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TRANSFORMATION OF BROMOBORATES ON THERMAL ANALYSIS

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ABSTRACT

The thermal decomposition of bromoborates has been studied. The first stage of decomposition shows the loss of 1 mol of alkyl bromide giving bromoborane, isolation of which was possible in the ethyl but not in the *n*-butyl system. Thermal decomposition of borates beyond the stage of the formation of bromoboranes leads to the formation of a further amount of butyl bromide together with boron tribromide. The final product was a polymeric material.

INTRODUCTION

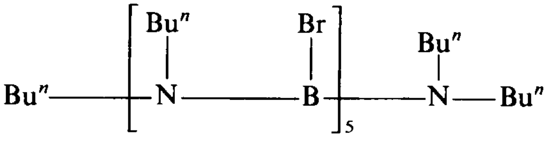
In the previous system we described the process of dealkylphenylation with the formation of polymers [1,2] having an open chain structure [3]. We introduce another interesting system where still higher molecular weight polymers are achieved. This paper describes the study of the thermal decomposition of bromoborates (R, Et, Bu^n) and of the equivalent 1 : 1 complex using both bench pyrolysis and thermoanalytical techniques.

DISCUSSION

Tetraalkylammonium bromoborate, $\mathrm{Et_4N^+BBr_4^-}$ on pyrolysis at 240–280°C for 12 h gave, in an ethyl system, triethylamine boron tribromide (1) and ethyl bromide

$$\mathrm{Et_4N^+BBr_4^-} \rightarrow \mathrm{Et_3NBBr_3} \qquad (1)$$

The residues obtained from tetra-*n*-butylammonium bromoborate were viscous oils and gums and could only be examined with difficulty. The polymers obtained, on examination, gave a molecular weight of 994 which, coupled with elemental analysis, indicates a polymeric structure approximating to that given below



$$\mathrm{Bu}^n-\left[\overset{\overset{\displaystyle \mathrm{Bu}^n}{|}}{\mathrm{N}}-\overset{\overset{\displaystyle \mathrm{Br}}{|}}{\mathrm{B}}\right]_5-\overset{\overset{\displaystyle \mathrm{Bu}^n}{|}}{\mathrm{N}}-\mathrm{Bu}^n \qquad (2)$$

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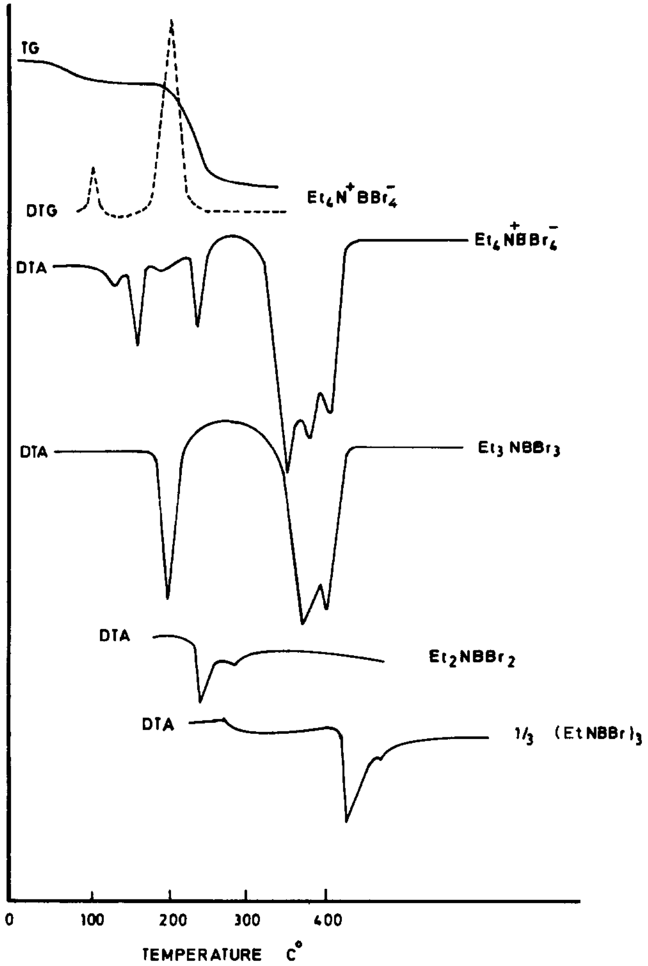


Fig. 1. Comparison of TG/DTG and DTA curves of tetraethylammonium bromoborate.

The fact that the 1 : 1 complex could not be isolated in the tetra-*n*-butylammonium compound is also shown in TG, where instead the loss of 2 mol butyl bromide was indicated (eqn. 3). However, the ethyl system shows an intermediate equivalent to the loss of (1 mol) ethylbromide, i.e., the formation of the 1 : 1 complex (Fig. 1). This is further supported by bench pyrolysis which shows that the loss of ethyl bromide (0.89 mol) was equivalent to the formation of the 1 : 1 complex (eqn. 1) which is distilled over.

$$Bu^n_4N^+BBr_4^- \rightarrow Bu^n_2NBBr_2 \qquad (3)$$

DTA affords no indication of the thermal decomposition sequence beyond the point of formation of the 1 : 1 complex except in the case of the tri-*n*-butylamine boron tribromide where there is an indication of the formation of di-*n*-butylaminoboron dichloride (eqn. 3). These indications are obtained by comparison of the equivalent DTA curves (Figs. 1 and 2).

EXPERIMENTAL

Tetraalkylammonium bromoborates, $R_4N^+BBr_4^-$ (R = Et, Bu^n), have been prepared by the interaction of the appropriate tetraalkylammonium halide and boron bromide. All values are tabulated in Table 1. $Et_4N^+BBr_4^-$ (5.22 g, 1.0 mol) was heated at 240–270°C for 12 h in an H-piece connected to a water condenser, then to a cold trap at −80°C, then to potassium hydroxide and finally to a bromine water trap.

Volatile matter (1.10 g) was collected in a flask cooled to 0°C. This volatile matter was shown to be ethylbromide (1.10 g, 6.89 mol) by elemental analysis, GLC and infrared spectroscopy.

The residue was a dark brown coloured specimen of triethylamine-boron tribromide (3.01 g).

Triethylamine-boron tribromide (28.61 g, 1.0 mol) was heated at

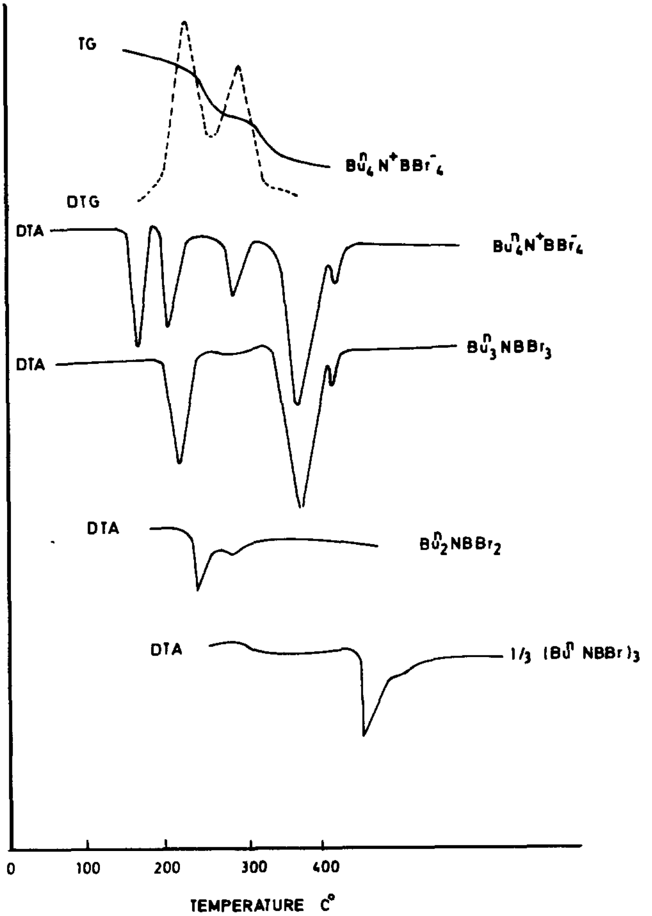


Fig. 2. Comparison of TG/DTG and DTA curves of tetra-*n*-butylammonium bromoborate.

TABLE 1
Data for the tetraalkylammonium bromoborates

Compound	Reactant	BBr_3 yield (%)	Melting point (°C)	Analysis		
				B	Br	N
$Et_4N^+BBr_4^-$	$Et_4N^+Br^-$	99.98	212 decomp.	2.20	68.9	3.04
$Bu^n_4N^+BBr_4^-$	$Bu_4^+Br^-$	96	180	1.85	55.8	2.69
Et_3NBBr_3	Et_3N	96	decomp.	3.11	69.3	3.90
Bu_3NBBr_3	Bu_3N	93	136	2.46	55.04	3.29

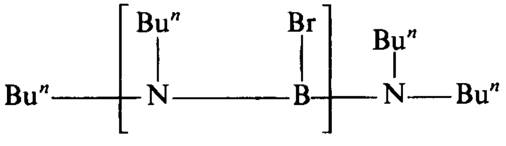
240–250°C for 48 h under reflux in the apparatus described previously.

Boron tribromide (8.80 g, 0.43 mol) was trapped at −80°C. The residue (18.43 g) was a dark coloured viscous liquid (found: B, 4.77; Br, 63.14; N, 6.53%) insoluble in toluene and chloroform. This residue (13.85 g) was heated at 140–180°C/0.01 mm. A distillate (3.69 g) was collected in a flask and ethylbromide (0.7 g, 0.8 mol) and boron tribromide (1.12 g, 0.5 mol) were trapped at −80°C. This distillate (3.69 g) (found: B, 5.30; Br, 58.08; N, 6.82%; b.p., 84–88°C/0.1 mm) was probably a mixture, and with petroleum (b.p., 30–40°C) it afforded a solid (0.93 g) which was filtered off and dried (m.p., 105–107°C; found: B, 4.29; Br, 71.06; N, 5.43; M.Wt., vapour pressure method in toluene at 37°C, 476; calc. for $C_8H_{20}B_2Br_4N_2$: B, 4.49; Br, 65.8; N, 5.78; M.Wt., 484). Evaporation of the solvent from the filtrate afforded a viscous polymeric liquid (2.09 g; found: B, 6.21; Br, 57.07; N, 7.82; M.Wt., vapour pressure method in toluene at 37°C, 497; calc. for $C_8H_{20}B_3Br_4N_3$: B, 6.07; Br, 62.6; N, 8.25; M.Wt. 509).

Tetra-*n*-butylammonium tetrabromoborate, $Bu^n_4N^+BBr_4^-$ (16.46 g, 1.0 mol) was heated at 240–270°C for 12 h. Volatile matter (10.53 g) was received in a flask and also (0.078 g) in the cold trap at −80°C. The volatile matter was examined by elemental analysis, GLC and infrared spectroscopy and shown to be:

(a) *n*-butyl bromide (6.62 g, 1.68 mol);
(b) *s*-butyl bromide (1.59 g, 0.40 mol);
(c) boron tribromide (0.078 g, 0.011 mol) in cold trap at −80°C;
(d) boron tribromide (1.11 g, 0.15 mol) in the flask.

The solid residue (5.48 g) was dark brown (found: B, 3.24; Br, 39.09; N, 4.89; B : Br : H = 1 : 1.6 : 1.1). Sublimation at 220–240°C/0.05 mm afforded what was possibly a linear polymer



$$\mathrm{Bu}^n-\left[\overset{\mathrm{Bu}^n}{\mathrm{N}}-\overset{\mathrm{Br}}{\mathrm{B}}\right]-\overset{\mathrm{Bu}^n}{\mathrm{N}}-\mathrm{Bu}^n$$

(4.82 g, 29.3%; found: B, 3.92; Br, 40.13; N, 7.65; calc. for $C_{32}H_{72}B_5Br_5N_6$: B, 5.4; Br, 40.24; N, 8.45; M.Wt., 994).

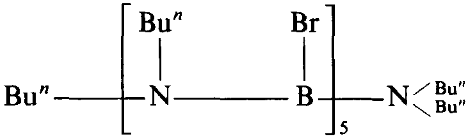
Pyrolysis of tri-n-butylamine-boron tribromide: 1 : 1 complex

Tri-*n*-butylamine-boron tribromide, $\mathrm{Bu}^n_3\mathrm{N,BBr}_3$ (16.34 g, 1.0 mol) was heated at 240–270°C for 12 h.

Volatile matter (0.97 g) was received in a flask and also (0.85 g) in a cold trap at −80°C. The volatile matter was examined by elemental analysis, GLC and infrared spectroscopy and shown to comprise the following substances:

(a) *n*-butyl bromide (5.98 g, 1.16 mol);
(b) *s*-butyl bromide (1.49 g, 0.29 mol);
(c) boron tribromide (0.85 g, 0.09 mol) in cold trap at −80°C;
(d) boron tribromide (1.64 g, 0.17 mol) in the flask.

There was a dark brown semi-solid residue (5.43 g; found: B, 3.92; Br, 38.65; N, 8.27; B : Br : N = 1.3 : 1 : 1.6). The residue was heated, and afforded a distillate (b.p. 85°C/0.1 mm; 0.68 g). The volatile matter in the cold trap at −196°C weighed 0.15 g and the sublimate at 200°C/0.15 mm (presumably a linear polymer)



$$\mathrm{Bu}^n-\left[\overset{\mathrm{Bu}^n}{\overset{|}{\mathrm{N}}}-\overset{\mathrm{Br}}{\overset{|}{\mathrm{B}}}\right]_5-\mathrm{N}{<}^{\mathrm{Bu}^n}_{\mathrm{Bu}^n}$$

weighed 1.83 g (found: C, 37.70; H, 7.79; B, 4.77; Br, 39.83; N, 7.59; calc. for $\mathrm{C}_{32}\mathrm{H}_{72}\mathrm{B}_5\mathrm{Br}_5\mathrm{N}_6$: C, 38.64; H, 7.26; B, 5.43; Br, 40.17; N, 8.44%). There was a residue of dark brown solid (2.07 g, 12.6%; found: B, 6.25; Br, 30.96; N, 10.96%; B : Br : N = 1.5 : 1 : 2), which was insoluble in solvents such as benzene, toluene, chloroform and methylene dichloride.

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