt/Pt-13%Rh thermocouples came within the base recess of each crucible. The platform was also connected to the microbalance in such a way that slight changes in the weight of the samples were indicated. Alumina was used as reference material. The furnace was controlled at a heating rate of 10 deg·min^{-1}. All experiments were performed in nitrogen atmosphere.

Results and discussion

The preparation of tetraphenylborates, $RNH_3^+BPh_4^-$, $R_2NH_2^+BPh_4^-$, $R_3NH^+BPh_4^-$ and $R_4N^+BPh_4^-$ (R = Me, Et, n-Bu), has already been described in the literature [7, 8]. Tetraphenylborates were prepared by the interaction of al-

kylhalides (1 M) with sodium tetraphenylborate (1 M) in aqueous medium. The white crystalline compounds were obtained after recrystallization. The results are given in Table 1. The thermal decomposition of all these tetraphenylborates was studied using TG and DTA techniques in nitrogen atmosphere.

Table 1 Preparation of tetraphenylborates

| Compounds | Yield/ % | M.P. | Analysis/% | | | |
| | | | Found | | Calculated | |
			N	B	N	B
MeNH$_3$BPh$_4$	83.5	139.7[a]	3.89	3.21	3.99	3.13
Me$_2$NH$_2$BPh$_4$	85.1	172.2[a]	3.81	2.99	3.84	3.00
Me$_3$NHBPh$_4$	85.6	224.5[a]	3.42	2.69	3.69	2.90
Me$_4$NBPh$_4$	86.3	350.0[a]	3.54	2.82	3.56	2.80
EtNH$_3$BPh$_4$	86.1	164.4[a]	3.88	3.15	3.84	3.01
Et$_2$NH$_2$BPh$_4$	81.6	110.2	3.60	2.85	3.56	2.80
Et$_3$NHBPh$_4$	82.5	116.2	3.31	2.63	3.33	2.61
Et$_4$NBPh$_4$	85.4	200.0[a]	3.14	2.47	3.12	2.45
Bu^{n}NH$_3$BPh$_4$	81.2	156.6[a]	3.61	2.85	3.56	2.80
Bu$^n{}_4$NH$_3$BPh$_4$	86.8	205.0[a]	2.46	1.95	2.49	1.96

[a]Melting with decomposition.

Alkylammonium tetraphenylborates

The TG curves are presented in Fig. 1 and the results are listed in Table 2 for alkylammonium tetraphenylborates, RNH$_3^+$BPh$_4^-$.

When R = Me, the first inflection indicates the loss of (1 mole, 20.87%) benzene leading to the formation 1:1 complex of methylammine triphenylborane MeNH$_2$BPh$_3$, the second inflection shows the loss of a mixture of benzene (2 moles) and methylbenzene (1 mole) (Total loss 70.84%). The residue appeared to be boron nitride.

When R = Et, the first inflection indicates the loss of (0.5 mole, 10.4%) benzene and the second inflection shows the loss of a mixture of benzene and ethylborazine (2.5 moles and 1 mole, respectively, total loss 89.3%).

When R = n-Bu, the loss of (2 moles, 40.12%) benzene leading to the formation of an intermediate butylamino diphenylborene, n-BuNHBPh$_2$. Further loss of (1 mole, 54.33%) mixture of benzene and n-butylbenzene was observed. The residue seemed to be composed of boron nitride.

Dialkylammonium tetraphenylborates

TG curves are presented in Fig. 1 and the results in Table 2 for dialkylammonium tetraphenylborates, $R_2NH_2^+BPh_4^-$.
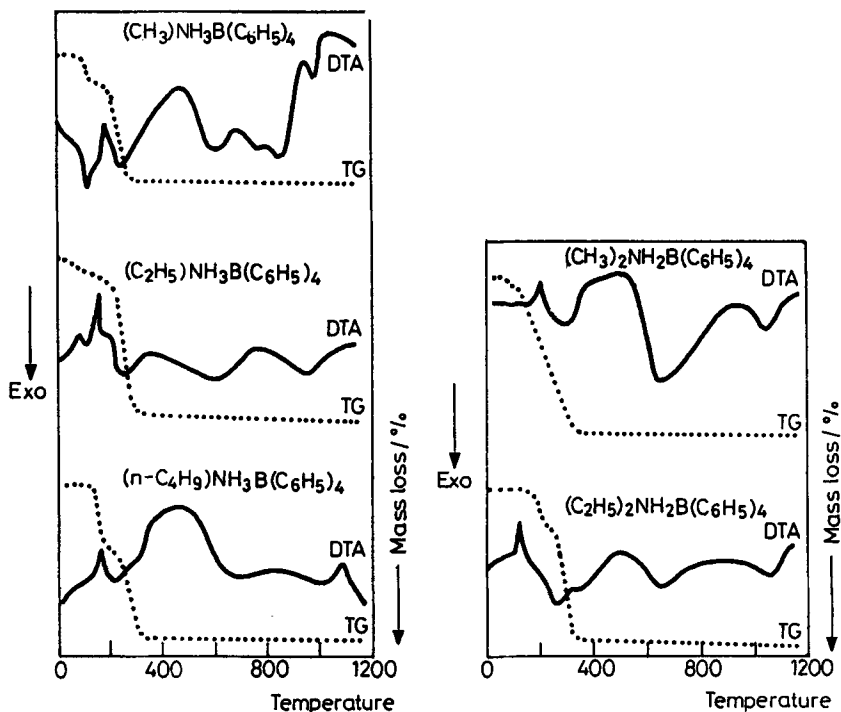

Fig. 1 TG/DTA curves of mono and dialkylammonium tetraphenylborates

When R = Me, the first inflection shows the loss of (0.17 mole, 3.83%) benzene. The second inflection shows the loss of (1.83 moles and 2 moles, respectively, total loss 92.7%) a mixture of benzene and methylbenzene. The residue is presumably boron nitride.

When R = Et, the loss of (1 mole, 20.5%) benzene results in the formation of the 1:1 complex of diethylamine triphenylborane, Et_2NHBPh_3 as an intermediate, which shows a further loss of a mixture of benzene and ethylbenzene (1 mole and 2 moles, respectively, total loss 76.18%). The residue appeared to be boron nitride.

Trialkylammonium tetraphenylborates

The TG curves are presented in Fig. 2 and results in Table 2 for trialkylammonium tetraphenylborates, $R_3NH^+BPh_4^-$.

Table 2

TG and DTA results

Compound	Temp.	Wt. loss/%		DTA	Nitrogen atmosphere	
		Found	Calcd.		Volatile matter	Intermediate and residue
$(CH_3)NH_3B(C_6H_5)_4$	139.3	20.87	22.22	Exo	C_6H_6	$CH_3NH_2B(C_6H_5)_4$
	263.4	70.24	70.66	Exo	$2(C_6H_6);CH_3C_6H_5$	BN
	620	–	–	Exo	–	–
	989	–	–	Exo	–	–
$(C_2H_5)NH_3B(C_6H_5)_4$	113.7	–	–	Endo	–	–
	169.0	10.4	10.7	Endo	$0.5(C_6H_6)$	$C_2H_5NH_{2.5}B(C_6H_5)_{3.5}$
	180	89.3	89.6	–	$2.5(C_6H_6);C_2H_5NBC_6H_5$	–
	640	–	–	Exo	–	–
	970	–	–	Exo	–	–
$(n-C_4H_9)NH_3B(C_6H_5)_4$	159	40.1	39.7	Endo	$2(C_6H_6)$	$n-C_4H_9NHB(C_6H_5)_2$
	200	54.8	53.9	Endo	$C_6H_6;C_4H_9-C_6H_5$	BN
	680	–	–	Exo	–	–
	1089	–	–	Endo	–	–
$(CH_3)_2NH_2B(C_6H_5)_4$	90	3.83	3.56	Endo	$0.17(C_6H_6)$	$(CH_3)_2NH_{1.83}B(C_6H_5)_{3.83}$
	190	92.8	89.6	Endo	$1.83(C_6H_6);2CH_3-C_6H_5$	BN
	645	–	–	Exo	–	–
	1035	–	–	Exo	–	–

Table 2 Continued

Compound	Temp.	Wt. loss/%		DTA	Nitrogen atmosphere	
		Found	Calcd.		Volatile matter	Intermediate and residue
$(C_2H_5)_2NH_2B(C_6H_5)_4$	109	–	–	Endo	–	–
	149	20.5	19.9	–	C_6H_6	$(C_2H_5)_2NHB(C_6H_5)_3$
	257	76.19	73.98	Exo	$C_6H_6;2(C_2H_5-C_6H_5)$	BN
	645	–	–	Exo	–	–
	1065	–	–	Exo	–	–
$(CH_3)_3NHB(C_6H_5)_4$	210	19.86	20.58	Endo	C_6H_6	$(CH_3)_3NB(C_6H_5)_3$
	400	70.95	72.82	Exo	$3(CH_3-C_6H_5)$	BN
	640	–	–	Exo	–	–
	1040	–	–	Exo	–	–
$(C_2H_5)_3NHB(C_6H_5)_4$	161	42.23	43.70	Endo	$C_6H_6;C_2H_5-C_6H_5$	$(C_2H_5)_2NB(C_6H_5)_2$
	170	53.21	50.35	–	$2(C_2H_5-C_6H_5)$	BN
	640	–	–	Exo	–	–
	1070	–	–	Exo	–	–
$(CH_3)_4NB(C_6H_5)_4$	360	–	–	Endo	–	–
	400	95.0	93.64	–	$4(CH_3-C_6H_5)$	BN
	630	–	–	Exo	–	–
	1075	–	–	Exo	–	–

Table 2 Continued

TG and DTA results

Compound	Temp.	Wt. loss/%		DTA	Nitrogen atmosphere	
		Found	Calcd.		Volatile matter	Intermediate and residue
$(C_2H_5)_4NB(C_6H_5)_4$	206	6.2	5.9	Exo	$0.25(C_2H_5-C_6H_5)$	$(C_2H_5)_{3.75}NB(C_6H_5)_{3.75}$
	370.9	86.48	88.53	Exo	$3.75(C_2H_5-C_6H_5)$	BN
	690	–	–	Exo	–	–
	1010	–	–	Exo	–	–
$(n\text{-}C_4H_9)_4NB(C_6H_5)_4$	220	94.5	95.54	Exo	$4(C_4H_9-C_6H_5)$	BN
	670	–	–	Exo	–	–
	1040	–	–	Exo	–	–
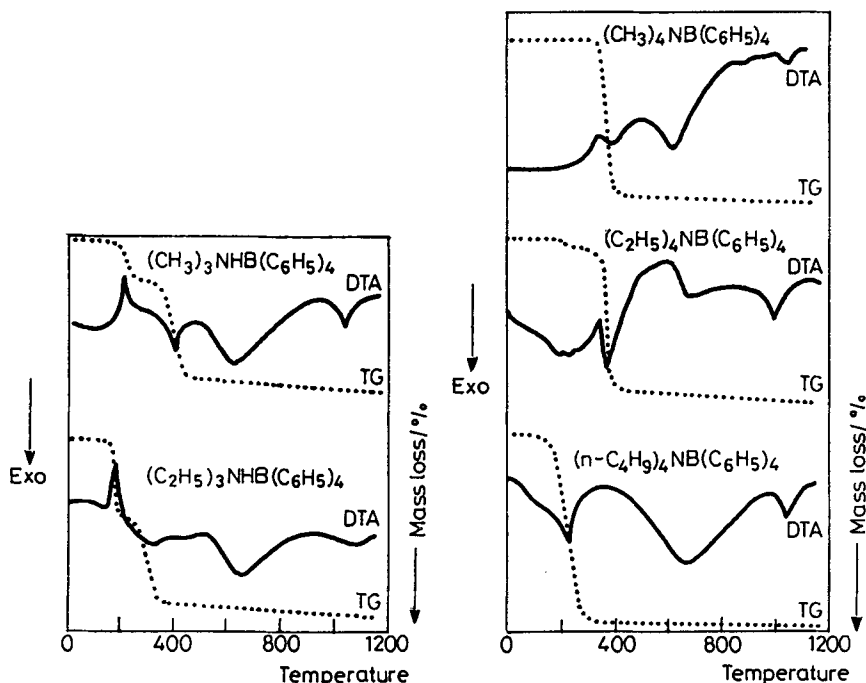
Fig 2 TG/DTA curves of tri- and tetraalkylammonium tetraphenylborates

When R = Me, the loss of (1 mole, 19.86%) benzene is observed, leading to the formation of an intermediate 1:1 complex of trimethylamino triphenylborane, Me_3NBPh_4. Further loss of (3 moles, 70.95%) methylbenzene gives rise to boron nitride.

When R = Et, the loss of (1 mole, 42.23%) a mixture of benzene and ethylbenzene is observed leading to the formation of the intermediate diethylamino diphenylborene, Et_2NBPh_2. Further loss of (2 moles, 53.21%) ethylbenzene occurs and the residue seems to be boron nitride.

Tetraalkylammonium tetraphenylborates

The TG curves are presented in Fig. 2 and the results in Table 2 for tetraalkyl- ammonium tetraphenylborates, $R_4N^+BPh_4^-$.

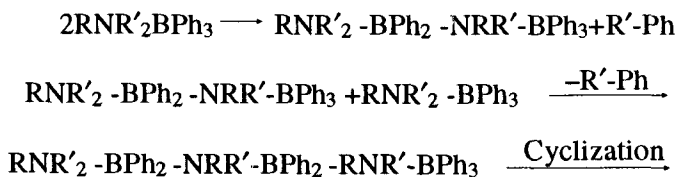When R = Me, the loss of (4 moles, 95.1%) methylbenzene occurs with the formation of boron nitride.

When R = Et, the loss of (0.25 mole, 6.2%) ethylbenzene is indicated. Further loss of (3.75 moles, 86.48%) ethylbenzene results in the formation of boron nitride residue.

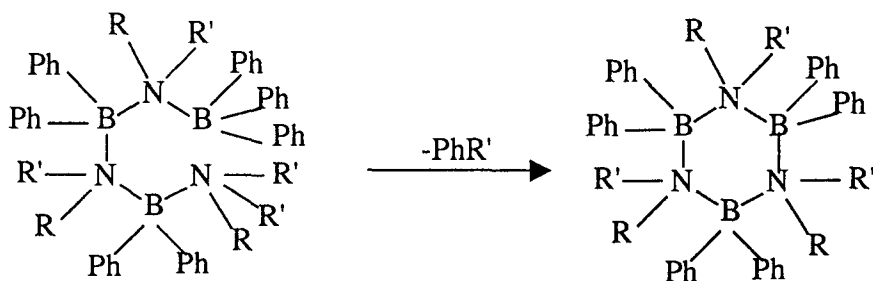When R = n-Bu, the loss of (4 moles, 94.5%) n-butylbenzene occurs with the formation of boron nitride residue.

The DTA traces of alkylammonium, dialkylammonium, trialkylammonium and tetraalkylammonium tetraphenylborates are presented in Figs 1 and 2 and results are given in Table 2. The DTA curve exhibits an endothermic decomposition in the range of 100–160°C indicating the elimination of benzene or alkylbenzene resulting in the formation of 1:1 complex, which is followed by an exothermic peak in the range of 200–400°C corresponding to the evolution of volatile matter and resulting in the formation of borazine. The volatilization of borazine is indicated by a broad exothermic peak in the range of 600–680°C. An other exothermic peak in the range of 980–1090°C indicates the polycyclic condensation of the borazine ring leading to the formation of boron nitride.
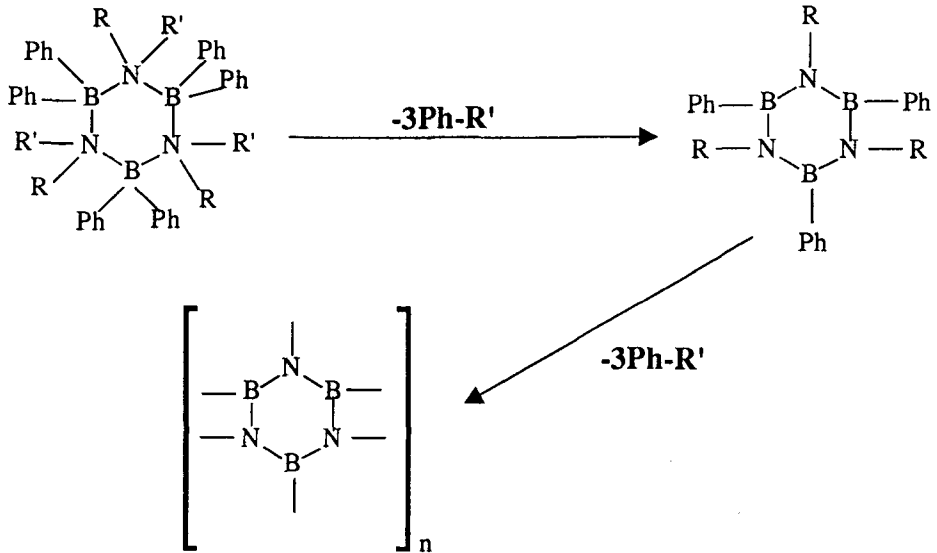
On the basis of TG and DTA results in was concluded that trimeric linear boranoamine was formed when the amino diphenyl borene or amino triphenyl borane was heated and both benzene and alkylbenzene evolved. The resulting trimer undergoes intermolecular ring closure to form borazane which loses benzene or alkylbenzene to yield borazine. On further heating ring fusion occurs with the evolution of one mole of alkylbenzene to give boron nitride.

The reaction sequence is given below.

$$2RNR'_2BPh_3 \longrightarrow RNR'_2\text{-}BPh_2\text{-}NRR'\text{-}BPh_3 + R'\text{-}Ph$$

$$RNR'_2\text{-}BPh_2\text{-}NRR'\text{-}BPh_3 + RNR'_2\text{-}BPh_3 \xrightarrow{\ -R'\text{-}Ph\ }$$

$$RNR'_2\text{-}BPh_2\text{-}NRR'\text{-}BPh_2\text{-}RNR'\text{-}BPh_3 \xrightarrow{\ Cyclization\ }$$

R = Me, Et and n-Bu. and R' = H, Me, Et and n-Bu

-3Ph-R'

-3Ph-R'

References

1 M. F. Lappert and M. K. Mujumdar, Proc. Chem. Soc., (1963) 88.
2 J. C. Sheldon and B. C. Smith, Quart. Rev., 14 (1960) 200.
3 B. C. Burg and J. Banus, J. Am. Chem. Soc., 76 (1964) 390.
4 H. S. Turner and R. J. Warne, Proc. Chem. Soc., (1962) 69.
5 S. U. Sheikh, Bull. Chem. Soc. Jpn., 49 (1976) 2879.
6 S. U. Sheikh, M. Naseem Akhtar and T. Ahmed, Thermochim. Acta, 165 (1990) 1.
7 S. U. Sheikh, T. Mahmood and Munir-ul-Haq, Proc. ESTA, 1–4 Sep. (1981) 131.
8 S. U. Sheikh, J. Thermal Anal., 18 (1980) 299.

Zusammenfassung — Es wurden verschiedene Alkylammonium-, Dialkylammonium-, Trialkylammonium- und Tetralkylammoniumtetraphenylborate hergestellt. Die thermischen Zersetzungskurven von RNH_3BPh_4, $R_2NH_2BPh_4$, R_3NHBPh_4 und R_4NBPh_4 (mit $R=$ Me, Et, n-Bu) in Stickstoff zeigen, daß die Eliminierung flüchtiger Substanzen zur Bildung eines 1:1-Komplexes von Trialkylaminotriphenylboran und Dialkylaminodiphenylboren führt. Die weitere Eliminierung flüchtiger Substanzen führt zur Bildung von Borazin bei 600 bis 680°C. Wird Borazin weiter erhitzt, zeigt eine exotherme Umsetzung bei 980–1090°C die polycyclische Kondensation von Borazin an, wobei Bornitrid gebildet wird. Die flüchtigen Substanzen dieser Reaktion wurden quantitativ bestimmt und ein Reaktionsmechanismus vorgeschlagen.