BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (10), 2879—2880 (1976)

Thermogravimetric Analysis of Tetraalkylammonium Haloborates. I.

S. U. Sheikh

Department of Chemistry, University of Islamabad, Islamabad, Pakistan

(Received April 28, 1976)

Synopsis. Thermogravimetric analysis of tetraalkylammonium haloborates lead to the formation of trialkylamine trihaloborane and dialkylamino dihaloborane followed by ill-predictable intermediates leading to the formation of boron-nitrogen polymers.

Pyrolysis and thermoanalytical techniques applied to tetraalkylammonium haloborates is a part of an extensive research investigation into the factors to develop chemically and thermally stable boron-nitrogen polymers.[1–2] Considerable interest is attached to prepare polymers in which main chain is composed of elements other than carbon, in the hope that the thermal stability would be greater than that of the known organic polymers. Although a number of useful thermally stable polymers have in fact been developed by organic chemists but the interest given to the development of some areas of organometallic chemistry has been inadequate. Our work which is being presented in this and succeeding papers is directed towards the preparation of boron-nitrogen polymers.

Polyborazynes $[XBNR]_n$ exist as cyclic dimers, trimers and linear polymers.[3–5] The great difficulty in the preparation of linear polyborazynes is the overwhelming propensity of polyborazynes to exist as small rings.[6] It was thought that one method to prevent the formation of small rings and constraining polymerization to only linear polymers was to introduce some measure of steric inhibition to ring formation. In our efforts to prepare linear polymers two approaches were devised. The first was to discover whether by a suitable choice of reactants or experimental conditions the formation of ring compounds might be suppressed in favor of linear polymers. The second approach was to devise means whereby ring compounds might be linked in linear chains either directly or through suitable bridging groups. This paper describes part of our work on the first approach namely the study of dealkylhalogenation of the 1: 1 adducts tetraalkylammonium haloborates[7] selected as suitable models for the study of the possible inhibition of ring compound formation and for the preparation of linear polymers.

Experimental

Appropriate tetraalkylammonium haloborates were prepared by interaction of equimolar quantities of tetraalkylammonium halides and trihaloborane in dichloromethane. Tetraalkylammonium tetraphenylborates were prepared in aqueous medium.

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

$$R_4N^+Cl^- + Na^+BPh_4^- \longrightarrow R_4N^+BPh_4^- + NaCl$$

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

$$X = \mathrm{Cl},\ \mathrm{Br}\text{ and } \mathrm{PhBCl_2}$$

Thermogravimetric analyses were carried out by using Stanton HT-SM Thermobalance. All samples of haloborates and haloboranes were subjected to heat in an atmosphere of nitrogen with a flow rate of 5 l/h. Nitrogen gas provided a blanket of an inert atmosphere by preventing ingress of air. Samples varied in weights from 0.1 g to 0.2 g were used. Platinum crucible with or without platinum lid was used and its capacity varied between 10 to 15 mm. To achieve better resolution heating rates from 0.5 to 6 °C per minute were employed depending on the relative rates of decomposition of each reaction intermediate.

Results and Discussion

Tetraalkylammonium haloborates $[R_4N^+BX_4^-]$ undergo interesting transformations. When in the above complex R was ethyl and X was chloride and phenylboron dichloride inflection corresponding to the ejection of one molecule of ethyl chloride was observed with the formation of 1: 1 complex $[R_3NBX_3]$. When R was butyl and X was chloride and bromide in the complex $[R_4N^+BX_4^-]$, the complex ejected two molecules of butyl halide in one step with the formation of dibutylamino dihaloborane. When R was butyl and X was

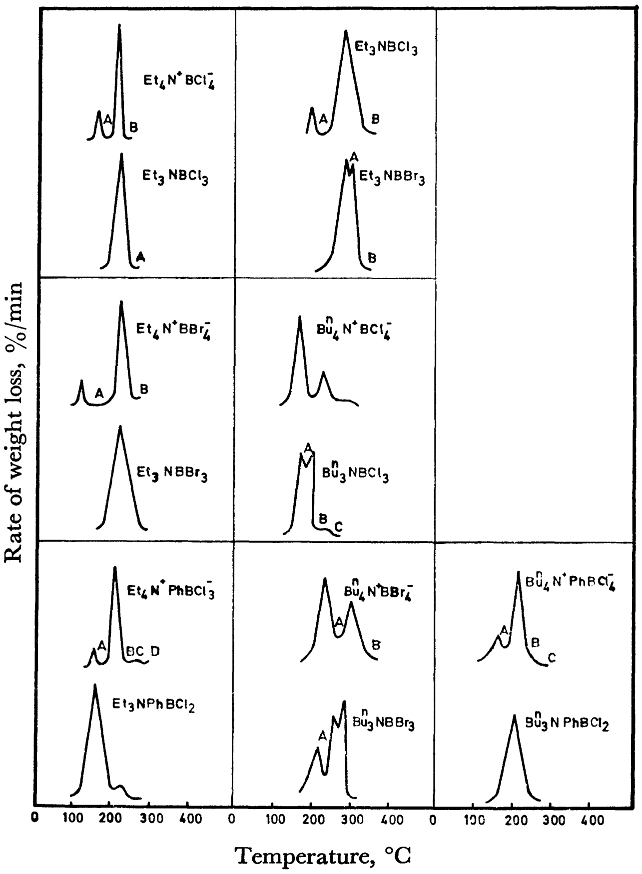

Fig. 1. Differential thermograms.

Table 1. Thermogravimetric analysis of tetraalkylammonium haloborate

Compound	Sample wt (mg)	% wt loss at inflection	% wt loss calculated for 1 : 1 complex	1 : 1 Complex formed
$Et_4N^+BCl_4^-$	178.2	22.4 at A	22.9	Et_3NBCl_3
		94.2 at B[a)]	—	—
$Et_4N^+BBr_4^-$	207.5	14.4 at A	23.6	—
		39.4 at B[a)]	—	—
$Et_4N^+BPhCl_3^-$	187.1	19.1 at A	19.7	$Et_3NBPhCl_2$
		37.8 at B	39.5	$Et_2NBPhCl$
		82.8 at C[a)]	—	—
		89.2 at D[a)]	—	—
$Et_4N^+BPh_4^-$	158.1	22.8 at A	23.6	Et_3NBPh_3
		88.6 at B[a)]	—	—
n-$Bu_4N^+BCl_4^-$	111.9	47.4 at A	46.9	n-Bu_2NBCl_2
		87.6 at B[a)]	—	—
n-$Bu_4N^+BBr_4^-$	156.9	48.4 at A	47.8	n-Bu_2NBBr_2
		89.8 at B[a)]	—	—
n-$Bu_4N^+BPhCl_3^-$	156.2	17.8 at A	21.1	n-$Bu_3NBPhCl_2$
		39.7 at B	40.2	n-$Bu_2NBPhCl$
		93.4 at C[a)]	—	—
n-$Bu_4N^+BPh_4^-$	100.4	No inflection	—	—

a) Undermined intermediates.

phenylboron dichloride, two molecules of butyl chloride were ejected in two separate steps with the formation of dibutylamino phenylchloride. The results are represented in the form of differential thermograms in Fig. 1 and Table 1.

$$Et_4N^+BCl_4^- \longrightarrow Et_3NBCl_3 + EtCl \qquad (1)$$

$$Et_4N^+BPhCl_3^- \longrightarrow Et_3NBPhCl_2 + EtCl \qquad (2)$$

$$Et_3NBPhCl_2 \longrightarrow Et_2NBPhCl + EtCl \qquad (3)$$

$$Bu_4N^+BX_4^- \longrightarrow Bu_2NBX_2 + 2BuX \qquad (4)$$

$$Bu_4N^+BPhCl_3^- \longrightarrow Bu_3NBPhCl_2 + BuCl$$

$$Bu_3NBPhCl_2 \longrightarrow Bu_2NBPhCl + BuCl. \qquad (5)$$

Thermogravimetric analysis of tetrabutylammonium tetraphenylborate did not give any indication for the formation of any resolvable intermediate. However, in the case of tetraethylammonium tetraphenylborate system an intermediate, equivalent to [Et_3NBPh_3] was indicated with possible loss of one molecule of ethylbenzene.

All the thermogravimetric analysis results were further supported by the differential thermal analysis. The latter technique afforded no identification of the thermal decomposition sequence beyond the point of formation of 1 : 1 complex except in the case of triethylamine and tributylamine trichloroboranes, where, there are some indications of the possible formation of diethylamino and dibutylamino dichloroborane respectively. These indications are obtained by comparison of relevant differential thermal analysis curves.

Helpful guidance of Dr. B. R. Currell during the course of this work is acknowledged.

References

1) W. Gerrard, *J. Oil. Col. Chem. Ass.*, **42**, 625 (1959).
2) W. Gerrard, *Soc. Chem. Ind. Mongr.*, No. 13 (1961).
3) M. F. Lappert and M. K. Majumdar, *Proc. Chem. Soc.*, **1963**, 88.
4) J. C. Sheldon and B. C. Smith, *Quart. Rev.*, **14**, 200 (1960).
5) A. B Burg and J. Banus, *J. Am. Chem. Soc.*, **76**, 3903 (1954).
6) C. A. Brown and A. W. Laubengayer, *J. Am. Chem. Soc.*, **77**, 3699 (1955).
7) I. M. Butcher and W. Gerrard, *J. Inorg. Nucl. Chem.*, **27**, 829 (1965).