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THERMAL DECOMPOSITION OF SUBSTITUTED TETRAPHENYLBORATES

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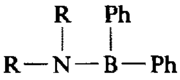
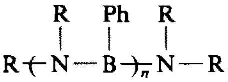
ABSTRACT

Combined TG/DTA and pyrolysis by a bench technique have been used to study alkylammonium, dialkylammonium, trialkylammonium and tetraalkylammonium tetraphenylborates, $RNH_3^+BPh_4^-$, $R_2NH_2^+BPh_4^-$, $R_3\overset{+}{N}HBPh_4^-$ and $R_4\overset{+}{N}BPh_4^-$ (where R ≡ Me, Et or Bu^n) with the formation of polymeric compounds of the type **I**, **II** and **III**, and elimination of benzene, alkylbenzene and traces of boron triphenyl.



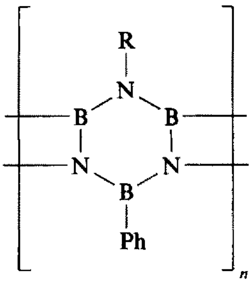
$$R-\overset{R}{\overset{|}{N}}-\overset{Ph}{\overset{|}{B}}-Ph$$

I



$$R\left(\overset{R}{\overset{|}{N}}-\overset{Ph}{\overset{|}{B}}\right)_n\overset{R}{\overset{|}{N}}-R$$

II



III

The volatiles evolved in these reactions were measured quantitatively and reaction mechanisms are suggested.

INTRODUCTION

During the last 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 and nitrogen compounds is to generate small rings (n = 3, 4). It was thought that it would be interesting to confine polymerisation to linear structural compounds only by introducing steric conditions to inhibit the

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formation of a ring-type structure. In an attempt to prepare linear polymers, a number of tetraalkylammonium haloborates were obtained and pyrolysis studies of these compounds using thermoanalytical [5] and macroscopic bench pyrolysis techniques have yielded very interesting results. In this paper we report the second part of the investigation to trace the reaction sequence in the preparation of linear polymers.

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 the 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 such 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 °C min^{-1}. All experiments were performed in normal atmosphere.

RESULTS AND DISCUSSION

The preparation of tetraphenyl borates, $R\overset{+}{N}H_3\overset{-}{B}Ph_4$, $R_2\overset{+}{N}H_2\overset{-}{B}Ph_2$, $R_3\overset{+}{N}H\overset{-}{B}Ph_4$ and $R_4\overset{+}{N}BPh_4$ ($R \equiv$ Me, Et or Bu^n), has already been described

TABLE 1

Preparation of tetraphenylborates

Compounds	Yield (%)	m.p. (°C)	Analysis (%)			
			Found		Calculated	
			N	B	N	B
$MeNH_3BPh_4$	83.5	139.7 [a]	3.89	3.21	3.99	3.13
$Me_2NH_2BPh_4$	85.1	172.2 [a]	3.81	2.99	3.84	3.01
Me_4NBPh_4	86.3	350.0 [a]	3.54	2.82	3.56	2.80
$EtNH_3BPh_4$	86.1	164.4 [a]	3.88	3.15	3.84	3.01
$Et_2NH_2BPh_4$	81.62	110.2	3.60	2.85	3.56	2.80
Et_3NHBPh_4	82.5	116.2	3.31	2.63	3.33	2.61
Et_4NBPh_4	85.35	200.0 [a]	3.14	2.47	3.12	2.45
$Bu^nNH_3BPh_4$	81.2	156.6 [a]	3.61	2.85	3.56	2.80
$(Bu^n)_4NBPh_4$	86.8	205.0 [a]	2.46	1.95	2.49	1.96

[a] Melting with decomposition.

in the literature [6,7]. Tetraphenylborates were prepared by the interaction of alkylammonium halides (1 M) with sodium tetraphenylborate (1 M) in aqueous medium. The white crystalline compounds were recovered after recrystallisation, see Table 1.

We have studied the decomposition of alkylammonium, dialkylammonium, trialkylammonium and tetraalkylammonium tetraphenylborates, $\mathrm{RN\overset{+}{H}_3\overset{-}{B}Ph_4}$, $\mathrm{R_2N\overset{+}{H}_2\overset{-}{B}Ph_4}$, $\mathrm{R_3N\overset{+}{H}\overset{-}{B}Ph_4}$ and $\mathrm{R_4\overset{+}{N}\overset{-}{B}Ph_4}$ (where R ≡ Me, Et or Bu^n), in the absence of solvent, by thermal analysis, and on a larger scale, by a macro bench pyrolysis technique.

Alkylammonium tetraphenylborates

Figure 1 shows the TG curves for alkylammonium tetraphenylborate when R ≡ Me, Et or Bu^n. The loss of 1 and 3 molecules of benzene, see Table 2, indicates the formation of the 1:1 complex, $\mathrm{RNH_2BPh_3}$, and *B*-triphenyl-*N*-trialkylborazine, $\frac{1}{3}\mathrm{(RNBPh)_3}$. When R represents Me or Et groups, it appears that decomposition beyond the 1 : 1 complex stage does not lead to the formation of borazine; instead, evolution of benzene (Table 2) increases to $\frac{2}{3}$ molecule, indicating the formation of an ill-defined polymer. It appears that the reaction of the 1 : 1 complex to yield borazine is complicated, no clearly discernable intermediates being isolated.

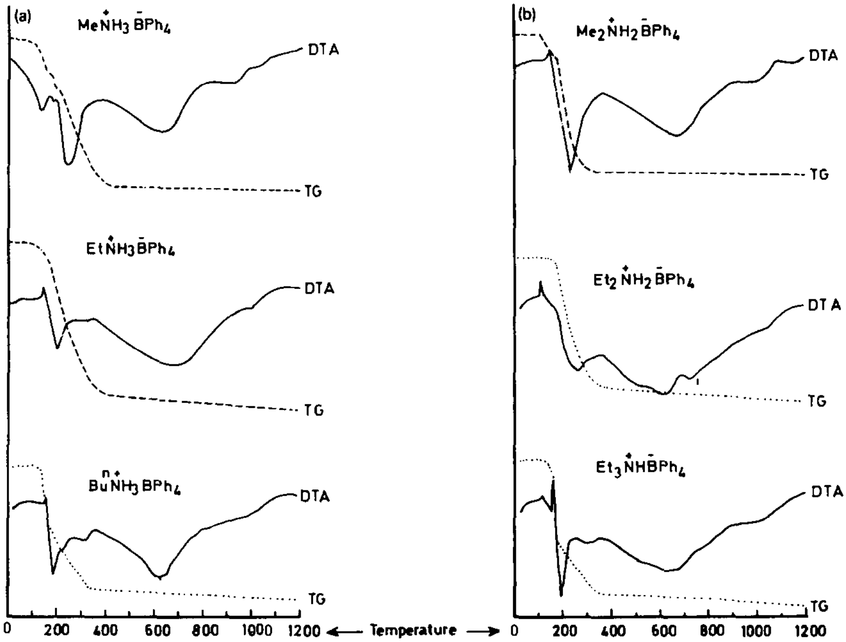


Fig. 1. Combined TG/DTA curves for mono-, di- and tri-alkylammoniumtetraphenylborates.

TABLE 2

TG and DTA results of tetraphenylborates

Compound	Temperature	Weight loss (%)		DTA	Volatile matter	Intermediates and residues
		Found	Calculated			
$MeNH_3BPh_4$	139.7	21.24	22.22	Exo	C_6H_6	$CH_3NH_2B(C_6H_5)_3$
	184.9	8.09	7.41	Exo	$\frac{1}{3}(C_6H_6)$	$CH_3NH_{5/3}B(C_6H_5)_{8/3}$
	284.7	55.79	54.51	Exo	$\frac{5}{3}(C_6H_6)$; $\frac{2}{3}(CH_3{-}C_6H_5)$	$(CH_3)_{1/3}NB(C_6H_5)_{1/3}$
$Me_2NH_2BPh_4$	121	10.40	10.70	Exo	$\frac{1}{2}(C_6H_6)$	$(CH_3)_2NH_{3/2}B(C_6H_5)_{7/2}$
	231.70	70.50	74.00	Exo	$\frac{3}{2}(C_6H_6)$; $\frac{5}{3}(CH_3{-}C_6H_5)$	$(CH_3)_{1/3}NB(C_6H_5)_{1/3}$
	700.00	8.90	8.40	Exo	$\frac{1}{3}(CH_3{-}C_6H_5)$	...B–N–...
$EtNH_3BPh_4$	164.40	–	–	Endo	–	–
	212.9	85.88	85.47	Exo	$3C_6H_6$; $\frac{2}{3}(C_2H_5{-}C_6H_5)$	$(C_2H_5)_{1/3}NB(C_6H_5)_{1/3}$
	670.3	–	–	Exo	–	–
$Et_2NH_2BPh_4$	110	–	–	Endo	–	–
	261.7	83.90	84.65	Exo	$2C_6H_6$; $\frac{5}{3}(C_2H_5{-}C_6H_5)$	$(C_2H_5)_{1/3}NB(C_6H_5)_{1/3}$
	628.4	–	–	Exo	–	–
Et_3NHBPh_4	116.2	–	–	Endo	–	–
	163.6	50.59	52.09	Endo	C_6H_6; $\frac{4}{3}(C_2H_5{-}C_6H_5)$	$(C_2H_5)_{5/3}NB(C_6H_5)_{5/3}$
	303	33.93	33.57	Exo	$\frac{4}{3}(C_2H_5{-}C_6H_5)$	$(C_2H_5)_{1/3}NB(C_6H_5)_{1/3}$
	680	–	–	Exo	–	–
Et_4NBPh_4	200.8	12.92	11.80	Exo	$\frac{1}{2}(C_2H_5{-}C_6H_5)$	$(C_2H_5)_{7/2}NB(C_6H_5)_{7/2}$
	320.7	81.07	82.62	Exo	$\frac{7}{2}(C_2H_5{-}C_6H_5)$	...NB...
	690	–	–	Exo	–	–
$Bu^nNH_3BPh_4$	137.6	59.04	59.54	Exo	$3C_6H_6$;	$\frac{1}{3}(C_4H_9NB(C_6H_5)_3$
	190.6	21.82	22.73	Exo	$\frac{2}{3}(C_4H_9{-}C_6H_5)$	$(C_4H_9)_{1/3}NB(C_6H_5)_{1/3}$
	324.0	19.0	17.73	Exo	$(C_4H_9)_{1/3}NB(C_6H_5)_{1/3}$	–
	650	–	–	Exo	–	–
$Bu^n_4NBPh_4$	180	43.98	45.81	Exo	$2C_4H^n_9{-}C_6H_5$	$(C_4H^n_9)_2NB(C_6H_5)_2$
	300	31.12	33.76	Exo	$\frac{5}{3}(C_4H^n_9{-}C_6H_5)$	$(C_4H^n_9)_{1/3}NB(C_6H_5)_{1/3}$
Me_4NBPh_4	349	95.0	93.64	Exo	4MePh	BN
	621	–	–	Exo	–	–

Dialkylammonium tetraphenylborates

The TG curves for dialkylammonium tetraphenylborates, $R_2NH_2BPh_4$, are shown in Fig. 1. When $R \equiv Me$, loss of $\frac{1}{2}$ and then $1\frac{1}{2}$ molecules of benzene (Table 2) was observed. Further loss of $1\frac{2}{3}$ molecules of methylbenzene was indicated. No borazine was isolated in the system.

When $R \equiv Et$, loss of 2 molecules of benzene and of $1\frac{2}{3}$ molecules of ethylbenzene (Table 2) was observed, no intermediate being isolated in the system.

Trialkylammonium tetraphenylborates

The TG curves for triethylammonium tetraphenylborate are shown in Fig. 1. The loss of 1 molecule of benzene and of $1\frac{1}{2}$ molecules of ethylbenzene (Table 2) corresponds to the formation of an ill-defined intermediate, $(C_2H_5)_{2/3}NB(Ph)_{2/3}$. A further loss of $1\frac{1}{3}$ molecules of ethylbenzene was observed.

Tetraalkylammonium tetraphenylborates

Figure 2 shows the TG curves for tetraalkylammonium tetraphenylborates, $R_4\overset{+}{N}\overset{-}{B}Ph_4$. When $R \equiv Me$, the loss of 4 molecules of methylbenzene

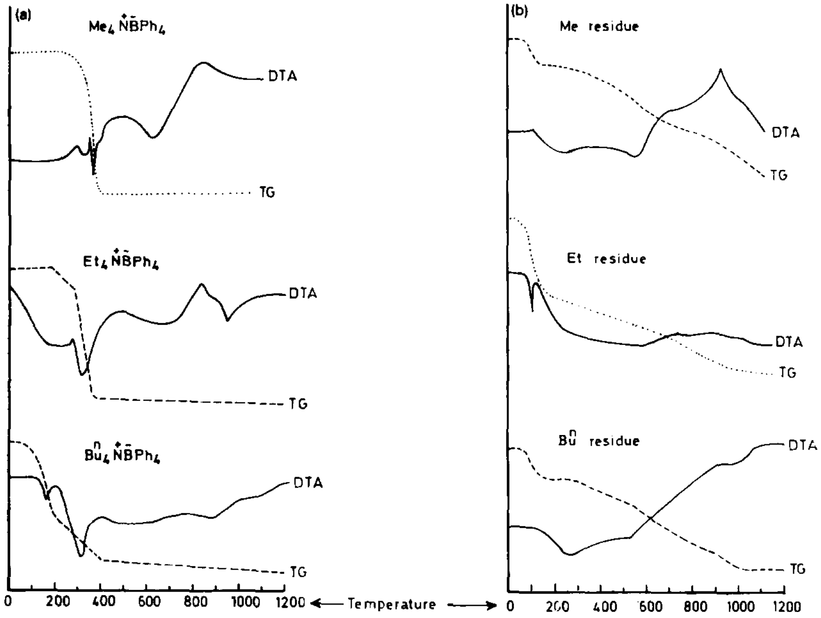


Fig. 2. Combined TG/DTA curves for the tetra-alkylammoniumtetraphenylborates (a) and for the residues (b).

leads to the formation of a probable boron nitride polymer. When R ≡ Et, the loss of a $\frac{1}{2}$ molecule of ethylbenzene and the further loss of $3\frac{1}{2}$ molecules of ethylbenzene probably results in the formation of boron nitride polymer.

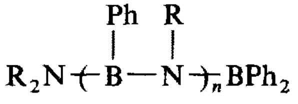
Where R ≡ Bu^n, loss of 2 molecules of butylbenzene leads to the formation of dibutylaminodiphenylborane intermediate. A further loss of $1\frac{2}{3}$ molecules of butylbenzene was observed.

DTA of alkylammonium tetraphenylborates

The DTA curves of alkylammonium tetraphenylborates, RNH_3BPh_4, $R_2NH_2BPh_4$, R_3NHBPh_4 and R_4NBPh_4 where R ≡ Me, Et or Bu^n, show interesting transformations. The DTA curves are represented in Figs. 1 and 2, and the results are tabulated in Table 2. A melting endotherm with decomposition was observed in these cases. An exothermic peak in the range 200–300 °C was observed corresponding to the borazine. The volatilisation exothermic peak was observed at 600–680 °C, corresponding to the decomposition of the borazine ring in the formation of polymeric material which was further confirmed by the glass transition ranging between 1000 and 1100 °C.

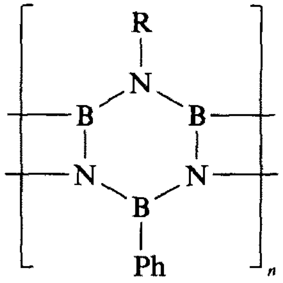
An examination of tetraphenylborates by macro bench pyrolysis shows the elimination of benzene and alkylbenzene leading to the formation of intermediates. The results are given in Table 3. The ultimate products are polymeric intermediates (residues), which were subjected to TG and DTA. The results are given in Table 4 and Fig. 2b.

It has been observed in our present work that formation of the trimeric linear boronamine occurs when the aminodiphenylborane or aminotriphenylborane adduct is heated and both benzene and traces of triphenylborane are evolved.



$$R_2N\left(\overset{\overset{\textstyle Ph}{|}}{B}-\overset{\overset{\textstyle R}{|}}{N}\right)_nBPh_2$$

(i)



(ii)

The production of polymeric material of type (i) can be accomplished by the reaction sequence given below

$$Bu^n_4NBPh_4 \longrightarrow Bu^n_2NBPh_2 + 2Bu^n{-}Ph$$

$$2Bu^n_2NBPh_2 \longrightarrow Bu^n_2N{-}BPh{-}NBu^n{-}BPh_2 + Bu^n{-}Ph$$

$$nBu^n_2NBPh_2 + nBu^n_2N{-}BPh{-}NBu^n{-}BPh_2 \longrightarrow$$
$$Bu^n_2N\left(BPh{-}NBu^n\right)BPh_2 + nBu^n{-}Ph$$

TABLE 3

Bench pyrolysis results of tetraphenylborates

Sample	Weight loss (%)		Time (h)	Temperature (°C)	Volatile matter	Residue
	Found	Calculated				
$Me_2NH_2BPh_4$	61.63	59.54	5.30	300	$2C_6H_6$; $\frac{2}{3}(CH_3{-}C_6H_6)$	$(CH_3)_{4/3}NB(C_6H_5)_{4/3}$
$Bu^nNH_3BPh_4$	75.80	70.90	7.40	300	$3(C_6H_6)$; $\frac{1}{3}(C_4H_9{-}C_6H_5)$	$(C_4H_5)_{2/3}NB(C_6H_5)_2$
$EtNH_3BPh_4$	87.84	83.74	3.00	300	$3C_6H_6$; $\frac{2}{3}(C_2H_5{-}C_6H_5)$	$(C_2H_5)_{1/3}NB(C_6H_5)_{1/3}$
$Et_2NH_2BPh_4$	72.29	75.85	7.00	300	$2C_6H_6$; $\frac{4}{3}(C_2H_5{-}C_6H_5)$	$(C_2H_5)_{2/3}NB(C_6H_5)_{2/3}$
Et_3NHBPh_4	76.21	77.28	4.00	300	C_6H_6; $\frac{7}{3}(C_2H_5{-}C_6H_5)$	$(C_2H_5)_{2/3}NB(C_6H_5)_{2/3}$

TABLE 4

TG and DTA results of bench pyrolysis residue

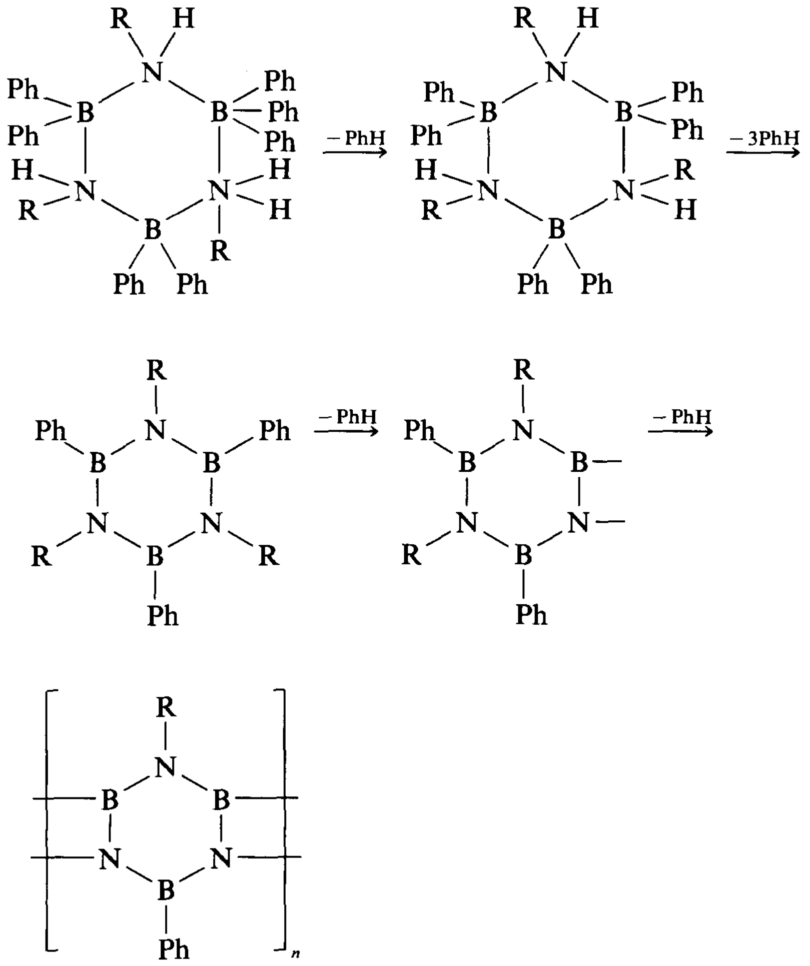
Residue	Temperature	Weight loss (%)		DTA	Volatile matter	Intermediate
		Found	Calculated			
$(CH_3)_{4/3}NB(C_6H_5)_{4/3}(0.8H_2O)$	114.0	8.99	8.88	Endo	$0.8H_2O$	$(CH_3)_{4/3}NB(C_6H_5)_{4/3}$
	555.1	18.47	18.92	Exo	$\frac{1}{3}(CH_3{-}C_6H_5)$	$\frac{1}{3}(CH_3NBC_6H_5)_3$
	935.4	15.57	18.92	Endo	$\frac{1}{3}(CH_3{-}C_6H_5)$	$(CH_3)_{2/3}NB(C_6H_5)_{2/3}$
$(C_2H_5)_{2/3}NB(C_6H_5)_{2/3}3H_2O$	102	38.03	36.1	Exo	$3H_2O$	$(C_2H_5)_{2/3}NB(C_6H_5)_{2/3}$
	–	23.82	23.6	–	$\frac{1}{3}(C_2H_5{-}C_6H_5)$	$(C_2H_5)_{1/3}NB(C_6H_5)_{1/3}$
	–	16.27	23.6	–	$\frac{1}{3}(C_2H_5{-}C_6H_5)$	$\ldots(B{-}N)_n\ldots$ incomplete decomposition
$(C_4H_9^n)_{2/3}NB(C_6H_5)_{2/3}H_2O$	111.1	14.6	13.6	Endo	H_2O	$(C_4H_9^n)_{2/3}NB(C_6H_5)_{2/3}$
	522.3	31.86	33.75	Exo	$\frac{1}{3}(C_4H_9^n{-}C_6H_5)$	$(C_4H_9)_{1/3}NB(C_6H_5)_{1/3}$
	–	10.69	16.80	–	$\frac{1}{6}(C_4H_9^n{-}C_6H_5)$	$(C_4H_9)_{1/6}NB(C_6H_5)_{1/6}$

However, when the alkyl group on the tetraphenylborate has a low molecular weight, such as Me, Et, etc., a very similar reaction sequence to the previous example may be postulated but on the basis of the dimerisation and trimerisation of aminotriphenylborane complexes, rather than that of aminodiphenylborane. The resulting trimer undergoes intermolecular ring closure to form the borazane, which then loses benzene or alkylbenzene to yield borazine. On further heating, ring fusion takes place with evolution of one molecule of alkylbenzene to give polymeric materials of type (ii). The reaction sequence is given below

$$2RNH_2BPh_3 \longrightarrow RNH_2{-}BPh_2{-}NHR{-}BPh_3 + Ph{-}H$$

$$RNH_2{-}BPh_2{-}NRH{-}BPh_3 + RNH_2BPH_3 \longrightarrow$$

$$RNH_2{-}BPh_2{-}NRH{-}BPh_2{-}NRH{-}BPh_3 + Ph{-}H$$



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