

ELECTRON-IMPACT INDUCED FRAGMENTATION OF 1:1 COMPLEX IN BORON-NITROGEN COMPOUNDS

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The species produced from the electron-impact induced fragmentation of 1:1 complexes of trialkylamines and haloboranes have been examined. However, when the same treatment is carried out with triethylamine borane complex some other species also appear.

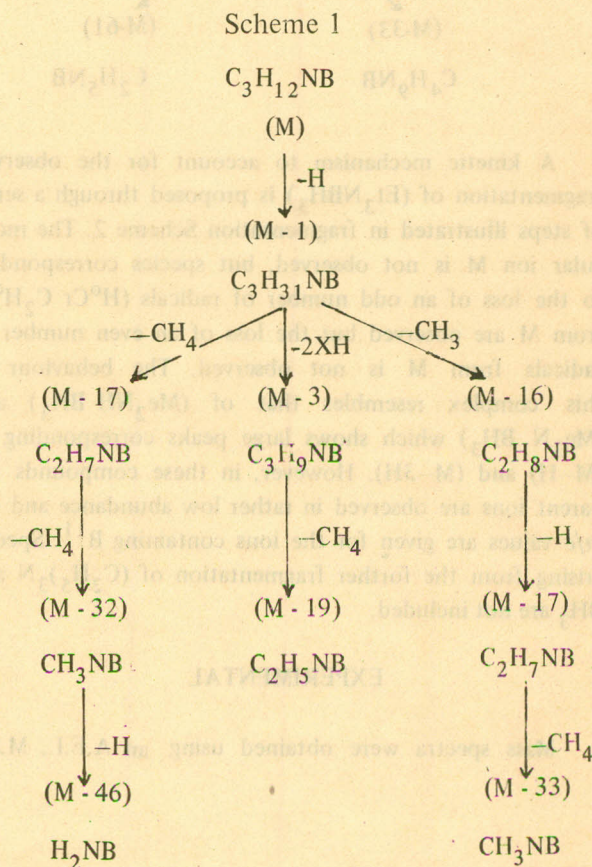
INTRODUCTION

One of the interesting transformations of trialkylamine haloborane complexes ($R_3N.BX_3$: where $R = Et$ and $n\text{-But}$, $X = H, Cl, Br$ or $PhCl_2$) concerns their conversions to polyborazynes [1-4] $(RNBX)_n$. The most important method for such conversions is the direct pyrolysis of the complexes leading to the formation of dialkylamino dihaloborenes and finally to polymeric products [5].

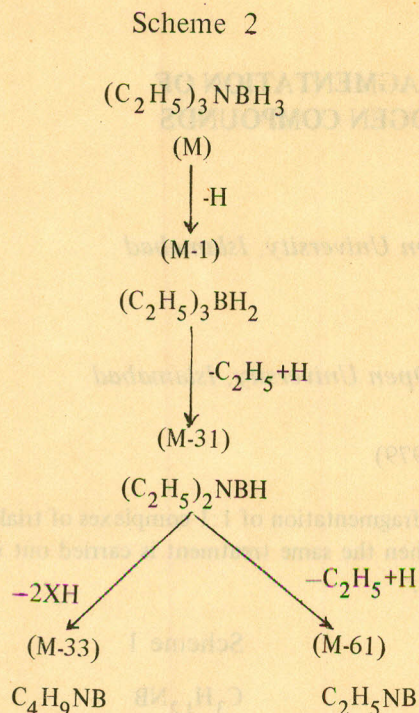
Knowing these results we were stimulated to study the electron impact induced fragmentation of trialkylamine haloborane complexes. Mass spectra of trimethylamine haloboranes ($X = Cl, Br, I$ and BF_nBr_m) ($n + m = 3$) and ethylamine haloboranes ($X = H, Cl, Br$ and I) are already known [6,7] showing the fragmentation pattern in which mainly the cleavages of boron-nitrogen and boron-halogen bonds are indicated. Their results were interpreted in terms of bond strength. Other species detected by them are shown in Scheme 1. The dissociation process of trialkylamine haloboranes ($R = Et$ and $n\text{-But}$ and $X = Cl, Br, PhCl_2$) which were studied by us resembles that of trimethyl series but we noticed some additional interesting species in the fragmentation of triethylamine borane complexes.

RESULTS AND DISCUSSION

The mass spectra of triethylamine haloborane ($R_3N.BX_3$: $R = Et$ and $n\text{-But}$, $X = H, Cl, Br$ and $PhCl_2$) produced from electronically induced reaction at 100° and 250° were obtained. The spectra of the complexes obtained mainly from fragmentation of R_3N and BX_3 were investigated. However, with $X = H$ the electron



induced dissociation of the complex of triethylamine borane ($Et_3N.BH_3$) leads to few other fragments as indicated from the record of fragmentation pattern given in Fig.1. The assignments of structures to these fragments were facilitated by the use of the isotopic pattern from naturally occurring isotopes of boron ($B^{10} = 19.6\%$ $B^{11} = 80.4\%$).



A kinetic mechanism to account for the observed fragmentation of $(\text{Et}_3\text{NBH}_3)$ is proposed through a series of steps illustrated in fragmentation Scheme 2. The molecular ion M is not observed, but species corresponding to the loss of an odd number of radicals (H° or $\text{C}_2\text{H}_5^\circ$) from M are observed but the loss of an even number of radicals from M is not observed. The behaviour of this complex resembles that of $(\text{Me}_2\text{NBH}_3)$ and $(\text{Me}_3\text{NBH}_3)$ which shows large peaks corresponding to (M-H) and (M-3H). However, in these compounds the parent ions are observed in rather low abundance and the m/e values are given for the ions containing B^{11} . Species arising from the further fragmentation of $(\text{C}_2\text{H}_5)_3\text{N}$ and BH_3 are not included.

EXPERIMENTAL

Mass spectra were obtained using an A.F.I., M.S.9

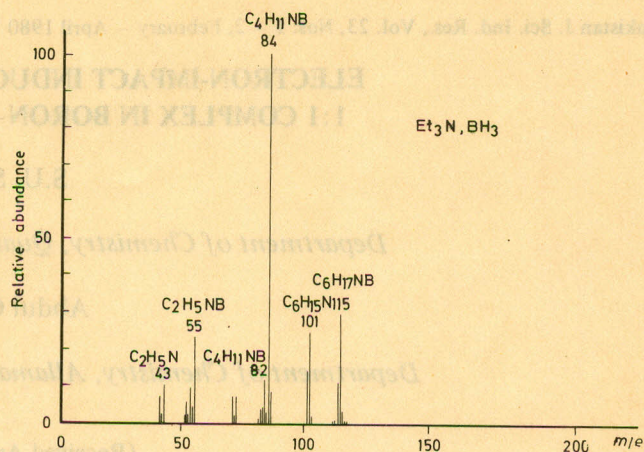


Fig. 1. Fragmentation pattern of triethylamine borane.

instrument at 70 eV and an accelerating voltage of 8 kV with the ionization chamber at 100–200°. Pure samples were introduced with a direct insertion probe.

Triethylamine haloborane were prepared by the interaction of triethylamine and haloborane (1:1) at 80° as described previously [8].

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