Ionisation Potentials and Electronic Spectra of Halogeno- and Amino-boranes, and a Study of Some Redistribution Reactions

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We have prepared, identified (by mass measurement), and characterised (by their ionisation potentials) the mixed halogenoboranes $X_nBX'_{3-n}$ (X and X′ are Cl and Br, or Cl and F, and $n = 1$ or 2), using redistribution reactions of the following type, carried out by introducing each of the simple halides successively into the mass spectrometer at ambient temperature.

$$BX_3 + BX'_3 \rightleftharpoons X_2BX' + XBX'_2$$

This class of reaction is capable of wide extension. For example, we have similarly examined the Et_nBCl_{3-n} system. Under laboratory conditions, BEt_3 and BCl_3 interact only at high temperatures.

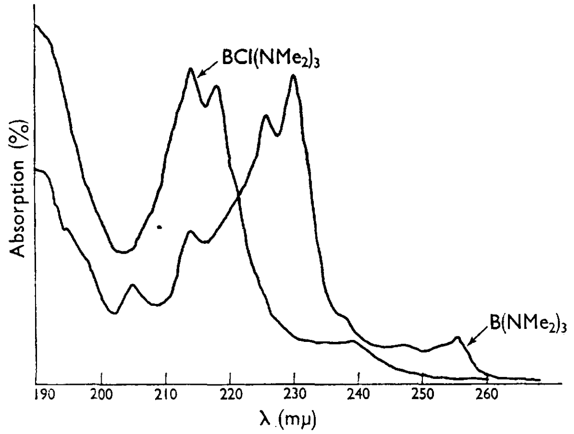
There has been much interest in the question of the existence of the mixed halides of boron, and these are only known as mixtures in equilibrium with the simple halides.[1] It is noteworthy, therefore, that their parent molecular ions are long-lived. The ions F_2BCl^+ and $FBCl_2^+$ have previously been identified mass-spectrometrically.[2]

TABLE

Series 1	Compound	$B(NMe_2)_3$	$ClB(NMe_2)_2$	Cl_2BNMe_2	Cl_3B
	I.P. (ev)	7·57 ± 0·05	8·0 ± 0·06	10·27 ± 0·08	11·67 ± 0·1
Series 2	Compound	BBr_3	$ClBBr_2$	Cl_2BBr	Cl_3B
	I.P. (ev)	10·62 ± 0·1	10·79 ± 0·3	11·13 ± 0·1	11·67 ± 0·1
Series 3	Compound	BF_3	$ClBF_2$	Cl_2BF	Cl_3B
	I.P. (ev)	15·97 ± 0·1	12·43 ± 0·1	12·18 ± 0·1	11·67 ± 0·1
Series 4	Compound	BEt_3	$ClBEt_2$	Cl_2BEt	Cl_3B
	I.P. (ev)	9·66 ± 0·1	10·28 ± 0·1	10·8 ± 0·3	11·67 ± 0·1

The mass-spectral redistribution reaction has been extremely convenient in advancing[3] our study on ionisation potentials of a series of boron compounds. The present data are shown in the Table. So far, we have analysed the results only by a simple Hückel treatment (*cf.*, ref. 3). The most important conclusion is that whereas π-bonding between boron and nitrogen is important, it is far less significant for BCl or BBr.

We propose to attempt more sophisticated treatments in order to evaluate the electronic levels of these molecules. For this purpose, electronic-spectral data are needed, and none were previously available on simple boron compounds. Absorption maxima (gaseous samples) in the range 185—350 mμ for the compounds examined to date are: $B(NMe_2)_3$, 256, 247, 237sh, 231, 227, 214, 205, $\sim$188; $ClB(NMe_2)_2$, 235sh, 218, 213, $\sim$187; $BrB(NMe_2)_2$, essentially similar to $ClB(NMe_2)_2$, particularly with regard to relative intensities; Cl_2BNMe_2, and Br_2BNMe_2, continuous intense absorption from $\sim$230 to $\sim$185 mμ; BCl_3, 208, $\sim$186; BBr_3, 252, 204 mμ. Further illustration, for two of the compounds, is provided by the Figure. At this time



FIGURE

we do not have available accurate results for extinction coefficients, mainly for the less volatile compounds. However, the high intensities ($\log_{10} \epsilon$ up to $\sim$3·8) of certain of the absorption bands of $B(NMe_2)_3$ and $XB(NMe_2)_2$ ($X = Cl$ or Br) are consistent with these arising from allowed n–$\pi \rightarrow \pi^*$ transitions; whilst the much lower intensities found for bands in BCl_3, BBr_3, and Cl_nBBr_{3-n} suggest that these arise from symmetry-forbidden transitions, such as n–$\sigma \rightarrow \pi^*$. The spectral and ionisation potential data are thus in qualitative agreement regarding the relative importance of π-bonding in the various systems. From electronic spectral data of mixtures of BCl_3 and BBr_3, evidence for mixed halides was obtained, and redistribution reactions are being studied by this technique also.

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