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A SYSTEMATIC STUDY OF THE THERMAL DECOMPOSITION OF TETRAALKYLAMMONIUM HALOBORATES

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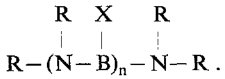
Thermal decompositions of tetraalkylammonium haloborates, $R_4N^+BX_4^-$ (where R = Et or n-Bu, and X = Cl, Br or $PhBCl_2$), have been studied by both bench pyrolysis and thermoanalytical techniques. The first stage in the thermal decomposition of the haloborates involves the loss of one mole of an alkyl halide with the formation of a 1 : 1 complex. Thermal decomposition of the haloborates beyond the stage of formation of haloboranes leads to the evolution of further quantities of alkyl halides together with the corresponding boron trihalide. In many instances the final products were polymeric materials of the general type:



$$R-(\overset{R}{N}-\overset{X}{B})_n-\overset{R}{N}-R\,.$$

During the past decade much interest has been shown in the study of thermal decompositions of primary alkylammonium haloborates leading to the syntheses of polyborazynes $(RNBX)_n$ [1—4]. The major tendency of reactions between boron and nitrogen compounds is to generate small rings (n = 2, 3, 4). It was thought that it would be interesting to constrain polymerization to obtain only linear structural compounds, by introducing steric conditions to inhibit the formation of ring-type structures.

In attempts to prepare linear polymers, a number of tetraalkylammon haloborates were taken, and pyrolysis studies of these compounds using thermoanalytical [5] and bench techniques have yielded very interesting results. This paper reports the second part of the findings of a continuing investigation to trace the reaction sequence in the preparation of linear polymers.

Experimental

Preparation of tetralkylammonium haloborates

Tetraalkylammonium halides were dissolved in dichloro methane (500 ml) and stirred with boron trihalides. The tetrahaloborates were filtered off and washed with the solvent (Table 1).

Table 1

Tetraalkylammonium haloborates ($R_4N^+BX_4^-$)

Compound	RX_3, g	$R_4N^+X^-$	Yield, %	Found, %			Required, %		
				B	X	N	B	X	N
$Et_4N^+BCl_4^-$	7.16	10.11	99	3.9	50.2	4.9	3.8	50.2	4.9
$Et_4N^+BBr_4^-$	20.96	17.57	95	2.4	69.4	3.1	2.4	69.4	3.0
$Et_4N^+BI_4^-$	27.55	18.10	71	1.6	78.2	2.3	1.6	78.2	2.2
$Et_4N^+BPhCl_3^-$	21.34	22.47	95	3.3	32.8	4.3	3.3	32.8	4.3
$Et_4N^+BPh_4^-$	8.5	4.2	72	2.4	—	3.1	2.4	—	3.1
n-$Bu_4N^+BCl_4^-$	5.85	13.14	94	2.7	35.9	2.5	2.7	35.9	2.4
n-$Bu_4N^+BBr_4^-$	25.05	32.2	96	1.9	55.8	2.7	1.9	55.8	2.7
n-$Bu_4N^+BPhCl_3^-$	6.35	12.20	93	2.5	27.4	3.6	2.5	27.3	3.5
n-$Bu_4N^+BPh_4^-$	17.12	16.12	78	1.2	—	1.6	1.2	—	1.6

Preparation of trialkylamine trihaloboranes

Trialkylamines were added dropwise to boron trihalides in dichloromethane (500 ml) at − 80°, resulting in white crystalline trialkylamine trihaloboranes (Table 2).

Table 2

Trialkylamine haloborate (R_3NBX_3)

Compounds	BX_3, g	R_3N, g	Yield, %	Found, %			Required, %		
				B	X	N	B	X	N
Et_3NBCl_3	58.58	58.58	99	5.0	48.7	6.4	4.9	48.7	6.4
Et_3NBBr_3	25.05	10.11	95	3.1	68.3	3.9	3.1	68.2	3.9
$Et_3NBPhCl_2$	15.87	10.11	92	4.2	27.3	5.3	4.2	27.3	5.4
n-Pr_3NBCl_3	39.56	47.76	95	4.1	40.6	5.4	4.1	40.7	5.4
n-Pr_3NBBr_3	50.11	28.66	98	2.8	60.9	3.5	2.7	60.9	3.5
n-$Pr_3NBPhCl_2$	39.72	35.82	99	3.6	23.4	4.6	3.7	23.5	4.6
n-Bu_3NBCl_3	29.29	46.34	96	3.6	35.2	4.7	3.6	35.2	4.6
n-Bu_3NBBr_3	25.05	18.53	93	2.5	55.0	3.3	2.5	55.0	3.2
n-$Bu_3NBPhCl_2$	39.72	46.34	98	3.0	20.1	3.9	3.0	20.0	3.9

Preparation of dialkylamino dihaloborenes

(i) Diethylamine (2.03 mole) in dichloromethane (500 ml) was added (4 hr) to borous trichloride (1.0 mole) at −80°. Volatile matter on distillation at 144−145° afforded a colourless liquid of diethylaminoboron dichloride (Found: B, 7.0; Cl, 46.1; N, 8.9; Calc. for $C_4H_{10}BCl_2N$: B, 7.0; Cl, 46.1; N, 8.9%).

(ii) Triethylamine (1.0 mole was added dropwise to a solution of di-*n*-butylamine boron trichloride (1.0 mole) in dichloromethane (500 ml), and the mixture was heated (24 hr) under reflux until hydrogen chloride evolution ceased. The dark brown liquid was distilled at 41° (0.1 mm), which gave a colourless liquid of di-*n*-butylaminoboron dichloride (Found; B, 5.2; Cl, 33.8; N, 6.7; Calc. for $C_8H_{18}BCl_2N$: B, 5.2; Cl, 33.8; N, 6.7%).

Pyrolysis of tetraaikylammonium haloborates and trialkylamine trihaloboranes

The flask containing the sample was fitted with an air condenser leading to a trap maintained at −80°, further connected to a potassium hydroxide trap. The flask was heated in a covered furnace. The temperature of pyrolysis was maintained at various levels until reaction ceased (3–6 hr), to evolve any volatile matter. The alkyl halides and boron trihalides were retained in the trap at −80°. The condensates were analyzed for boron, nitrogen and the halogens. Separations were carried out by GLC, and identification by IR spectroscopy.

Pyrolysis residues were obtained which were analyzed to obtain a mass balance. These residues were further subjected to distillation under vacuum to recover linear structure polymers, and final identifications were achieved by mass spectrometry, infrared spectroscopy and molecular weight determinations.

Preparation of borozines

Equimolecular proportions of reagents were mixed in chlorobenzene and the system was heated under reflux (6–7). Sublimations or distillations afforded B-trichloro-N-triethyl borozine or B-trichloro-N-tri-*n*-butyl borazine, respectively.

Differential thermal analysis

The results were obtained using a Standata 6–25 (manufactured by Stanton instruments Ltd., London). All runs were of sample (100–150 mg) against alumina as reference. The sample and reference material were contained in platinum crucibles (8 mm diam. × 10 mm depth) with a central base recess. These crucibles can be mounted (i) in wells within a stainless steel sample block mounted on ceramic stems; (ii) in a sintox ceramic block similarly mounted; (iii) on a palladium–ruthenium crucible support platform on twin ceramic stems. In each case the crucibles are mounted so that the beads of two Pt/Pt 13% Rh thermocouples come within the base recess of each crucible. The sample temperature (T) is taken from the sample thermocouple, the differential temperature (ΔT) is amplified, and then (T) and (ΔT) are recorded on a Leeds – Northrop X_1-X_2 10 in. recorder. The furnace is controlled. Heating rates were varied from 2°/min to 16.75°/min, but all results reported in this paper were obtained at 16.76°/min. All experiments were performed under a nitrogen atmosphere with a flow rate of 200 ml/min.

Thermogravimetry

The technique used for TG is described in Part 1 [5].

Results and discussion

Tetraalkylammonium haloborates ($R_4N^+BX_4^-$) and trialkylamine trihaloboranes (R_3NBX_3) were prepared by the interaction of the appropriate alkylammonium halide and trialkylamine with boron trihalide:

$$R_4N^+X^- + BX_3 \rightarrow R_4N^+BX_4^-$$

$$R_4N^+Cl^- + NaBPh_4 \rightarrow R_4N^+BPh_4^- + NaCl$$

$$R_3N + BX_3 \rightarrow R_3NBX_3$$

$$R = \text{Et}, n\text{-Pr or } n\text{-Bu}$$

$$X = \text{Cl, Br or PhCl}_2$$

Thermal decompositions of tetraalkylammonium haloborates and trialkylamine trihaloboranes were studied by bench and thermal analytical techniques and their results are summarized in Tables 3–4 and Fig. 1(a–b). In the thermal decomposi-

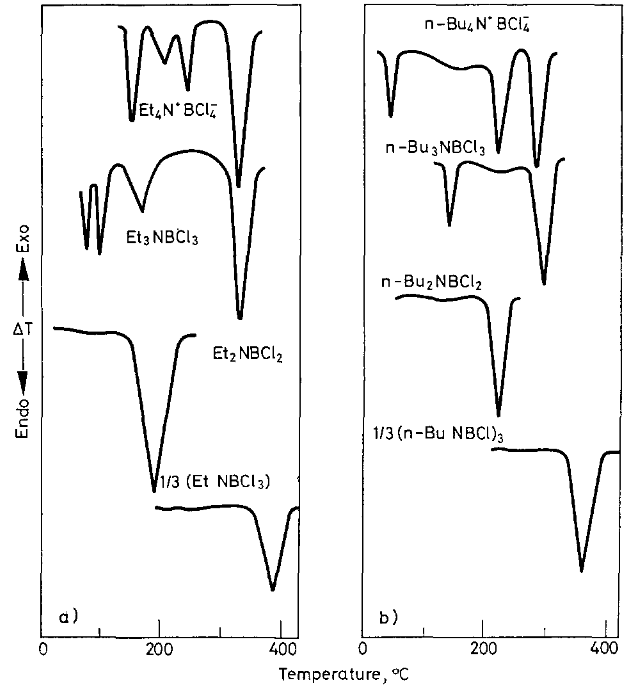


Fig. 1. DTA curves of compounds investigated

Table 3

Volatiles obtained on pyrolysis of borates

Borates	RX mols	BX_3 mols	Ph H mols	Pyrolysis conditions
Et_4NBCl_4	0.91	–	–	260 – 280°/2.15 h
Et_4NBBR_4	0.89	–	–	240 – 270°/2 h
$Et_4NPhBCl_3$	0.81	–	–	200 – 250°/5 h
Et_4NBPh_4	–	–	1.10	350 – 370°/26 h
$Bu^n_4NBCl_4$	1.56	0.05	–	260 – 280°/2.1 h
$Bu^n_4NBBr_4$	2.08	0.16	–	280 – 290°/3.1 h
$Bu^n_4NPhBCl_3$	1.08	0.03 ($PhBCl_2$)	0.83	260 – 280°/10.3 h
$Bu^n_4NBPh_4$	–	–	2.6	280 – 290°/7.45 h

No volatiles were obtained.

Table 4

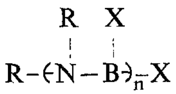
Volatiles obtained on pyrolysis of haloborane

Haloborane	RX, mols	BX_3, mols	PhH, mols	Pyrolysis conditions
$Et_3N \cdot BCl_3$	0.026	–	–	140 – 165°/24 h
$Et_3N \cdot BCl_3$	–	–	–	280 – 300°/40 h*
$Et_3N \cdot BBr_3$	–	.007	–	280 – 300°/31 h*
$Et_3N \cdot PhBCl_2$	–	–	–	270 – 295°/28 h*
$Et_3N \cdot BCl_3$	(2.16 g)$^+$	.006	–	260 – 280°/42 h*
Et_3NBBr_3	0.08	0.48	–	240 – 250°/48 h*
$Pr^n_3NBCl_3$	0.87	0.16	–	110 – 180°/20 h* 210 – 260°/21 h
$Bu^n_3NBCl_3$	1.20	0.43	–	140 – 165°/24 h 240 – 260°/48 h
$Bu^n_3NBCl_3$	1.31	0.42	–	260 – 300°/26 h
$Bu^n_3NBCl_3$	0.51	0.17	–	240 – 260°/48 h
$Bu^n_3NBCl_3$	0.82	0.23	–	240 – 260°/71 h
$Bu^n_3NBCl_3$	1.0	0.31	–	240 – 280°/72 h
$Bu^n_3NBBr_3$	1.45	0.26	–	280 – 280°/5.1 h
$Bu^n_3NPhBCl_2$	0.68	0.12 ($PhBCl_2$)	1.0	280 – 310°/24 h

* In these experiments, pyrolysis was carried out under reflux conditions

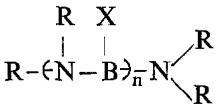
$^+$ Mixture of ethyl chloride and boron trichloride tion of tetraalkylammonium haloborates (R_4NBX_4) when *R* was ethyl and *X* was chloride, bromide or phenyl dichloride, the first stage of thermal decomposition involves loss of 1 mole of ethyl halide with the formation of triethylamine trihaloborane, but the isolation of the 1 : 1 complex was not possible in the system where *R* was *n*-butyl and *X* was chloride or phenyl dichloride. The residues recovered were intractable and no identification was accomplished. When *X* was bromide the residue gave a polymeric product (ii) of molecular weight 994 (where $n = 5$).

Pyrolysis of trialkylamine trihaloboranes, under reflux at 240–280° for 41–71 hr, when *R* is ethyl or *n*-butyl and *X* is chloride, bromide or phenyl dichloride, indicated the formation of dialkylamino dihaloborene, R_2NBX_2, together with a mixture of alkyl halides, boron trihalide and short-chain polymers (i) where $n = 1$, 2 and 3). When *R* is *n*-butyl and *X* was chloride, bromide or phenyl dichloride the residue obtained consisted of varying amounts of *n*-butylammonium halide and polymeric materials possibly of structure (ii) (where n = 2 to 4)



$\mathrm{R}\text{-}(\overset{\mathrm{R}}{\mathrm{N}}-\overset{\mathrm{X}}{\mathrm{B}})_{n}\text{-}\mathrm{X}$

(i)



$\mathrm{R}\text{-}(\overset{\mathrm{R}}{\mathrm{N}}-\overset{\mathrm{X}}{\mathrm{B}})_{n}\text{-}\mathrm{N}{<}^{\mathrm{R}}_{\mathrm{R}}$

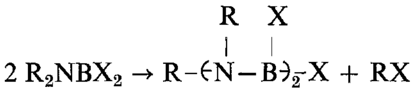
(ii)

The TG curves of tetraalkylammonium haloborates show that a loss in weight corresponding to the formation of the 1 : 1 complex is possible in the ethyl series but not in the *n*-butyl series; instead, the compound ejects two molecules of butyl halide in one step. TG of the trialkylamine trihaloboranes, R_3NBX_3, shows a further loss in weight corresponding to the formation of dialkylamino dihaloborene, R_2NBX_2, when *R* is ethyl or *n*-butyl and *X* is $PhBCl_2$.

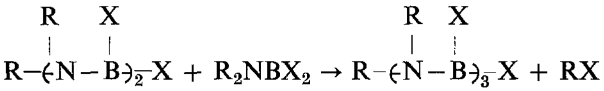
A comparison of DTA traces is presented in Fig. 1(a–b). Tetraalkylammonium haloborates (R_4NBX_4), trialkylamine trihaloboranes (R_3NBX_3), dialkylamino dihaloborenes (R_2NBX_2) and B-trihalo-N-trialkyl borazines ($1/3\,(RNBX)_3$) all show interesting transformations. DTA affords no evidence of the thermal decomposition sequence beyond the point of formation of 1 : 1 complexes, except in the cases of triethylamine and tri-*n*-butylamine trihaloboranes, when there are indications of the possible formation of diethylamino and di-*n*-butylamino borenes. Indication of the formation of borazines is not obtained from comparison of the relevant DTA curves. Tetraalkylammonium haloborates and trialkylamine trihaloboranes (as shown by the results of bench pyrolysis DTA and TG) yield products consistent with a reaction involving intramolecular loss of alkyl halides from 1 : 1 complexes to give dialkylamino dihaloborenes, followed by intermolecular loss of alkyl halides between molecules of dialkylamino dihaloborene. The formation of BX_3 could be explained on the basis of reaction (5) below:

$$R_4N^+BX_4^- \rightarrow R_3NBX_3 + RX \tag{1}$$

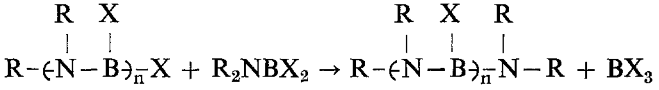
$$R_3NBX_3 \rightarrow R_2NBX_2 + RX \tag{2}$$



$$2\,R_2NBX_2 \rightarrow R\text{-}\left(\overset{R}{\underset{|}{N}}-\overset{X}{\underset{|}{B}}\right)_{2}\text{-}X + RX \qquad (3)$$



$$R\text{-}\left(\overset{R}{N}-\overset{X}{B}\right)_{2}\text{-}X + R_2NBX_2 \rightarrow R\text{-}\left(\overset{R}{N}-\overset{X}{B}\right)_{3}\text{-}X + RX \qquad (4)$$



$$R\text{-}\left(\overset{R}{N}-\overset{X}{B}\right)_{n}\text{-}X + R_2NBX_2 \rightarrow R\text{-}\left(\overset{R}{N}-\overset{X}{B}\right)_{n}\text{-}\overset{R}{N}-R + BX_3 \qquad (5)$$

R = Et or n − Bu

X = Cl, Br or $PhBCl_2$

$n = 1-5$

Polymers with these end-groups were not isolated in the ethyl systems, but were obtained in the *n*-butyl systems. It is possible that they were formed in the ethyl systems but were not amenable to isolation. A study of the effects of heating diethylamino dichloroborenes and di-*n*-butylamino dichloroborene under reflux has not provided any support for these reaction sequences. In the case of diethylamino dichloroborene the temperature of reflux (144 – 146°) was not high enough to effect decomposition. At 320 – 380° (96 hr) di-*n*-butylamino dichloroborene partially decomposed (36.6%) to give di-*n*-butylamine boron trichloride, presumably by intermolecular abstraction of hydrogen chloride.

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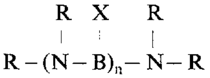
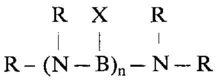
ZUSAMMENFASSUNG — Die thermische Zersetzung von Tetraalkylammoniumhaloboraten, $R_4N^+BX_4^-/R$=Et und n—Bu, X=Cl, Br, $PhBCl_2$) wurde durch Pyrolyse und Thermische Analyse untersucht. In der ersten Stufe der thermischen Zersetzung verlieren die Haloborate ein Mol eines Alkylhalids unter Bildung eines 1 : 1 Komplexes. Nach der Stufe der Haloboranbildung führt die thermische Zersetzung der Haloborate zur Entstehung weiterer Mengen von Alkylhaliden und dem entsprechenden Bortrihalid. In vielen Fällen waren die Endprodukte Polymer Typ



$$R-(\overset{R}{N}-\overset{X}{B})_n-\overset{R}{N}-R$$

Резюме — Изучено термическое разложение тетраалкиламмониевых солей галогенборатов общей формулы $Я_4И^+BX^-$, где Я = этил и н-бутил, а X = Cl, Вг, $ФBCl_2$ с помощью стендового пиролиза и термоаналитическим методом. Первая стадия термического разложения галогенборатов включает потерю одного моля алкилгалоида с образованием комплекса состава 1 : 1. Термическое разложение галогенборатов выше стадии образования галогенборанов приводит к выделению последующих количеств алкилгалоидов вместе с соответствующими тригалоидпроизводными бора. Во многих случаях конечными продуктами распада являлись полимерные соединения общего типа



$$R-(\overset{R}{N}-\overset{X}{B})_n-\overset{R}{N}-R$$