APPLICATION OF THERMAL ANALYSIS TO THE STUDY OF ASPECTS OF BORON-NITROGEN CHEMISTRY—II

DIFFERENTIAL THERMAL ANALYSIS OF SOME ALKYLAMMO-NIUM TETRACHLORO- TETRAPHENYL- AND TRICHLORO-PHENYLBORATES

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Abstract—Thermal analysis studies of the alkylammonium tetrachloro-, tetraphenyl- and trichlorophenylborates demonstrates formation of 1:1 complex by loss of hydrogen chloride or benzene. Further decomposition in both the tetrachloro- and the trichlorophenylborate systems leads to formation of the B-trichloro-N-trialkylborazine. Decomposition of the tetraphenylborates stops at the borazene stage with formation of the alkylaminodiphenylborane.

OF the polyborazynes $(-N - B -)_n$ linear⁽¹⁾ derivatives and also cyclic dimers,⁽²⁾ trimers⁽³⁾ and tetramers⁽⁴⁾ have been reported. Which oligomer is obtained in any particular preparation depends on both the substituents X and Y and also the mode of preparation. In order to formulate methods for the preparation of particular polyborazynes it is necessary to have a clear understanding of their mechanism of formation. Polyborazynes may be obtained by the thermal decomposition of alkyl-ammonium tetrachloro-, and trichlorophenylborates and we are studying the decomposition of these systems, as well as that of the alkylammonium tetraphenylborates, by normal macroscopic bench techniques and by thermal analysis. In this paper we report the application of DTA to these systems.

Alkylammonium tetrachloroborates

Part I⁽⁵⁾ of this series, and its' companion paper,⁽⁶⁾ describe the investigation of the decomposition of alkylammonium tetrachloroborates by bench technique and by thermogravimetric analysis and suggest the reaction sequence:

$$RNH_{3}^{+}BCl_{4}^{-} \rightarrow RNH_{2}BCl_{3} + HCl \rightarrow \frac{1}{3}(RNBCl)_{3} + 2HCl \qquad (1)$$

$$R = Me, Et, Pr^{n}, Pr^{i}, Bu^{n}, Bu^{i}, Bu^{s} \text{ and } Oct^{n}.$$

We have now examined the ethyl, n-propyl, n-butyl, s-butyl and n-octylammonium

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tetrachloroborates by differential thermal analysis combined with gas evolution analysis. A comparison of the DTA traces obtained from each tetrachloroborates $(RNH_3^+BCl_4^-)$, 1:1 complex $(RNH_2:BCl_3)$, and •B-trichloro-N-trialkyl borazine $[(RNBCl)_3]$ provides further confirmation of the reaction sequence (1); as a typical example of the traces from the Pr^n system are reproduced (Fig. 1). Initial decomposition of the tetrachloroborate to give the 1:1 complex involves both endothermic and exothermic steps, decomposition of the 1:1 complex is indicated by a single broad endotherm with a peak at 240°, followed by another endotherm at 355° corresponding to the volatilisation of the B-trichloro-N-tri-n-propylborazine. The corresponding 1:1 complex gave a melting endotherm at 140°, a single decomposition endotherm at 265°, followed again by the B-trichloro-N-tri-n-propylborazine volatilisation endotherm at 355°. The B-trichloro-N-tri-n-propylborazine itself gave the melting endotherm at 115° and again the volatilisation endotherm at 355°.

Alkylammonium trichlorophenylborates

An examination by bench techniques^(7,8) indicated that the pyrolysis of alkylammonium trichlorophenylborates occurs with elimination of benzene and hydrogen chloride to give the B-trichloro-N-trialkylborazine; the decomposition appears to involve two concurrent reaction paths.

and

$$RNH_{3}+PhBCl_{3}- \rightarrow RNH_{2}:PhBCl_{2} + HCl$$

$$RNH_{3}+PhBCl_{3}- \rightarrow RNH_{2}:BCl_{3} + PhH$$

$$RNH_{2}:PhBCl_{2} \rightarrow \frac{1}{3}(RNBCl)_{3} + PhH + HCl$$

$$RNH_{2}:BCl_{3} \rightarrow \frac{1}{3}(RNBCl)_{3} + 2HCl$$

$$R = Pr^{n} \text{ and } Bu^{i}$$

$$(2)$$

Thermogravimetric analysis of the alkylammonium trichlorophenylborates, due to the existence of concurrent reaction paths, has not given easily interpreted results. A comparison of the DTA traces of each trichlorophenylborate ($RNH_3^+PhBCl_3^-$), both 1:1 complexes ($RNH_2:BCl_3$ and $RNH_2:PhBCl_2$), and the corresponding Btrichloro-N-trialkylborazine ($RNBCl_3$ and B-triphenyl-N-trialkylborazine ($RNBPh_3$ is consistent with the above reaction scheme; clearly showing that the trichlorophenylborate and both 1:1 complexes all give the B-trichloro-N-trialkylborazine with no indication of formation of the B-triphenyl-N-trialkylborazine. The results of the n-propyl system are reproduced in Fig. 1 as being typical examples. The n-propylammonium trichlorophenylborate shows two decomposition endotherms at 130° and 260° followed by the volatilisation endotherm of the B-trichloro-N-trialkylborazine at 355°. The n-propylamine, dichlorophenylborane (1:1) complex shows an initial melting endotherm at 150°, a broad decomposition endotherm at 260° involving loss of benzene and hydrogen chloride followed by the volatilisation endotherm of the chloroborazine at 355°.

Alkylammonium tetraphenylborates

Previous workers^(9.10) have studied the decomposition of various alkylammonium tetraphenylborates (RNH_3 +BPh₄⁻), but this work has been aimed mainly at the

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FIG. 1.—DTA and GEA curves for n-propylammonium tetrachloroborate and trichlorophenylborate systems.

determination of drying temperatures of tetraphenylborate precipitates in the gravimetric determination of amines. For this reason thermogravimetric analysis was performed in air, and the eludication of the decomposition route was hampered by oxidation effects. We have studied the decomposition under nitrogen on a large scale by bench techniques,^(7,8) and now report on the application of DTA.

Pyrolysis of alkylammonium tetraphenylborates gives formation of the alkylamine, triphenylborane, 1:1 complex, with evolution of benzene (1 mole), on further pyrolysis more benzene (1 mole) is eliminated with formation of the alkylaminodiphenylborane.

$$\begin{array}{l} \text{RNH}_3^+\text{Ph}_4\text{B}^- \to \text{RNH}_2, \, \text{Ph}_3\text{B} + \text{PhH} \\ \text{RNH}_2, \text{Ph}_3\text{B} \to \text{RNHBPh}_2 + \text{PhH} \\ \text{R} = \text{Pr}^n, \, \text{Bu}^i \text{ and } \text{Bu}^s \end{array}$$

$$(3)$$

Thermogravimetric analysis has indicated a two step reaction but resolution was too poor to allow further interpretation. Comparison of the DTA traces of each tetraphenylborate, 1:1 complex (RNH_2 , Ph_3B) and alkylaminodiphenylborane ($RNHBPh_2$) supports the reaction sequence (3). Once again the results of the n-propyl system are reproduced (Fig. 2) as being typical. The n-propylammonium tetraphenylborate shows a sharp initial exotherm at 167° followed by a decomposition endotherm

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at 202° which is then followed by the volatilization endotherm of the n-propylaminodiphenylborane at 336°. The n-propylamine, triphenylborane complex (Pr^nNH_2 , Ph_3B) shows a single decomposition endotherm followed again by the volatilization endotherm of the n-propylaminodiphenylborane.



FIG. 2.-DTA and GEA curves for n-propylammonium tetraphenylborate system.

Comparison of DTA results

The alkylammonium tetrachloroborates, trichlorophenylborates and tetraphenylborates all seem to show the same pattern from the 1:1 complex stage onwards i.e. a single decomposition endotherm followed by the volatilization endotherm of the product. The initial decomposition leading to formation of the 1:1 complex appears to be very complicated; the tetrachloroborates show an endotherm and an exotherm, the trichlorophenylborates only an endotherm and the tetraphenylborates an exotherm only. It should be noted that, in the case of the tetrachloroborates, resolution depends upon heating rate, that is endotherm and exotherm are resolved at heating rates of 12:0 and 16.75° per min, whereas at lower heating rates only the endotherm is resolved.

It can be visualized that the chemical reaction involving decomposition of the borate to give the 1:1 complex, which involves formation of a N—B bond, will be exothermic. This, however, is not the only heat change involved and we must take into account the fact that both volatilization of the product, benzene or hydrogen chloride, and the possible melting of the 1:1 complex will be endothermic; in addition there may be further changes which, at the moment, we cannot visualize. The total heat effect observable by DTA at any one moment will be the sum of all these effects.

HOWICK and PFLAUM^($\hat{\Psi}$) report the DTA of methyl, dimethyl, ethylammonium and pyridinium tetraphenylborates as occurring by a series of wholly exothermic steps, the initial exotherm is probably of the same origin as that which we report, but the complete difference of the rest of the trace is probably due to the fact that HOWICK and PFLAUM carried out their investigations in air, their further exothermic peaks being due to oxidation.

EXPERIMENTAL

Differential thermal analysis. These results were obtained using the 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. imes 10 mm depth) with a central base recess. These crucibles can be mounted in (i) wells within a stainless steel sample block mounted on ceramic stems, (ii) a "Sintox" ceramic block similarly mounted (iii) on palladium-ruthenium crucible support platforms on twin ceramic steams. In each case the crucibles are so mounted that the beads of two Pt/Pt 13% Ph 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 X₁-X₂ 10 in. recorder. The furnace is controlled by a West programme controller. Heating rates were varied from 2° /min. to 16.75° /min., all results reproduced in this paper were, however, obtained at 16.75° /min. All experiments were performed under a nitrogen atmosphere. Gas evolution analysis was based on the technique described by Wendlandt.⁽¹¹⁾ Nitrogen was passed through the reference side of Gow Mac hot wire detector (150°), then through the DTA chamber and into the sample side of the detector. The cell bridge circuit was of conventional design, and the output was fed into a Leeds-Northrop recorder. Evolution of volatile material was represented by a peak in the gas evolution analysis. In this way a distinction was made between DTA peaks due to chemical reactions entailing loss of volatile products, and those due to other reactions and change of phase.

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