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DIFFERENTIAL THERMAL ANALYSIS OF TETRAALKYLAMMONIUM HALOBORATES

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DTA of a series of compounds of the type $R_4N^+BX_4^-$ (where R = Et or n-But and X = Cl, Br, Ph or $PhCl_2$) indicates the formation of trialkylamine trihaloboranes and dialkylamino dihaloborenes as intermediates in the formation of linear polymers instead of cyclic borazines as the end-products.

INTRODUCTION

Several attempts have been reported in the literature [1–3] to obtain boron–nitrogen linear polymers in preference to the formation of small ring compounds. The paration of linear polymers was considered interesting because it is expected that such linear polymers will be chemically and thermally more stable compared to small ring compounds[4–6]. It was, therefore, decided to substitute different tertiary alkyl groups in place of primary or secondary alkyl groups in tetraalkylammonium haloborates $[R_4N^+BX_4^-]$ in the hope to obtain linear boron–nitrogen polymers instead of small ring compounds on pyrolysis. This paper investigates the comparative differential thermal analysis study of tetraalkylammonium trichlorophenylborates and their intermediates with different alkyl groups.

EXPERIMENTAL

All the haloborates and their intermediate compounds were prepared by the known procedures [7,8]. DTA was carried out by using the Standate model 6–25 (Stantan Instruments, England). For these experiments sample sizes (from 0.1 to 0.15 g) were used alongwith calcined alumina as the reference material. Platinum crucibles of 8 mm with 10 mm depth were found suitable. Nitrogen atmosphere was maintained over the samples at the rate of 200 ml/min throughout these experiments. Heating rates were maintained in steps varying from 2 to 16.75°/min.

RESULTS AND DISCUSSION

The compounds tetraalkylammonium trichlorophenylborates $[R_4N^+BPhCl_3]$, trialkylamine dichlorophenylborane $[R_3NBPhCl_2]$, trialkylamine trichloroborane $[R_3NBCl_3]$, dialkylamino chlorophenylborene $[R_2NBPhCl]$, dialkylamino dichloroborene $[R_2NBCl_2]$, B-trichloro-N-trialkylborazine $[1/3\ (RNBCl)_3]$, B-triphenyl-*N*-trialkylborazine $[1/3\ (RNBPh)_3]$, were subjected to DTA showing interesting results (Fig. 1 showing DTA curves).

When R in $[R_4N^+BPhCl_3^-]$ is ethyl it undergoes decomposition giving endothermic peak at 225°. On raising the temperature decomposition proceeds to triethylamine dichlorophenylborane and not triethylamine trichloroborane. When tetraethylammoniumtrichlorophenylborate and triethylamine dichlorophenylborane are subjected to DTA a common volatilization endothermic peak at 268° corresponding to the diethylamino chlorophenylborene is obtained. This, therefore, confirms that during the decomposition, diethylamino dichloroborene has no part to play as an intermediate with DTA of tetraethylammonium trichlorophenylborate. Further increase in the temperature

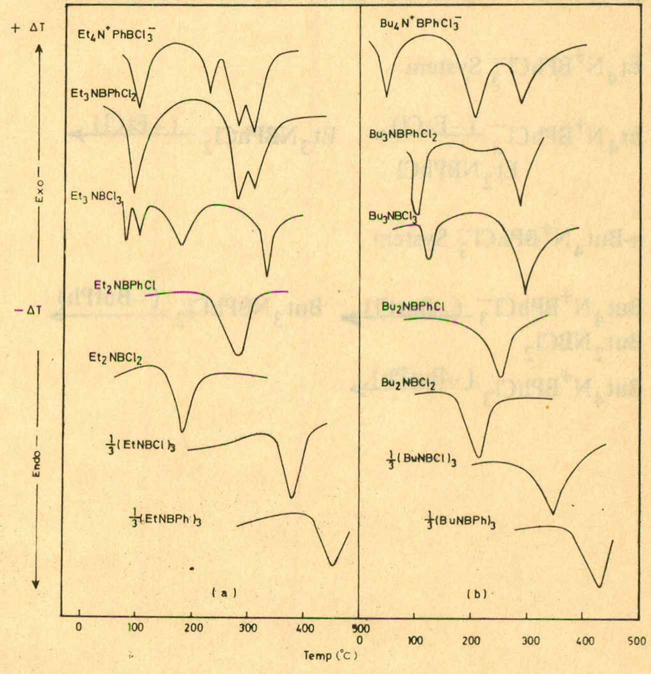

Fig.1 DTA of tetraalkylammonium haloborates.

of the sample containing tetraethylammonium trichlorophenylborate, triethylamine dichlorophenylborane, triethylamine trichloroborane and diethylamine chlorophenylborene, diethylamino dichloroborene gave no indication of cyclic borazines formation because of the absence of their characteristic endothermic peak (DTA peak for B-trichloro-*N*-triethylborazine is at 365° and B-triphenyl *N*-triethylborazine is at 425°).

When R is n-butyl in $[R_4N^+BPhCl_3^-]$ tetra-n-butylammonium trichlorophenylborate exhibits an intense volatilization endothermic peak at 235°. Further increase in the temperature results in the decomposition to tri-n-butylamine dichlorophenylborane and/or tri-n-butylamine trichloroborane. This is because two peaks are so close to each other that their differentiation from each other is extremely difficult. Similar to ethyl system a common volatilization endothermic peak corresponding to the formation of di-n-butylammino dichloroborene is obtained. When tetra-n-butylammonium trichlorophenylborate and tri--n-butylamine trichloroborane are subjected to DTA, peak corresponding to di-n-butylamino dichloroborene is observed. Tetra-n-butylammonium trichlorophenylborates, tri-n-butylamine dichlorophenylborane, tri-n-butylamine trichloroborene , di-n-butylamino chlorophenylborene and di-n-butylamino dichloroborene on DTA studies give no indication of the formation of cyclic borazines. B-trichloro-N-tri-n-butylborazine and B-triphenyl-*N*-tri-n-butylborazine gave broad volatization endothermic peaks at 378° and 456° respectively. DTA results of tetraethylammonium haloborates, tetra-n-butylammonium haloborates and their intermediates support the following reaction sequences.

$Et_4N^+BPhCl_3^-$ System

$$Et_4N^+BPhCl_3^- \xrightarrow{(-EtCl)} Et_3NBPhCl_2 \xrightarrow{(-EtCl)} Et_2NBPhCl$$

n-$But_4N^+BPhCl_3^-$ System

$$But_4N^+BPhCl_3^- \xrightarrow{(-ButCl)} But_3NBPhCl_2 \xrightarrow{(-ButPh)} But_2NBCl_2$$

$$But_4N^+BPhCl_3 \xrightarrow{(-ButPh)} But_3NBCl_3 \xrightarrow{(-ButCl)} But_2NBCl_2$$

Tetraethylammonium trichlorophenylborate differs from tetra-n-butylammonium trichlorophenylborate in giving different end-products on DTA. In ethyl system diethylamino chlorophenylborene is formed and in n-butyl system dibutylamino dichloroborene is formed. The preferential elimination of phenyl group instead of chloride in the n-butyl system can be easily explained on steric consideration, n-butyl groups are considerably larger than ethyl groups and in the end-product removal of phenyl group is necessitated to relieve strain in the butyl system.

Primary alkylammonium haloborates on pyrolysis leads to the formation of borazines as the end-product. Tri - and tetraalkylammonium haloborates preferentially give linear polymers of variable length. Further work is in progress to determine the exact nature of these polymers.

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