THERMOGRAVIMETRIC ANALYSIS OF TRIALKYLAMINE HALOBORANES. PART III

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Abstract. Thermogravimetric analysis of trialkylamine haloboranes [R_3NBX_3] shows loss in weight corresponding to the ejection of 1 mol. of alkyl halides with the formation of dialkylamine dihaloboranes.

This work is a continuation of our investigations for the preparation of boron–nitrogen polymers in the hope that their thermal stabilities would be greater than those of the known organic polymers. Part 1 of this series described the thermogravimetric analysis of tetraalkylammonium haloborates[1] and Part II of this series deals with the application of differential thermal analysis (DTA) on tetraalkylammonium haloborates.[2] The results of these studies are consistent with the following proposed schemes :

$$R_4N^+BX_4^- \longrightarrow R_3NBX_3 + RX \qquad (a)$$

R, Et and n—Pr ; X, Cl, Br, I and $PhCl_2$

$$R_4N^+BX_4^- \longrightarrow [?] \longrightarrow R_2NBX_2 + RX \qquad (b)$$

R, n—Bu; X, Cl, Br, I and $PhCl_2$
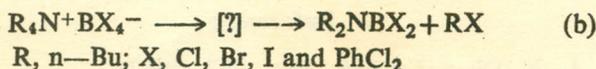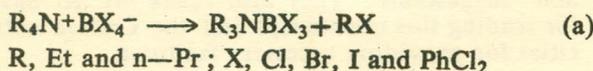
In order to formulate methods for the preparation of particular linear[3] or cyclic[4-6] polyborazynes $\begin{bmatrix} R & X \\ | & | \\ N{-}B \end{bmatrix}_n$ it is necessary to have a clear understanding of the mechanism of their formation. A number of routes (c–f) leading to the formation of polyborazynes have been suggested earlier.[7-10]

$$3RNH_2BX_3 \xrightarrow{-3HX} [3RNHBX_2] \xrightarrow{-3HX}$$

$$[3RN{=}BX] \longrightarrow [RNBX]_3 \qquad (c)$$

$$3RNH_2BX_3 \xrightarrow{-3HX} [3RNHBX_2] \longrightarrow$$

$$[RNHBX_2]_3 \xrightarrow{-3HX} [RNBX]_3 \qquad (d)$$

$$3RNH_2BX_3 \xrightarrow{-HX} \begin{bmatrix} RNH_2BX_2RNHBX_3 \\ + \\ RNH_2BX_3 \end{bmatrix} \xrightarrow{-2HX}$$

$$[RNHBX_2]_3 \xrightarrow{-3HX} [RNBX]_3 \qquad (e)$$

$$3RNH_2BX_3 \xrightarrow{-3HX} [3RNHBX_2] \xrightarrow{-HX}$$

$$\begin{bmatrix} RNHBXRNBX_2 \\ + \\ RNHBX_2 \end{bmatrix} \xrightarrow{-2HX} [RNBX]_3 \qquad (f)$$
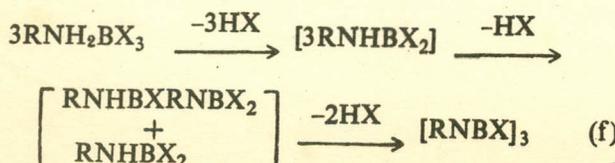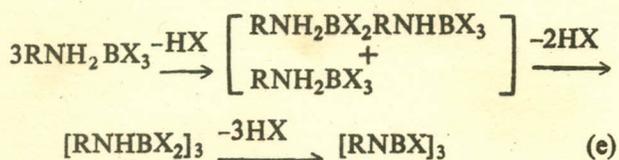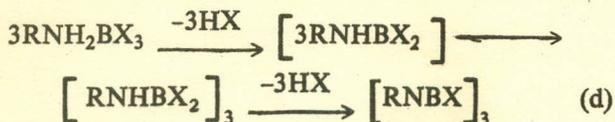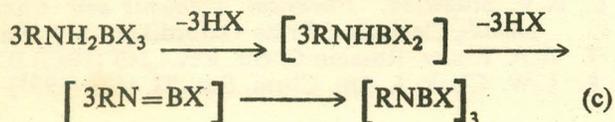
We have already reported the decomposition of tetraalkylammonium haloborates [$R_4N^+BX_4^-$] system by normal macroscopic bench technique and thermal analysis with a view to trace the reaction sequence leading to the formation of linear polyborazynes $\begin{bmatrix} R & X \\ | & | \\ N{-}B \end{bmatrix}_n$
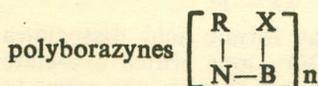
Since trialkylamine haloboranes are formed by the decomposition of tetraalkylammonium haloborates it was considered necessary to know the fate of trialkylamine haloboranes [R_3NBX_3] on extension of the same treatment. Therefore, this paper, reports the results obtained by using the same technique on different trialkylamine haloboranes.

Experimental

Trialkylamine haloboranes were prepared by the interaction of suitable trialkylamine and trihaloborane in 1:1 ratio at –80°.

$$R_3N + BX_3 \longrightarrow R_3NBX_3$$

R, Et, n–Pr, n–Bu; X, Cl, Br, I, $PhCl_2$
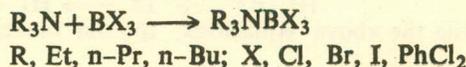
Thermogravimetric analysis technique has been described in Part I. The results were obtained by using heating rates from 3 to 6°/min. Slower heating rates gave variable results which were difficult to reproduce. This difficulty is probably due to some side reactions and volatility of intermediates.

Results and Discussion

Thermogravimetric analysis of 1:1 complexes of trialkylamines and haloboranes [R_3NBX_3] undergo the following interesting changes. When R is ethyl and X is chloride or bromide, no transformation is recorded due to any loss in weight of the complex. In instances where R is ethyl and X is dichlorophenyl, the inflection corresponding to the ejection of one mol. of ethyl chloride indicates the formation of diethylaminodihaloborane [R_2NBX_2]. When R is n-butyl and X is chloride or bromide in the 1:1 complex of tri-n-butylamine and haloborane, decomposition corresponds with the formation of di-n-butylaminodihaloborane [R_2NBX_2] with the elimination of one mol. of butylhalide. But when R is n-butyl and X is dichlorophenyl no

TABLE 1. THERMOGRAVIMETRIC ANALYSIS OF TRIALKYLAMINE HALOBORANE.

1 : 1 Complex	Sample wt (mg)	% wt loss at inflection	% wt loss calculated for dialkylamine dihaloborane	Dialkylamine dihaloborane formed
Et_3NBCl_3	195.9	14.3 A*	—	—
		99.7 B*	—	—
Et_3NBBr_3	226.5	68.4 A*	—	—
		97.3 B*	—	—
$Et_3NBPhCl_2$	222.8	20.6 A	20.8	$Et_2NBPhCl$
		62.4 B*	—	—
		80.3 C*	—	—
$n\text{-}Bu_3NBCl_3$	127.5	35.5 A	35.7	$n\text{-}Bu_2NBCl_2$
		80.7 B*	—	—
		94.9 C*	—	—
$n\text{-}Bu_3NBBr_3$	115.2	29.0 A	29.8	$n\text{-}Bu_2NBBr_2$
		99.8 B*	—	—
$n\text{-}Bu_3NBPhCl_2$	130.4	No inflection	—	—

*Undetermined intermediates.
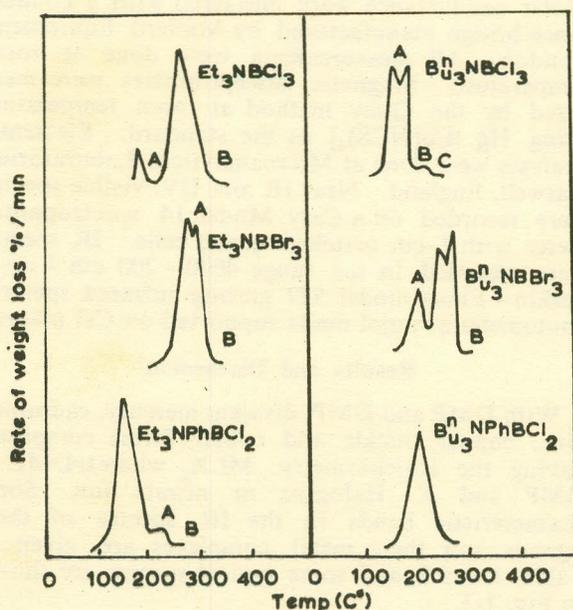
Fig. 1. Differential thermograms.

change in weight was observed. These reactions are indicated in equations (g–i) and results are presented as differential thermograms in Fig. 1 and Table 1.
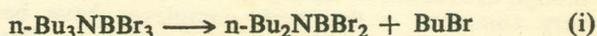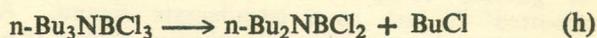
$$Et_3NBPhCl_2 \longrightarrow Et_2NBPhCl + EtCl \qquad (g)$$

$$n\text{-}Bu_3NBCl_3 \longrightarrow n\text{-}Bu_2NBCl_2 + BuCl \qquad (h)$$

$$n\text{-}Bu_3NBBr_3 \longrightarrow n\text{-}Bu_2NBBr_2 + BuBr \qquad (i)$$

References

1. S.U. Sheikh, Bull. Chem. Soc. Japan (1976), in press.
2. S.U. Sheikh, Bull. Chem. Soc. Japan (1976) submitted.
3. A.B. Burg and J. Banus, J. Am. Chem. Soc., **76**, 3903 (1954).
4. M.F. Lappert and M.K. Majumdar, Proc. Chem. Soc., 88 (1963).
5. J.C. Sheldon and B.C. Smith, Quart. Rev., **14**, 200 (1960).
6. H.S. Turner and R.J. Warne, Proc. Chem. Soc., 69 (1962).
7. P.I. Paetzold and W.M. Simson, Angew. Chem. Intern. Ed. (English) 5, 842 (1966).
8. *Boron-Nitrogen Chemistry*, edited by M. F. Lappert and M.K. Majumdar, Advance in Chemistry Series, No. 42, American Chemical Society, Washington D.C. (1964), p. 208.
9. O.T. Beachley, Inorg. Chem., **6**, 870 (1967).
10. B.R. Currell and I. Atkinson, unpublished work (1970).