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Cationic Boron Complexes

O.P.Shitov, S.L.Ioffe, V.A.Tartakovskii, and S.S.Novikov

The review deals with studies on an interesting class of boron compounds constituting a very rapidly developing field at the boundary between inorganic and "organoelemental" chemistry.
The bibliography includes 189 references.

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I. INTRODUCTION

The chemistry of cationic boron complexes† began with the work of Diltey, who obtained in 1906 the first boronium cations by the interaction of β-diketones with boron trichloride[1].

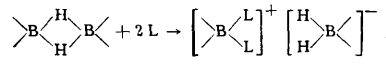
In the last decade, after the work of Parry and coworkers[2-9] who determined the structure of "diammoniate of diborane", this field in boron chemistry has developed extensively.

A number of fundamental monographs[10-21] dealing with various aspects of boron chemistry have now been published. In the first place mention must be made here of the books by Mikhailov[17], Zhigach[19], Steinberg[15], and Muetterties[18]. These monographs contain isolated data on the methods of synthesis and the properties of boronium salts but they do not provide complete information about these compounds. Moreover, in recent years many new results have accumulated, which have not been reviewed anywhere. This review gives a compilation of the literature on the cationic boron complexes up to the middle of 1969.

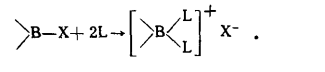
II. PREPARATION OF CATIONIC BORON COMPLEXES

The methods of preparation of numerous boron complexes with a wide variety of structures may be divided into four principal groups.

1. Asymmetric cleavage of boranes by Lewis bases:

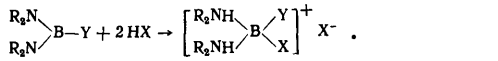


2. Conversion of substituted boranes under the action of amines:

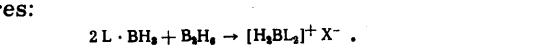


† Boron complexes with boron as the central atom of the cation are called cationic boron complexes or boronium salts. In the present review both terms are used.

3. Addition of hydrogen halides to aminoboranes:

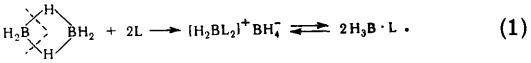


4. Reaction of boranes with aminoboranes at elevated temperatures:



1. ASYMMETRIC CLEAVAGE OF BORANES BY LEWIS BASES

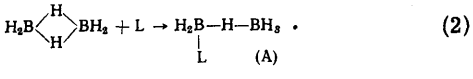
At the present time there exist two views on the mechanism of the formation of cationic boron complexes by the reaction of Lewis bases with diborane. According to Beachley[22], at a low temperature bases always cause an asymmetric cleavage of diborane and the cationic boron complexes can rearrange to the corresponding aminoboranes when the latter are thermodynamically more stable at a given temperature:



(1)

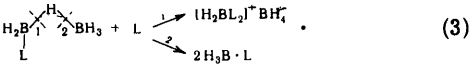
However, Shore and Parry[3] and also Inoue and Kodama[23] showed that in liquid amines and in ether there is no equilibrium between cationic boron complexes and the corresponding aminoboranes.

According to another view[5,24] the reaction of diborane with Lewis bases begins with the dissociation of one bridge bond and the formation of an intermediate product (A):



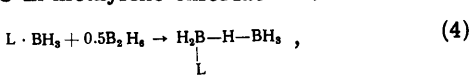
(2)

The nature of the final compound is determined by the mode of dissociation of the three-centre bond $H_2B-H-BH_3$ as a result of the attack by a second molecule of the base on product (A):



(3)

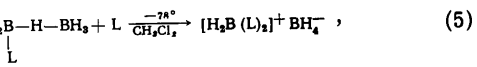
The mode of attack depends both on the structure of the reactants and on the reaction temperature. In many cases the reaction can proceed via both pathways simultaneously. This mechanism of the formation of boronium salts was confirmed by the preparation of compounds of type (A) in the tensimetric titration of aminoboranes by diborane at −78°C in methylene chloride[24,25]:



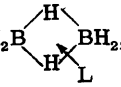
(4)

where L = NH_3, CH_3NH_2, or $N(CH_3)_3$. The presence of H_2B and BH_3 groups in these compounds was established by ^{11}B NMR spectroscopy‡.

The addition of a second mole of the amine leads to compounds indicated below:



(5)

‡ Eastham[26] suggests that compounds (A) have the structure , i. e. the diborane molecule is linked to the ligand by a π-bond formed by a free orbital of diborane and the electron pair of the amine. However, this structure was rejected on the basis of tracer atom studies and the determination of the heats of reaction[27].

where L = NH_3 or CH_3NH_2;

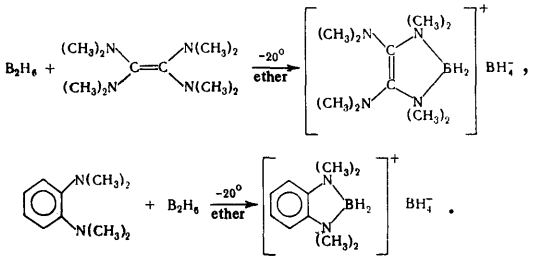
(6)

Thus the same products were obtained in reactions (5) and (6) as in the reaction between diborane and an excess of the corresponding amine at a low temperature.

It is interesting to note the effect of the degree of methylation of amines on the proportions of the final products in the reaction with diborane. Whereas in the reaction with ammonia[28-32] the boronium salt is mainly formed§, in the reaction with trimethylamine the product was exclusively a neutral complex[39]. Methylamine and dimethylamine[22,23,39] form mixtures of both possible compounds, with the boronium salt predominating in the first case and the neutral complex in the second:

(7)

Apparently the cleavage of the intermediate (A) is determined mainly by steric factors. This is confirmed by Wiberg's data[40] on the synthesis of boronium salts in the reaction of tertiary diamines with diborane:



(8)

The ease of preparation of such salts has been explained by the formation of a sterically favourable cyclic system[14].

Other Lewis bases can also react with diborane via mechanism (2)−(3) with formation of cationic boron complexes. In a tensimetric study of the reaction of diborane with dimethyl sulphoxide in methylene chloride at −78°C, McAchran and Shore[41] showed that in this case a boronium salt is formed:

(9)

The formation of the hydrated ion BH_2^+ has been postulated in the reaction between diborane and 8 *N* hydrochloric acid at −70°C:[42,43]

(10)

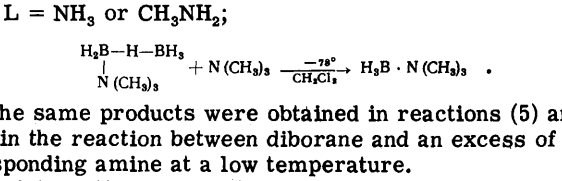
The cation may be formed as a result of the asymmetric cleavage of diborane by water¶:

(11)

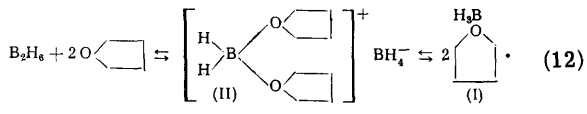
On the basis of the electrical conductivity of diborane solutions in tetrahydrofuran (THF) and diglyme, Brown and Wallace[44] and Mikhailov et al.[45] concluded that the corresponding cationic boron complexes exist in such

§ For the structure of "diammoniate of diborane" $[H_2B(NH_3)_2]^+BH_4^-$, see the appropriate literature[2-9,28,33-38].

¶ However, one cannot exclude also other mechanisms of this reaction, for example:

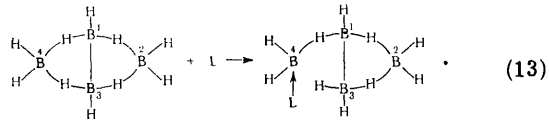


solutions. Mikhailov et al.[45] believe that in a tetrahydrofuran solution of diborane there is an equilibrium between the neutral complex (I) and the cationic boron complex (II):



(12)

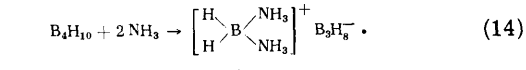
Apart from diborane, higher boranes can also undergo asymmetric cleavage by Lewis bases. The mechanism of the reaction of tetraborane with Lewis bases is similar to that of the cleavage of diborane and consists in the dissociation of one of the bridge bonds in the first stage of the reaction[46]:



(13)

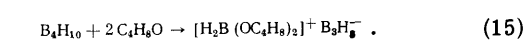
A second molecule of the base attacks the B^4-H-B^1 bond, which is ruptured with the formation of the cation $(H_2BL_2)^+$ and the anion $B_3H_8^-$ (asymmetric cleavage) or the complexes $H_3B.L$ and $B_3H_7.L$ (symmetrical cleavage).

Stock et al.[47], who investigated the reaction of tetraborane with ammonia, concluded that its products are unstable compounds with the compositions $B_4H_{10}.4NH_3$ and $B_4H_{10}.2.5NH_3$. However, Kodama and Parry[48,49] showed that the product of the reaction of an ethereal solution of tetraborane with ammonia at −78°C is diammineboronium octahydrotriborate:



(14)

Schaeffer et al.[50] detected by ^{11}B NMR spectroscopy the anion $B_3H_8^-$ in solutions of tetraborane in tetrahydrofuran at −53°C, which is evidence of the formation of the boronium salt:

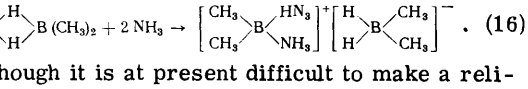


(15)

However, they did not detect the corresponding cation $[H_2B(OC_4H_8)_2]^+$.

These data are somewhat inconsistent with earlier studies, where it was found that the reactions of tetraborane with amines, ethers, or dialkyl sulphides lead exclusively to the formation of products of the symmetrical cleavage of tetraborane[51-53].

Moews and Parry[54] described the asymmetric cleavage of tetramethyldiborane by ammonia at −78°C†:

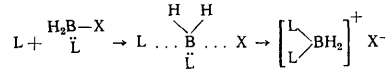


(16)

Thus, although it is at present difficult to make a reliable *a priori* prediction of the structure of the final products of the reaction of boranes with Lewis bases, the published data makes it possible to follow fairly clearly the effect of the structure of the reactants on the process.

2. THE CONVERSION OF SUBSTITUTED BORANES UNDER THE ACTION OF AMINES

The reaction of substituted boranes with bases is the most widely used method for the synthesis of cationic boron complexes. In most cases the formation of such complexes by this method may be regarded as nucleophilic substitution by the base of an electronegative substituent X at the boron atom, probably via an S_N2 mechanism[56-58]:

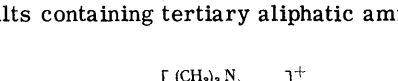


(17)

In many cases in the presence of bulky substituents in the amine–borane molecule or when charged intermediate species may be stabilised, one cannot exclude also the possibility of a reaction by an S_N1 mechanism. This possibility was discussed by Ryschkewitsch and coworkers[59], who investigated the reaction of $(CH_3)_3N.BH_2I$ with methylpyridines and also by Nöth et al.[56] in the case of pyridine-chloroborane, for which there is a possibility of the formation of a cation stabilised by mesomerism. However, in a later study of Nainan and Ryschkewitsch[58] the ionisation of iodoboranes in non-polar solvents and the formation under these conditions of boronium salts by an S_N1 mechanism was fully excluded.

In the synthesis of boronium salts via mechanism (17) it is necessary to take into account a number of factors which influence the stability of boronium salts under the reaction conditions: (1) the dimensions and nature of the anion; (2) the steric and electronic effects of the substituents at the boron atom; (3) the structure of the bases.

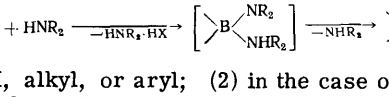
An increase in the size of the anion leads to considerable stabilisation of the boronium salt. Thus, when trimethylamine-iodoborane was used instead of trimethylamine-chloroborane[56,58,60], it was possible to obtain boronium salts containing tertiary aliphatic amines in the cation:



(18)

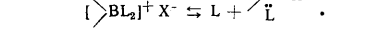
where L = $(CH_3)_3N$, $(C_2H_5)_3N$, or 4-methylpyridine.

The salts formed by the anions of weak acids (SR^-) are stable only in the presence in the cation of relatively small ligands[61]. An increase of the bulk of the substituents at the boron atom or the heteroatom of the base leads to a decrease of the stability of the boronium cation, the decomposition of which in the reaction may be represented by two mechanisms: (1) in the case of primary and secondary amines the final reaction products may be aminoboranes:



(19)

where R = H, alkyl, or aryl; (2) in the case of tertiary amines we believe that there is a possibility of the regeneration of the initial complex:



(20)

A number of boron compounds have been used to synthesise cationic boron complexes by the substitution method: (a) complexes of halogenoboranes with Lewis bases; (b) amine-boranes; (c) mercaptoboranes and their amine complexes; (d) aryl-, alkyl-, amino-, and alkoxy-boron halides; (e) boron trihalides BX_3 (X = Cl, Br, I, or F).

a. Preparation of Boronium Salts from Complexes of Halogenoboranes with Lewis Bases

Nöth and coworkers[56,62-64] observed in a study of the reaction of ether and amine complexes of chloroboranes

† This reaction was investigated for the first time by Schlesinger et al.[55], but they did not establish the composition and the structure of the reaction product.

with amines that the latter takes place with formation of boronium salts‡:

$$H_2BCl \cdot OR_2 + 2\,L \rightarrow \left[H_2B\begin{matrix}L\\L\end{matrix}\right]^+ Cl^- + R_2O;\ H_2BCl \cdot L + L' \rightarrow \left[H_2B\begin{matrix}L'\\L\end{matrix}\right]^+ Cl^-, \quad (21)$$

where L and L′ = NH_nR_{3-n} ($n = 1-2$) or C_5H_5N.

Ryschkewitsch and coworkers[58-60,66] obtained boronium salts containing various tertiary amines in the cation:

$$L \cdot BH_2I + L' \rightarrow \left[H_2B\begin{matrix}L\\L'\end{matrix}\right]^+ I^- , \quad (22)$$

where L = R_3N (R = CH_3 or C_2H_5) or pyridine and L′ = substituted pyridines, quinoline, or *NN*-dimethylaniline.

Douglass et al.[67] isolated boronium salts with alkyl substituents at the boron atom:

$$R'R''B \cdot I \cdot NC_5H_5 + C_5H_5N \rightarrow [R'R''B\,(NC_5H_5)_2]^+ I^- , \quad (23)$$

where R′ = 1,1,2-trimethylpropyl and R″ = H or R′ = R″ = cyclohexyl.

It has also been observed that the bis(pyridine)boronium cation is formed when pyridine-iodoborane is refluxed in an ether–benzene solution at 40°C.[68] The authors quote the following reaction mechanism:

$$\begin{gathered} C_5H_5N \cdot BH_2I + (C_2H_5)_2O \rightarrow [C_5H_5NBH_2O\,(C_2H_5)_2]^+ I^- , \\ [C_5H_5NBH_2O\,(C_2H_5)_2]^+ + I^- \rightarrow C_5H_5N \cdot BH_2OC_2H_5 + C_2H_5I , \\ C_5H_5N \cdot BH_2OC_2H_5 \leftrightarrows C_5H_5N + H_2BOC_2H_5 , \\ C_5H_5N \cdot BH_2I + C_5H_5N \rightarrow [(C_5H_5N)_2\,BH_2]^+ I^- . \end{gathered} \quad (24)$$

The preparation of cationic boron complexes containing in the cation alkylthio-groups linked directly to the boron atom has been described[69]:

$$(CH_3)_3N \cdot BH_2SCH_3 + BH_2I \cdot N(CH_3)_3 \rightarrow \left[\begin{matrix}CH_3\\|\\(CH_3)_3NBH_2SBH_2N(CH_3)_3\end{matrix}\right]^+ I^- , \quad (25)$$

$$CH_3)_3NBH_2SCH_3 + (CH_3)_3N \cdot BH_2SBH_2I \rightarrow \left\{\left[\begin{matrix}CH_3\\|\\(CH_3)_3NBH_2S\end{matrix}\right]_2 BH_2\right\}^+ I^- ,$$

and also the synthesis of boronium salts with polyfunctional bases[70,71], tertiary amines, phosphines, arsines, sulphides[72], and their oxides[73].

A monobrominated boronium cation was obtained by the reaction of trimethylamine-dibromoborane with *NNN′N′*-tetramethylethylenediamine[72]:

$$(CH_3)_3N \cdot BHBr_2 + (CH_3)_2NCH_2CH_2N(CH_3)_2 \rightarrow \left[\begin{matrix}CH_2-CH_2\\(CH_3)_2N\quad N(CH_3)_2\\B\\H\quad Br\end{matrix}\right]^+ Br^- . \quad (26)$$

b. Preparation of Boronium Salts from Amine-boranes

Douglass[74,75], who investigated the reaction of amine complexes of borane or its derivatives with iodine in an excess of the amine isolated cationic boron complexes:

$$RBH_2 \cdot L + I_2 + 2\,L \rightarrow [RBHL_2]^+ I^- + L{+}HI{\cdot}L , \quad (27)$$

‡ Nöth and coworkers[56] initially isolated the boronium salts as side products in the reduction of benzoyl chloride by the complexes $H_3B.NH_2R$ (R = CH_3, n-C_3H_7, or t-C_4H_9). The formation of these salts may be represented by the following equations[17]:

$$\begin{gathered} C_6H_5COCl + H_3B \cdot NH_2R \rightarrow H_2BCl \cdot NH_2R + C_6H_5CHO , \\ C_6H_5CHO + H_3B \cdot NH_2R \rightarrow C_6H_5CH_2OBH_2 + RNH_2 , \\ H_2BCl \cdot H_2NR + RNH_2 \rightarrow [H_2B\,(NH_2R)_2]^+ Cl^- . \end{gathered}$$

where (a) R = phenyl or cyclohexyl and L = C_5H_5N and (b) R = H and L = $(CH_3)_3N$ or C_9H_7N. Initially a two-stage reaction mechanism was proposed: in the first stage an amine complex of iodoborane is formed and is then converted further into a boronium salt under the influence of the excess amine:

$$\begin{gathered} RBH_2 \cdot L + I_2 + L \rightarrow RBHI \cdot L{+}HX{\cdot}L , \\ RBHI \cdot L + L \rightarrow [RBHL_2]^+ I^- . \end{gathered} \quad (28)$$

However, further study of the reaction[67] showed that amine-boranes containing bulky substituents at the boron atom do not react with iodine in the excess amine. Therefore Douglass suggested another mechanism with a four-membered transition complex:

$$\begin{gathered} 2\,C_5H_5N + I_2 \longrightarrow (C_5H_5N)_2I^+ I^- , \\ R_2BH\ NC_5H_5 + (C_5H_5N)_2I^+ \longrightarrow \left[\begin{matrix}NC_5H_5\\R_2B\cdots H\\|\\C_5H_5N\cdots INC_5H_5\end{matrix}\right] \longrightarrow [R_2B(NC_5H_5)_2]^+ + C_5H_5N \cdot HI . \end{gathered} \quad (29)$$

This mechanism agrees better with the experimental data, since it is known that cyclic transition states are very sensitive to steric factors.

Ryschkewitsch[76] obtained dipyridineboronium salts by the reaction of sodium borohydride or trimethylamine-borane with iodine in the presence of an excess of pyridine. The author believes that the formation of the dipyridineboronium cation from sodium borohydride may be represented by the following sequence of reactions:

$$\begin{gathered} BH_4^- + I_2 + 2\,C_5H_5N \rightarrow C_5H_5N \cdot BH_3 + C_5H_5NH^+ + 2\,I^- , \\ BH_4^- + C_5H_5NH^+ \rightarrow C_5H_5N \cdot BH_3 + H_2 , \\ C_5H_5N \cdot BH_3 + I_2 + C_5H_5N \rightarrow (C_5H_5N)_2\,BH_2^+ + C_5H_5NH^+ + 2\,I^- . \end{gathered} \quad (30)$$

The author concludes from the measurements of the rates of reaction of deuterated and normal trimethylamine-borane with iodine that the rate-determining stage of the reaction [Eqn. (31)] is hydride transfer from trimethylamine-borane to iodine:

$$H_3B \cdot N(CH_3)_3 + I_2 + 2\,C_5H_5N \rightarrow [H_2B\,(NC_5H_5)_2]^+ I^- + (CH_3)_3N \cdot HI . \quad (31)$$

A similar boronium cation is formed when trimethylamine-borane is refluxed with mercury(I) chloride in pyridine[76].

Borane complexes with phosphorus and arsenic derivatives can also be introduced into the Douglass reaction[70]:

$$(CH_3)_3SiCHL \cdot BH_3 + I_2 + N(CH_3)_3 \rightarrow \{(CH_3)_3N \cdot BH_2CH\,[Si\,(CH_3)_3]\,L\}^+ I^- , \quad (32)$$

where L = $P(CH_3)_3$ or $As(CH_3)_3$.

$$(C_6H_5)_3PCH_2BH_3 + I_2 + N(CH_3)_3 \rightarrow [(CH_3)_3NBH_2CH_2P\,(C_6H_5)_3]^+ I^- .$$

c. Preparation of Boronium Salts from Mercaptoboranes

Mikhailov and coworkers[61,77] showed that in the reaction of trimers of alkylthioboranes with primary amines bis-(alkylamine)boronium mercaptides are formed regardless of the proportions of the reactants:

$$(RSBH_2)_3 + 6\,RNH_2 \rightarrow 3\,[H_2B\,(NH_2R)_2]^+ SR^- , \quad (33)$$

where R = CH_3, C_2H_5, or n-C_4H_9. When the reaction is carried out with higher amines in the presence of benzyl chloride, bis(alkylamine)boronium chlorides are formed:

$$(RSBH_2)_3 + R'NH_2 + 3\,C_6H_5CH_2Cl \rightarrow 3\,[H_2B\,(NH_2R')_2]^+ Cl^- + C_6H_5CH_2SR , \quad (34)$$

where R = CH_3, C_2H_5, or n-C_4H_9 and R′ = iso-C_3H_7, n-C_3H_7, iso-C_4H_9, n-C_4H_9, t-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, or $C_6H_5CH_2$.

The authors proposed two schemes for the formation of bis(alkylamine)boronium chlorides without giving preference to either. The first is a modification of Nöth's method, based on the use of a halogenoborane as the initial component:

$$\begin{gathered}{}^1/_3\,(RSBH_2)_3 + 3\,R'NH_2 \rightarrow RSBH_2 \cdot NH_2R',\\ RSBH_2 \cdot NH_2R' + C_6H_5CH_2Cl \rightarrow ClBH_2 \cdot NH_2R' + C_6H_5CH_2SR,\\ H_2BCl \cdot NH_2R + RSBH_2 \cdot NH_2R' \rightarrow [H_2B\,(NH_2R')_2]^+\,Cl^- + {}^1/_3\,(RSBH_2)_3.\end{gathered} \quad (35)$$

The second scheme presupposes the partial conversion in ether of alkylamine-alkylthioborane into bis(alkylamine)-boronium mercaptide, which then reacts further with benzyl chloride:

$$\begin{gathered}2\,R'NH_2 \cdot BH_2SR \leftrightarrows [H_2B\,(NH_2R')_2]^+\,SR' + RSBH_2,\\ [H_2B\,(NH_2R')_2]^+\,SR^- + C_6H_5CH_2Cl \rightarrow [H_2B\,(NH_2R')_2]^+\,Cl^- + C_6H_5CH_2SR.\end{gathered} \quad (36)$$

We believe that the second scheme [Eqn. (36)] is less likely, because, as stated above[5,23], complexes of amine-boranes and their boronium salts are probably not interconverted in ether.

Cationic boron complexes are also formed when hydrogen chloride and halogeno-derivatives of hydrocarbons react with dimethylamine-alkylthioborane complexes[78,79]:

$$2\,RSBH_2 \cdot NH\,(CH_3)_2 + R'X \rightarrow \{H_2B\,[NH\,(CH_3)_2]_2\}^+\,X^- + RSR' + {}^1/_3\,(RSBH_2)_3, \quad (37)$$

where R = CH_3 or C_2H_5, H′ = CCl_3, $CHBr_2$, C_2H_5, $C_6H_5CH_2$, or H, and X = Cl or Br. Similar reactions take place with pyridine-alkylthioboranes under the action of carbon tetrachloride:

$$2\,RSBH_2 \cdot NC_5H_5 + CCl_4 \rightarrow [H_2B\,(NC_5H_5)_2]^+\,Cl^- + {}^1/_3\,(RSBH_2)_3 + RSCCl_3. \quad (38)$$

Only the amine complexes of halogenoboranes and dialkyl sulphides were isolated in the reactions of trialkylamine-alkylthioboranes with halogeno-derivatives of hydrocarbons[79]:

$$RSBH_2 \cdot NR''_3 + R'X \rightarrow R''_3N \cdot BH_2X + RSR'. \quad (39)$$

However, later a boronium salt was also obtained[80]:

$$(CH_3)_3N \cdot BH_2SCH_3 + CH_3I \rightarrow [(CH_3)_3NBH_2S\,(CH_3)_2]^+\,I^-. \quad (40)$$

Evidently, the formation of boronium salts in all the examples quoted takes place via mechanism (35).

d. Preparation of Boronium Salts from Alkyl-, Aryl-, Amino-, and Alkoxy-boron Halides

Many cationic boron complexes were synthesised by Mikhailov and coworkers[78,81-86] in a study of the reaction of diaryl- and dialkyl-boron halides with amines:

$$\begin{matrix}R'\\ R''\end{matrix}\!\!>\!B\!-\!X + 2\,L \rightarrow \left[\begin{matrix}R'\\ R''\end{matrix}\!\!>\!B\!<\!\begin{matrix}L\\ L\end{matrix}\right]^+ X^-, \quad (41)$$

where R′ and R″ = alkyl or aryl, X = Cl, or Br, and L = amine.

Similar boronium salts were also obtained by Nöth[63,87,88] and other investigators[89,90] by mixing the reactants in an inert solvent (ether, benzene, pentane) at room or a lower temperature.

It is noteworthy that one can undoubtedly include among the boronium salts also the ternary complexes of dibutylboron chloride and bromide with pyridine, $(C_4H_9)_2BX.2C_5H_5N$ (X = Cl or Br),[91] and a group of complexes of alkoxyarylboron chlorides[92-94], alkoxyboron dichlorides[95-97], and dialkoxyboron dichlorides[98] with two moles of pyridine, the preparation of which was reported by Gerrard, Lappert, and coworkers.

Diphenyl-($\alpha\alpha'$-dipyridyl)boronium chloride was obtained in 50% yield by refluxing diphenylboronic acid or its 2-aminoethyl ester with $\alpha\alpha'$-dipyridyl in 5 *N* solution of hydrochloric acid for 2–3 h:[89]

$$(C_6H_5)_2BOR + (NC_5H_4)_2 + HCl \rightarrow [(C_6H_5)_2B\,(NC_5H_4)_2]^+\,Cl^-, \quad (42)$$

where R = H or $OCH_2CH_2NH_2$.

A unique case of the synthesis of a cationic boron complex from borate has been described[98]:

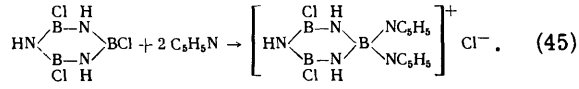
$$(C_6H_5O)_3B + NH_3 \rightarrow [(C_6H_5O)_2B\,(NH_3)_2]^+\,OC_6H_5^-. \quad (43)$$

It proved possible also to obtain boronium salts by the reaction of aminoboron halides with amines[89,99]:

$$\begin{matrix}(CH_3)_2N\\ R\end{matrix}\!\!>\!B\!-\!X + 2\,L \rightarrow \left[\begin{matrix}(CH_3)_2N\\ R\end{matrix}\!\!>\!B\!<\!\begin{matrix}L\\ L\end{matrix}\right]^+ X^-, \quad (44)$$

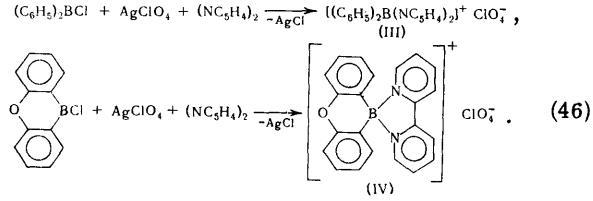
where R = $(CH_3)_2N$ or Cl, X = Cl, and L = pyridine, 4-$CH_3C_5H_4N$, or $\alpha\alpha'$-dipyridyl.

An unusual boronium salt is formed in the reaction of *B*-trichloroborazine with pyridine[99]:



(45)

The boronium salts (III) and (IV) were synthesised by Davidson and French by the reaction of a stoichiometric amount of $\alpha\alpha'$-dipyridyl with an equimolar mixture of diphenylboron chloride or 10-chloro-9-hydroxy-10-boraanthracene with silver perchlorate in nitromethane[100,101]:



(46)

They showed[100,101] that, depending on the amount of $\alpha\alpha'$-dipyridyl taken, diphenylboron chloride forms 1 : 1 and 2 : 1 complexes, to which ionic structures are attributed:

$$[(C_6H_5)_2B\,(NC_5H_4)_2]^+\,Cl^- \quad [(C_6H_5)_2B\,(NC_5H_4)_2]^+\,[Cl_2B\,(C_6H_5)_2]^-.$$

On the basis of the conductivities of $(C_6H_5)_2BCl$, $AlCl_3$, and $(C_6H_5)_2Br-AlCl_3$ solutions in nitrobenzene and also the ultraviolet spectra of these systems in ethyl methyl ketone, Davidson and French[102] believe that the boronium cation $(C_6H_5)_2B^+$, isoelectronic with the diphenylmethylcarbonium cation $(C_6H_5)_2CH^+$, is formed from $(C_6H_5)_2BCl$ in ionising solvents in the presence of ionic additives.

However, Moodie and coworkers[103], having analysed the ^1H NMR spectra of the products of the reaction of diphenylboron chloride and silver perchlorate in sulpholane, concluded that in solution the $(C_6H_5)_2B^+$ ion is coordinated to two solvent molecules and is therefore a boronium cation $[(C_6H_5)_2B\,(sulpholane)_2]^+$.

Armstrong and Perkins[104] arrived at a similar conclusion in view of the agreement between the electronic transition calculated by the Pariser–Parr–Pople method with the absorption observed in the ultraviolet spectrum of the diphenylboron cation.

Thus Davidson and French's conclusion that the $(C_6H_5)_2B^+$ ion is present must be evidently regarded as erroneous and the appreciable increase of the conductivity of the diphenylboron chloride solution in nitrobenzene following the addition of aluminium chloride may be accounted

for by the formation of a cationic boron complex according to the following mechanism:

$$(C_6H_5)_2BCl + Solv \leftrightarrows (C_6H_5)_2BCl \cdot Solv , \quad (47)$$

$$(C_6H_5)_2BCl \cdot Solv + AlCl_3 + Solv \rightarrow Solv \ldots \overset{\overset{(C_6H_5)_2}{|}}{\underset{Solv}{B}} \ldots Cl \ldots AlCl_3 \rightarrow$$

$$\rightarrow [(C_6H_5)_2B(Solv)_2]^+ AlCl_4^- ,$$

where Solv = $C_6H_5NO_2$.

Mikhailov and coworkers [45] observed that ethereal solutions of certain diarylboron chlorides [$(C_6H_5)_2BCl$, $(o\text{-}CH_3C_6H_4)_2BCl$, $(p\text{-}CH_3C_6H_4)_2BCl$, $(\alpha\text{-}C_{10}H_7)_2BCl$, and $(C_4H_9)_2BCl$] conduct electricity and explain this phenomenon by the existence in ether of an equilibrium between organoboron chlorides and the corresponding boronium salts:

$$R_2BCl + 2(C_2H_5)_2O \leftrightarrows \{R_2B[O(C_2H_5)_2]_2\}^+ Cl^- . \quad (48)$$

However, Moodie et al. [103] demonstrated by ^1H NMR spectroscopy that the cation of the boronium salt $\{(C_6H_5)_2B[O(C_2H_5)_2]\}^+ClO_4^-$ § is insufficiently stable and is fully decomposed in several hours via the following mechanism:

$$\{(C_6H_5)_2B[O(C_2H_5)_2]_2\}^+ \rightarrow (C_6H_5)_2BOC_2H_5 + (C_2H_5)_2O^+ . \quad (49)$$

e. Preparation of Boronium Salts from Boron Trihalides

A number of cationic boron complexes have been obtained by the reaction of boron trihalides with amines. The reaction consists of many stages and the final products depend on many factors [105-111]. Thus Nöth et al. [112] showed in a study of the reaction of boron trichloride with dimethylamine that the aminolysis of boron trichloride proceeds via a stage involving the formation of a boronium salt—dichlorobis(dimethylamine)boronium chloride (V) and dimethylaminoboron dichloride is formed only in the thermal decomposition of (V) in the course of aminolysis:

$$BCl_3 \xrightarrow{HN(CH_3)_2} Cl_3B \cdot HN(CH_3)_2 \xrightarrow{HN(CH_3)_2} \rightarrow \{Cl_2B[HN(CH_3)_2\}^+Cl^- \xrightarrow[-HN(CH_3)_2 \cdot HCl]{\Delta} Cl_2BN(CH_3)_2 ,$$

$$\downarrow (V) \quad \downarrow -2HN(CH_3)_2 \cdot HCl \quad (50)$$

$$ClB[N(CH_3)_2]_2 \xrightarrow[-HN(CH_3)_2 \cdot HCl]{HN(CH_3)_2} B[N(CH_3)_2]_3 .$$

Boronium salts containing various amines in the cation have been prepared by the reaction of dimethylamine – boron trichloride with amines in ether or benzene [112,113]:

$$Cl_3B \cdot NH(CH_3)_2 + L \rightarrow \left[Cl_2B\begin{matrix}NH(CH_3)_2\\ \diagup\\ L\end{matrix}\right]^+ Cl^- , \quad (51)$$

where L = NH_3, iso-$C_3H_7NH_2$, $C_4H_9NH_2$, $(CH_3)_2NH$, $(C_2H_5)_2NH$, $N(CH_3)_3$, pyridine, or 4-methylpyridine.

When trimethylamine-boron tribromide was refluxed with 3-chloropyridine, a boronium salt were also isolated: $[Br_2B(NC_5H_4Cl)_2]^+Br$. [114] Similar salts were obtained by the action of amines on solutions of boron trihalides in benzene or chloroform [115-118]¶:

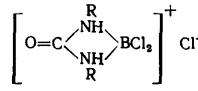
$$BX_3 + 2L \rightarrow [X_2BL_2]^+X^- , \quad (52)$$

where (a) X = Cl or Br and L = $NH(CH_3)_2$, RNH_2, or C_5H_5N and (b) X = I and L = C_5H_5N.

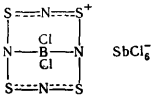
§ It is noteworthy that Mikhailov and coworkers [45] considered salts with the anion Cl^-, while boronium salts with the anion ClO_4^- are as a rule more stable [67].

¶ It is interesting that, in an ^1H NMR spectroscopic study of solutions of boron trihalides in pyridine derivatives in the temperature range between −50° and +35°C, the formation of boronium salts was not observed [119].

On the basis of conductimetric data, Greenwood and Robinson [120] attributed an ionic structure to the adducts formed by the reaction of boron trichloride with urea derivatives:



We may mention that the infrared spectrum of the compound isolated in the reaction between $SbCl_5$ and the adduct of sulphur nitride and boron trichloride corresponds very closely to the structure of a boronium salt [121]:



A similar cationic boron complex was detected in a study of $BCl_3-SbCl_5-CH_3CN$ phase diagrams at 25°C: [122]

$$BCl_3 + SbCl_5 + 2CH_3CN \rightarrow [Cl_2B(CH_3CN)_2]^+ SbCl_6^- . \quad (53)$$

Analysis of the spectroscopic characteristics and conductimetric data for solutions of boron trichloride and tribromide in acetonitrile led Schmulbach and Ahmed [123,124] to the conclusion that the ion pairs $[(CH_3CN)_2BX_2]^+BX_4^-$ exist in solution. However, the authors' conclusion probably requires confirmation. The same workers [125] suggest that the boronium cation $[I_2B(CH_3CN)_2]^+$ is formed on dissolution of $(C_2H_5)_4NBI_4$ in acetonitrile:

$$(C_2H_5)_4NBI_4 \xrightarrow{CH_3CN} (C_2H_5)_4N^+ + [I_2B(CH_3CN)_2]^+ + 2I^- . \quad (54)$$

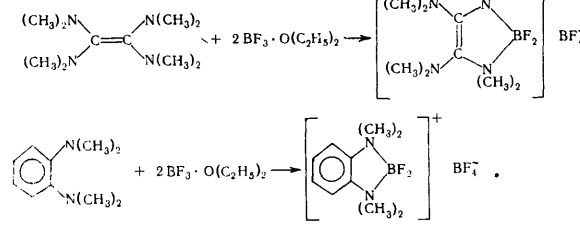
The formation of a boronium cation was postulated in the synthesis of arylboron halides from aromatic hydrocarbons and boron trichloride in the presence of aluminium and aluminium trichloride [126,127]:

$$ArH + BCl_3 \rightarrow ArH \cdot BCl_3 \xrightarrow{AlCl_3} ArHBCl_2^+ AlCl_4^- , \quad (55)$$

$$ArHBCl_2^+ \rightarrow ArBCl_2 + H^+ ,$$

$$3H^+AlCl_4^- + Al \rightarrow {}^3/_2H_2 + 4AlCl_3 .$$

The sole example of the preparation of cationic boron complexes from boron trifluoride is the reaction of boron trifluoride-ether with tertiary diamines [40,128]:



(56)

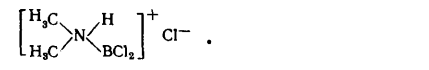
The majority of investigators assume a covalent structure for the boron trihalide complexes with amines: $R_{3-n}H_nN \rightarrow BX_3$. However, in a number of studies ionic structures were attributed to the amine complexes of boron trichloride:

$$[R_{3-n}H_nNBCl_2]^+Cl^- \quad [(R_{3-n}H_nN)_2BCl_2]^+BCl_4^- .$$

Thus the formation of an ionic complex in the dimethylamine–boron trichloride system was suggested by Brown and Osthoff [111], who concluded on the basis of a study of the vapour pressure of dimethylamine–boron trichloride that the following equilibrium exists in the gas phase:

$$(CH_3)_2NH \cdot BCl_3 \leftrightarrows (CH_3)_2NBCl_2 \cdot HCl \leftrightarrows (CH_3)_2NBCl_2 + HCl . \quad (57)$$

This observation enabled them to formulate the structure of amine-borane also in the form of the salt



The reaction of this complex with iron(III) chloride, which leads to the formation of $[Cl_2BNH(CH_3)_2]^+FeCl_4^-$, may be regarded as a confirmation of the ionic structure[129]. Moreover, dimethylamine–boron trichloride is readily hydrolysed in aqueous silver nitrate with formation of AgCl, this being in sharp contradiction with the behaviour of trimethylamine-boron trichloride, which is difficult to hydrolyse and which does not react with $FeCl_3$. At the same time the low conductivity of solutions of this complex in chloroform indicates a non-ionic structure[130].

Gerrard et al.[131] suggested that complexes of boron trichloride with aliphatic secondary amines be regarded as dichlorobis(dialkylamine)boronium tetrachloroborates:

$$[Cl_2B(NHR_2)_2]^+\ BCl_4^-\ ,$$

where R = CH_3 or iso-C_4H_9. This hypothesis is based on an analysis of the infrared spectra of these compounds, which contain absorption bands characteristic of the BCl_2 group and also frequencies corresponding to the anion BCl_4^-.

In a study of the viscosity and conductivity of melts of boron trichloride complexes with pyridine and piperidine over a wide range of temperatures, Greenwood and Wade[132] concluded that these complexes dissociate into ions to the extent of approximately 1%. On this basis, the following equilibrium between covalent and ionic forms was proposed:

$$2\,BCl_3 \cdot NC_5H_x \leftrightarrows [Cl_2B(NC_5H_x)_2]^+\ BCl_4^- \ , \qquad (58)$$

where x = 5 or 11.

The infrared spectra of the solid complex of pyridine with boron trichloride and its solutions in benzene[132] and also the ^{11}B NMR spectra of complexes of pyridine with BX_3 (X = Cl or Br) in acetonitrile and methylene chloride correspond to the covalent structure $C_5H_5N.BX_3$.[118,123] Boronium salts with ether ligands in the cation were synthesised by Mikhailov and coworkers[115-117] by the reaction of iron(III) or tin(IV) chloride with ethereal solutions of boron trichloride:

$$BCl_3 + 2\,L + FeCl_3 \xrightarrow{-70^\circ} [Cl_2BL_2]^+\ FeCl_4^- \ , \qquad (59)$$

where L = $(C_2H_5)_2O$ or C_4H_8O;

$$2\,BCl_3 + 4\,C_4H_8O + SnCl_4 \xrightarrow{-70^\circ} [Cl_2B(OC_4H_8)_2]_2^+\ SnCl_6^{2-} \ .$$

The results of this reaction and also the determinations of the molecular weights of boron trihalide-ether compounds in ether by Singer's method† and the capacity of ethereal solution of boron trihalides to conduct electricity led to the conclusion[45] that in ether there is an equilibrium between the neutral complex (VI) and the boronium salts (VII) and (VIII):

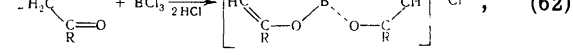
$$\underset{\text{(VI)}}{X_3B \cdot O(C_2H_5)_2} + (C_2H_5)_2O \leftrightarrows \underset{\text{(VII)}}{\{X_2B[O(C_2H_5)_2]_2\}^+}\ X^- \xrightleftharpoons{BX_3 \cdot O(C_2H_5)_2}$$

$$\rightarrow \underset{\text{(VIII)}}{\{X_2B[O(C_2H_5)_2]_2\}^+}\ BX_4^- \ , \qquad (60)$$

where X = Cl, Br, or F.

† The molecular weights determined for the other compounds of boron trichloride, trifluoride, and tribromide exceed the values for the neutral complexes by 50, 40, and 20% respectively[45].

However, these results can be accounted for also from other standpoints. For example, the conductivity of the complex of boron trifluoride with anisole was explained by Pechalin and Panchenko by the formation of a charge-transfer complex[133]. Fratiello et al.[134] observed that ethereal solutions of the complexes $BCl_3.OC_4H_8$ and $BBr_3.O(C_2H_5)_2$ are unstable and therefore their conductivity may be caused by the presence of decomposition products. Moreover, the NMR spectra of the ether complexes of boron trihalides, which always contain one ^{11}B signal and one signal corresponding to each of the protons in the ether bound in the complex, are also inconsistent with the presence of ionic structures[134]. Bearing in mind the results of Fratiello et al.[134], structures of the type $[(R_2O)_2BX_2]^+X^-$ for the ether complexes of boron trihalides can be rejected altogether. The reaction of ethereal solutions of boron trichloride with Lewis acids need not necessarily be accompanied by their ionisation but may involve an S_N2 mechanism:



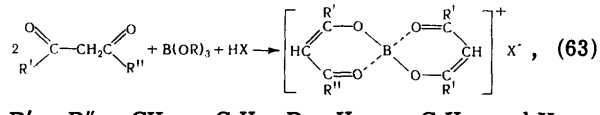
(61)

All these findings show that the problem of the existence of an equilibrium in ethereal solutions of boron trihalides cannot be regarded as finally solved.

Boron trichloride may react with β-diketones to form cationic boron complexes. Diltey in fact obtained in 1906 the first cationic boron complexes precisely by this reaction[1]:

(62)

where R = CH_3 or C_6H_5. Subsequently the method was improved by Barabas et al.[135] and extended to other β-diketones:



(63)

where R′ = R″ = CH_3 or C_6H_5, R = H or n-C_4H_9, and X = Cl or ClO_4^-.

Cationic chelate complexes of boron containing tropone derivatives as ligands were synthesised by Muetterties and coworkers[136-142] by the reaction between the tropone derivatives and BBr_3 in chloroform or methylene chloride:

$$BBr_3 + 2\,T \xrightarrow[-HBr]{} [BT_2]^+\ Br^- \ , \qquad (64)$$

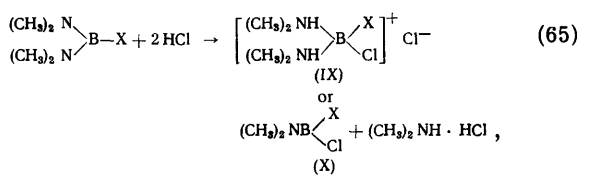
where T = tropolone, thiotropolone, or the lithium salt of *NN*-dimethylaminotroponimine and *N*-methylaminothiotropone.

In the case of tropolone the chelate complexes of boron can be obtained from boric acid and tropolone in aqueous solution in the presence of inorganic acids.

3. PREPARATION OF CATIONIC COMPLEXES BY THE ADDITION OF HYDROGEN HALIDES TO AMINOBORANES

The reaction of aminoboranes with hydrogen halides was investigated in greatest detail by Nöth and coworkers[63,87,143-147], who established that the reaction can lead to two different products, the structure of the compound depending mainly on the nature of the substituents at the boron atom. In the presence of bulky substituents,

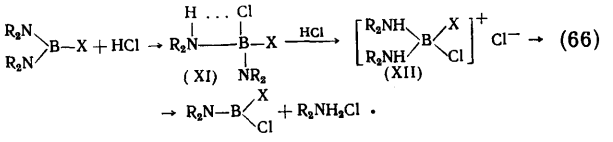
aminoborane derivatives are formed, but when the substituents are small the products are boronium salts:



(65)

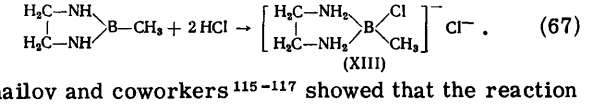
where in compound (IX) X = H, CH_3, C_2H_5, C_6H_5, Cl‡, F, or $N(CH_3)_2$ and in compound (X) X = C_3H_7, C_4H_9, $Si(CH_3)_3$, $Si(C_6H_5)_3$, $B[N(CH_3)_2]_2$, or $N(C_2H_5)_2$.

The mechanism of the reaction of aminoboranes with hydrogen chloride probably consists in the addition of HCl to the B–N bond of the aminoborane with formation of compound (XI). Subsequent addition of a second HCl molecule leads to the formation of the boronium salt (XII), the cation of which is unstable in the presence of bulky substituents and decomposes with formation of substitution products:



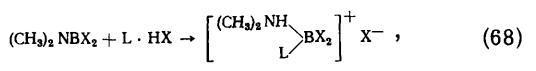
(66)

The reactions of hydrogen chloride with aminoboranes have been investigated in a number of studies. Thus, the preparation of the cationic boron complex (XIII) by the reaction of *B*-methyldiazaboroline with hydrogen chloride has been described[148]:



(67)

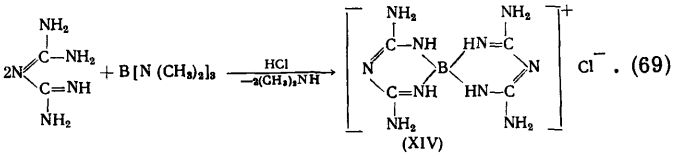
Mikhailov and coworkers[115–117] showed that the reaction of dimethylaminoboron dihalides with amine hydrogen halides in chloroform leads to the formation of boronium salts:



(68)

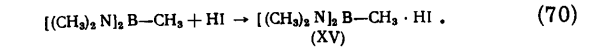
where X = Cl or Br and L = $(CH_3)_2NH$ or C_5H_5N.

The cationic boron complex (XIV) was synthesised by the reaction of biguanidine with tris(dimethylamino)borane in boiling pyridine followed by treatment with 0.5 *N* hydrochloric acid[149]:



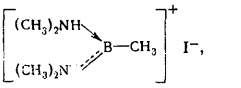
(69)

The unusual behaviour of hydrogen iodide in relation to aminoboranes is noteworthy. In contrast to the reactions with hydrogen chloride and bromide, methyl bis(dimethylamino)borane combines in toluene with only one mole of hydrogen iodide forming the insoluble complex (XV):

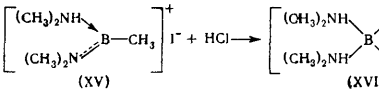


(70)

On the basis of infrared spectroscopic data, Nöth and coworkers[145] attribute to (XV) the structure

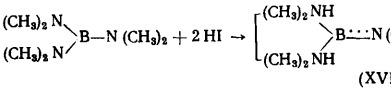


in which the cation is stabilised by the formation of a π-bond between the boron and nitrogen atoms. Additional confirmation of this structure is provided by the reaction of (XV) with hydrogen chloride, which leads to the formation of the boronium salt (XVI) and the disappearance from the infrared spectrum of the 1576 cm^{-1} absorption band characteristic of the B...N bond:



(71)

Hydrogen iodide reacts similarly also with tris(dimethylamino)borane:

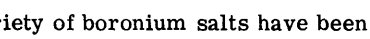


(72)

The structure of compound (XVII) is based on infrared spectroscopic data.

4. INTERACTION OF BORANES WITH AMINE-BORANES AT ELEVATED TEMPERATURES

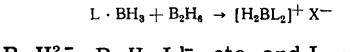
One of the general methods for the preparation of cationic boron complexes is the reaction proposed by Miller, Muetterties, and coworkers[70,138,140,150] between borane complexes and 'onium salts at an elevated pressure and a temperature in the range 100–180°C:



(73)

A wide variety of boronium salts have been synthesised by this method, containing in the inner sphere of the cation amines, phosphines, arsines, and dialkyl sulphides and with various acid residues as the anions. Equivalent amounts of a base and an acid may be employed instead of the 'onium salts.

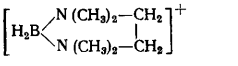
Cationic boron complexes are also obtained by the reaction of borane–base complexes with diborane or higher boranes at 100–250°C:[138,151–155]



(74)

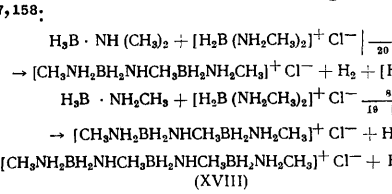
where X = $B_{12}H_{12}^{2-}$, $B_{12}H_{11}L^{1-}$, etc. and L = $(CH_3)_3N$, $(CH_3)_3P$, $(CH_3)_3As$, or $(CH_3)_2S$.

Boronium salts containing the cation



are formed when adducts of pentaborane(9) with *NNN'N'*-tetramethylethylenediamine (TMED) and B_4H_8.TMED are decomposed at 140–150°C.[156]

Beachley, who investigated the pyrolysis of the amine complexes of borane both in the presence of bis(methylamine)boronium chloride and in its absence, isolated boronium salts with cations containing several boron atoms[157,158]:



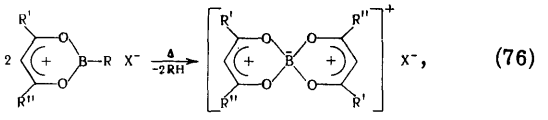
(75)

(XVIII)

‡ It is interesting to note that Weiberg and Schuster[109] described a product with the same composition more then 30 years before the work of Nöth.

The same products were obtained on partial pyrolysis of 1,3,5-trimethylcyclotriborazane in the presence of methylamine hydrochloride. The structure of the boronium salt (XVIII) was proposed by Beachley on the basis of infrared and ^1H NMR spectroscopic data.

The preparation of bis(1,3-diketonato)boronium salts by the decomposition of 1,3-dioxaborinium salts at 100°C both in the solid state and in inert solvents (toluene and acetonitrile) has been described[159,160]:



(76)

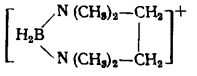
where X = Cl^- or ClO_4^-, R = C_6H_5, R′ = CH_3 or C_6H_5, and R″ = CH_3 or C_6H_5.

5. OTHER METHODS OF PREPARATION

A method for the synthesis of boronium salts with the composition $[H_2BL_2]^+X^-$, where L = tertiary amine, phosphine, or nitrile and X^- = ClO_4^- or BF_4^-, consisting in the treatment of borohydrides or amine-boranes with triphenylmethyl perchlorate or fluoroborate in the presence of bases, has been patented[161,162]:

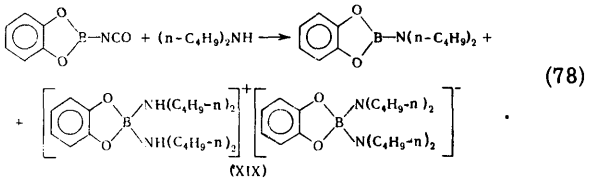
$$(C_6H_5)_3CBF_4 + (CH_3)_4NBH_4 + 2\,C_5H_5N \xrightarrow[CH_3CN]{-55^\circ} \rightarrow [H_2B(NC_5H_5)_2]^+BF_4^- + (C_6H_5)_3CH + (CH_3)_4NBF_4\ . \quad (77)$$

The acid hydrolysis of the adducts of pentaborane(9) with TMED and B_4H_8.TMED leads to the formation of the cation



in quantitative yield. The same cation is obtained by the hydrolysis of the adducts under neutral conditions[156].

After allowing two moles of dibutylamine to react with one mole of 2-isocyanato-1,3,2-benzodioxaboronate, Lappert and coworkers[163] isolated a complex with the composition $C_{22}H_{41}O_2N_2B$, which proved to be resistant to pyrolysis and alcoholysis. On the basis of infrared spectroscopic data, the structure of a boronium salt (XIX) was attributed to the complex:



(78)

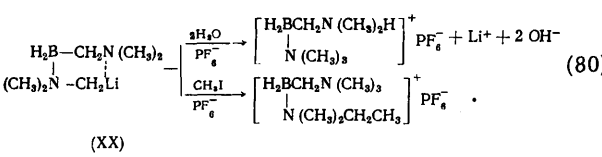
(XIX)

The boronium salts $[C_5H_5NBH_2N(CH_3)_3]^+I^-$ and $\{[(CH_3)_3NBH_2]_2SCH_3\}^+I^-$ were isolated after treating $H_3BN(CH_3)_2CH_2SCH_3$ with methyl iodide and pyridine or with methyl iodide and water respectively[80].

The preparation of ionic compounds of boron (the authors regard them as boronium salts) by the reaction of trimethylamine-dimethylaminomethylborane with ethyl bromoacetate or hydrogen chloride has been described[71,164]:

$$(CH_3)_3N\cdot BH_2CH_2N(CH_3)_2 + HCl \xrightarrow{PF_6^-} [(CH_3)_3NBH_2CH_2N(CH_3)_2H]^+PF_6^-\ . \quad (79)$$

Similar compounds are also formed in the methylation with methyl iodide or in the hydrolysis of the lithio-derivative of borane (XX):[71,164]



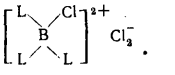
(80)

(XX)

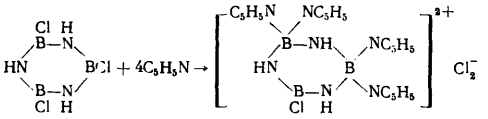
Di- and Tri-valent Cationic Complexes of Boron

The data presented above show that considerable advances have been achieved in the development of methods for the synthesis of singly charged cationic boron complexes. Until recently almost nothing was known about cationic boron complexes with charges greater than +1. The first mention of this class of compound dates back to 1951 when Sowa[165] reported the preparation of a series of boronium cations with charges ranging from +1 to +3. However, he did not prove the structure of these compounds. Only in the last three years has a series of papers appeared on the preparation of doubly and triply charged cationic boron complexes in which the structural data for the compounds are confirmed by the results of elemental analyses, infrared spectra, and conductimetric data.

When boron trichloride reacts with various primary, secondary, and tertiary amines in benzene, complexes with the composition $BCl_3.3L$ (L = amine) are obtained[166-168]; the structure of a divalent cationic complex was attributed to them:



Similar complexes were prepared by the reaction of *B*-trichloroborazine and diethylaminoboron dichloride with an excess of pyridine in benzene or petroleum ether at 0°C:[99]



(81)

$$(C_2H_5)_2NBCl_2 + 3\,C_5H_5N \rightarrow [(C_2H_5)_2NB(NC_5H_5)_3]^{2+}Cl_2^-\ .$$

Tri- and divalent boron complexes were synthesised by refluxing $(CH_3)_3N.BBr_3$ with an excess of pyridine or its derivatives[114]:

$$(CH_3)_3NBBr_3 \xrightarrow[3L']{4L} \begin{matrix}[BL_4]^{3+}Br_3^- + (CH_3)_3N \\ [BrBL'_3]^{2+}Br_2^- + (CH_3)_3N\ ,\end{matrix} \quad (82)$$

where L = 4-ethylpyridine and L′ = pyridine or 3-bromopyridine.

It is noteworthy that the complexes $3C_5H_{10}NH.BBr_3$ and $3(C_6H_5)_2NH.BBr_3$ obtained in reactions of boron tribromide with aromatic and cyclic amines and also the complexes $[(CH_3)_2N]_3B.3HI$ and $3(CH_3)_2NH.BCl_3$ should probably be regarded as divalent cationic boron complexes[112,145,169].

A divalent cationic complex has been synthesised by the reaction of tris-2,4,6-trichlorophenyl borate with ammonia[98]:

$$(Cl_3C_6H_2O)_3B + 3\,NH_3 \rightarrow [Cl_3C_6H_2OB(NH_3)_3]^{2+}[Cl_3C_6H_2O]_2^-\ . \quad (83)$$

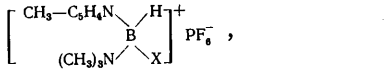
III. PHYSICAL PROPERTIES OF CATIONIC BORON COMPLEXES

Cationic boron complexes are crystalline substances. Most of them are insoluble in hydrocarbon solvents, carbon tetrachloride, and ethers. Boronium salts with small anions (Cl^-, NO_3^-, SO_4^-, etc.) are hygroscopic. They dissolve appreciably in halogenohydrocarbons (chloroform, methylene chloride, and dichloroethane), acetonitrile, acetone, alcohols, and water§, some salts crystallising as hydrates from the last solvent [89,150]. The water of hydration is readily eliminated by drying in a vacuum over phosphorus pentoxide or by recrystallisation from acetonitrile or chloroform. Boronium salts with large anions (PF_6^-, $B_{12}H_{12}^{2-}$, etc.) are much less soluble in organic solvents and water.

The boronium salts isolated from reactions in chloroform or carbon tetrachloride frequently contain between 0.2 and 0.9 mole of the solvent [75,76,136].

The saltlike nature of the cationic complexes of boron is confirmed by their capacity to conduct electricity in aqueous solutions [89,114], organic solvents [56,99,102,125,145], or amines [54]. The ionic structure of diammineboronium chloride $[H_2B(NH_3)_2]^+Cl^-$ and "diammoniate of tetraborane" $[H_2B(NH_3)_2]^+B_3H_8^-$ was also confirmed by X-ray diffraction data [170-172]. The molecular weights of these complexes have been determined in liquid ammonia [49,173,174].

Cationic boron complexes with an asymmetric boron atom should exist in optically active forms. After a number of unsuccessful attempts [135,150] optically active cationic complexes were isolated [60,66,175]:



where X = Cl or Br.

NMR Spectra of Cationic Boron Complexes

The ^{11}B NMR spectra of cationic boron complexes with 2 BH bonds consist of triplets with intensity ratios of 1 : 2 : 1 and J_{BH} constants in the range 90–120 Hz, [39,40,58-60,67,72,75,76,150,176,177] and the spectra of cations with only one BH bond consist of symmetrical doublets with J_{BH} = 134–160 Hz. [60,66,67,150]. The spectrum of bis(trimethylphosphine)-boronium consists of a quintet (0.5 : 4.4 : 5.5 : 4.4 : 0.5). [150] The ^1H NMR spectra of various cationic boron complexes have also been described [40,58-60,66,67,69-73,76,88,103,128,135,147,150,151,178].

Infrared and Ultraviolet Spectra of Cationic Boron Complexes

In the infrared spectra of boronium salts of the type $[H_2BL_2]^+X^-$ (where L is a Lewis base) there is a doublet in the region of 2380–2600 cm^{-1} associated with the stretching vibrations of the BH bonds. It is symmetrical for bisarsine and bisphosphine cations and asymmetric for bisamine cations, the band with the lower intensity lying at higher wavelengths. The frequencies due to the deformation vibrations of the BH_2 group are in the region of 1065–1170 cm^{-1}. In the deuterium-substituted cation $[D_2BL_2]^+$ the stretching and deformation vibration frequencies of the BD_2 group are displaced to 1900–1760 and 915 cm^{-1} respectively. In the region of 2430–2600 cm^{-1} cations of the type $[HB(R)L_2]^+$ have a singlet with a much lower intensity than the doublet of the BH_2 group [22,23,40,56-59,67,69-76,143,150,158].

The Raman spectra of diammineboronium and bis(dimethyl sulphoxide)boronium borohydrides each have two bands associated with the BH_2 group (2371–2315 and 2437–2422 cm^{-1} [8,41]).

The infrared spectra of the boronium salts $(R'R''BL_2)^+X^-$ containing various substituents at the boron atom (R′ and R″ = halogen, alkyl, aryl, etc.) [40,54,67,88,90,99-101,114,123,128,144,145,163], the infrared spectra of Diltey's complexes [135,159,178,179], and the ultraviolet spectra of various boronium cations [40,59,76,101,102,104,114,118,135,179] have been described.

§ The solubilities of a number of boronium salts in water have been determined [90].

IV. CHEMICAL PROPERTIES OF CATIONIC BORON COMPLEXES

The chemical reactions of cationic boron complexes can be divided into three groups.

1. Reactions with breakdown of the boronium salt (pyrolysis, hydrolysis, alcoholysis, and reactions with bases).
2. Reactions involving changes in the boronium cation but not resulting in its breakdown (substitution reactions and ligand exchange reactions).
3. Reactions of the anions of the boronium salts.

1. REACTIONS WITH BREAKDOWN OF THE BORONIUM SALT

a. Thermal Stability and Pyrolysis of Boronium Salts

The thermal stability of boronium salts depends both on the nature of the ligand and the substituents at the boron atom in the cation and on the nature and dimensions of the anions. Mikhailov [46] quotes the following series of bases bound in a complex with boron in terms of decreasing stability of the boronium cations: diamines > amines > phosphines > arsines > ethers > sulphides. Within the limits of each of the above types of bases, the stability of the boronium cation is determined mainly by steric factors. For example, for amine ligands it is possible to establish the following series in terms of decreasing thermal stability of boronium salts [56]:

$$[(C_6H_5)_2B(NH_3)_2]^+Cl^- > [(C_6H_5)_2B(NH_2CH_3)_2]^+Cl^- > \{(C_6H_5)_2B[HN(CH_3)_2\}^+Cl^-.$$

While diammineboronium borohydride is stable up to 80°C, the borohydrides of bis(methylamine)boronium and bis-(dimethylamine)boronium are stable at room temperature only in a vacuum [10,23].

The stability of boronium salts is appreciably influenced also by the dimensions of the substituent at the boron atom, the stability as a rule decreasing with increase in the size of the substituent. Thus ethylbis(dimethylamine)boronium chloride decomposes at room temperature and methylbis-(dimethylamine)boronium remains unchanged at the same temperatures in the absence of moisture [145].

The dimensions and the nature of the anion also have a significant effect on the thermal stability of the salts. The boronium salts formed with the anions of weak acids are stable only when small ligands are present in the inner sphere of the cation (NH_3, CH_3NH_2). [61] Boronium salts with anions of strong acids are distinguished by greater stability. While the boronium salt $[(CH_3)_2B(NH_3)_2]^+[H_2B.(CH_3)_2]^-$ decomposes at 10°C, its chloride is stable under

the same conditions[54]. When salts with strong acid anions and bulky ligands are formed, the dimensions of the anion become of decisive importance for their stability, since small anions are capable of displacing the ligand from the cation at elevated temperatures:

$$[H_2BL_2]^+Cl^- \xrightarrow{\Delta} H_2BCl \cdot L + L\ , \qquad (84)$$

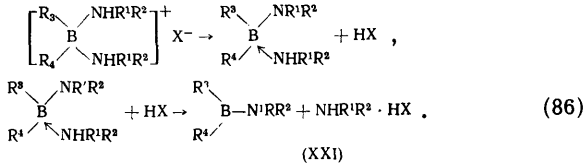
On the other hand, large anions ($B_{12}H_{12}^{2-}$, PF_6^-) permit the synthesis of stable boronium salts with ligands such as trimethylamine, ethyldimethylamine, triethylamine, and 2,6-dimethylpyridine[58,59,140,150].

Two types of thermal transformations are characteristic of boronium salts, depending on the nature of the ligand. The pyrolysis of boronium salts with tertiary amines as ligands and small anions leads to the displacement of the amine from the inner sphere of the cation by the anion and formation of complexes of the amine with boron derivatives[138,140,150,180]:

$$\{H_2B[N(CH_3)_3]_2\}^+X^- \xrightarrow{125-195^\circ} H_2B{-}X \cdot N(CH_3)_3 + N(CH_3)_3\ , \qquad (85)$$

where X = Cl, Br, or N_3.

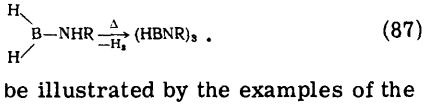
Another type of thermal transformation is characteristic of boronium salts containing primary and secondary aliphatic amines in the cation. When these salts are heated, aminoboranes and derivatives of cycloborazanes and borazines are produced, and their formation may be represented by the following equations:



(86)

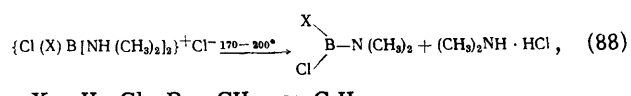
(XXI)

When R^3 and $R^4 = C_nH_{2n+1}$, C_6H_5, or Cl, the pyrolysis stops at this stage. When $R^1 = R^3 = H$, the product (XXI) may cyclise with formation of cycloborazanes $(H_2BNHR)_3$ or undergoes further reactions leading to borazine derivatives:



(87)

This mechanism may be illustrated by the examples of the reactions of boronium salts on heating quoted below. The wide melting point range of the boronium salts $\{Cl(X)B.[NH(CH_3)_2]_2\}^+Cl^-$ can probably be accounted for by their partial decomposition on heating. This reaction, which leads to the formation of aminoboranes, occurs smoothly at 170–200°C:[63,88,112,143-145]



(88)

where X = H, Cl, Br, CH_3, or C_6H_5.

It is noteworthy that the introduction of bulky substituents linked to boron into the cation of the boronium salt leads to a lowering of the temperature at which the transformation takes place[81,84]:

$$[(C_6H_5)_2B(NH_2R)_2]^+Cl^- \xrightarrow{200-250^\circ} (C_6H_5)_2B{-}NHR + RNH_2 \cdot HCl\ , \qquad (89)$$

where R = CH_3, C_2H_5, or iso-C_4H_9;

$$[(p\text{-}CH_3C_6H_4)_2B(NH_2R)_2]^+Cl^- \xrightarrow{150-170^\circ} (p\text{-}CH_3C_6H_4)_2BNH_2 + RNH_2 \cdot HCl\ ,$$

where R = C_2H_5 or iso-C_4H_9.

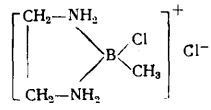
The decomposition of the salts $[H_2B(NH_2CH_3)_2]^+X^-$ and $[CH_3NH_2BH_2NHCH_3BH_2NH_2CH_3]^+X^-$, where X = BH_4 or Cl, at 100–125°C results in the formation of 1,3,5-trimethylcyclotriborazane and 1,3,5-trimethylborazine[157,158,181].

The pyrolysis of the "diammoniates" of diborane and tetraborane at 180–190°C leads to the formation of borazine[47,182]. *N*-Tri-n-burylborazine, bis-(n-butylamino)borane, and n-butylamine-borane were isolated in the thermal decomposition of bis-(n-butylamine)boronium ethylmercaptide[77].

A completely different type of thermal decomposition was observed on heating dicyclohexylbis(pyridine)boronium perchlorate in chloroform. This results in the formation of cyclohexene and cyclohexylbis(pyridine)boronium perchlorate[67]:

$$[(C_6H_{11})_2B(NC_5H_5)_2]^+ClO_4^- \xrightarrow{\Delta} [C_6H_{11}(H)B(NC_5H_5)_2]^+ClO_4^- + C_6H_{10}\ . \qquad (90)$$

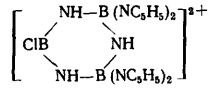
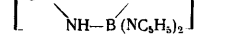
The pyrolysis of the boronium salt



at 300°C in the presence of hydrogen chloride results in the formation of methane and CH_3BCl_2 in low yields[148].

The decomposition of diphenylbis(ethyl ether)boronium[103]:

$$\{(C_6H_5)_2B[O(C_2H_5)_2]_2\}^+ \rightarrow (C_6H_5)_2B{-}OC_2H_5 + (C_2H_5)_3O^+ \qquad (91)$$

and the transformation[99] on vacuum sublimation of the divalent cationic complex  $2Cl^-$ into the univalent complex  Cl^- have also been described.

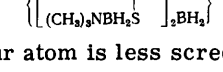
b. Hydrolysis and Alcoholysis

The hydrolysis and alcoholysis of boronium salts are the most important reactions of cationic boron complexes. It is noteworthy that the majority of boronium salts are stable in relation to water and acids but are fairly rapidly decomposed by alkalies[39,56,58,66,67,69-71,73-76,88,89,114,158]. Thus this reaction evidently reduces to nucleophilic attack on the boronium cation.

Although there has been no systematic study of the behaviour of boronium salts in hydrolysis, examination of the literature data permits the isolation of a number of factors which determine the stability of cationic boron complexes in relation to hydrolysis.

The hydrolytic stability of boronium salts is determined primarily by the basicity of the ligands in the cation. The salts become more stable with increase in the basicity of the ligands. Thus boronium cations containing thioether ligands with a relatively low basicity, $[H_2B(SR_2)_2]^+$, are readily hydrolysed by water¶.

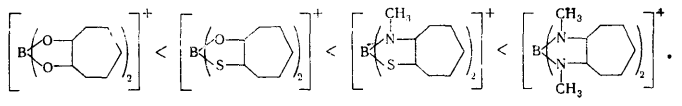
¶ However, a boronium cation containing the S–CH_3 group, $[(CH_3)_2NBH_2SBH_2N(CH_3)_3]^+$, which is resistant to acids and alkalies, has been described. Rowatt and Miller[69] explain its enhanced hydrolytic stability by the screening of the sulphur atom by $H_2BN(CH_3)_3$ groups, which are isoelectronic with the neopentyl group. The cation



in which the sulphur atom is less screened, is hydrolysed by water.

Bis(trialkylarsine)boronium salts, $[H_2B(AsR_3)_2]^+X^-$, in which the ligands are more basic, can be actually recrystallised from water, but water hydrolyses them slowly. Cations with even more basic tertiary phosphines, $[H_2B(PR_3)_2]^+$, are stable even in relation to boiling inorganic acids but are slowly decomposed in hot alkalies. Diamineboronium cations, $[H_2B(NR_3)_2]^+$, are not susceptible to the action of concentrated acids (HCl, HNO_3, H_2SO_4), and 10% alkali even on heating [70,140,150]. However, the replacement of NR_3 in the boronium cation by 4-methylpyridine leads to a sharp lowering of the hydrolytic stability of the salt [58].

An analogous variation of hydrolytic stability in relation to alkalies on passing to more basic ligands was observed by Muetterties [136-138,140-141] also for chelate cationic boron complexes:



The rate of hydrolysis of the boronium cations $[H_2BL_2]^+$, where L is a pyridine derivative, is inversely proportional to the relative strength of the base [114]. Boronium salts with weakly basic ligands such as dimethylformamide and dimethylacetamide [70] and the *N*-oxides of tertiary bases [73], exhibit an unexpectedly high stability in relation to hydrolysis.

On the basis of data for the solvolysis of a number of bis(alkylamine)boronium chlorides, Mikhailov and coworkers [183] established that, with increase in the bulk of the molecules of nitrogen-containing bases, the hydrolytic stability of the salts decreases in the series

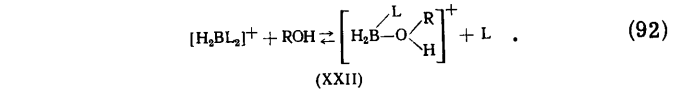
(a) $NH_3 > CH_3NH_2 > C_2H_5NH_2 > n\text{-}C_3H_7NH_2 > C_4H_9NH_2 > n\text{-}C_5H_{11}NH_2 > n\text{-}C_6H_{13}NH_2$;
(b) $NH_3 > CH_3NH_2 > (CH_3)_2NH$;
(c) $n\text{-}C_3H_7NH_2 > iso\text{-}C_3H_7NH_2$;
(d) $n\text{-}C_4H_9NH_2 > iso\text{-}C_4H_9NH_2 > t\text{-}C_4H_9NH_2$.

Bulky or electronegative substituents at the boron atom reduce the hydrolytic stability of boronium salts [54,56,61,112]. Thus the stability of salts of the type $\{(Cl)XB[NH(CH_3)_2]_2\}^+ .Cl^-$ decreases with increase in the bulk of the substituent X in the following sequence [88,143,147]: $H > F > Cl \sim C_6H_5$.

The nature of the anion of the boronium salt probably also influences its hydrolytic stability. Boronium salts with anions of weak acids $[(CH_3)_2BH_2^-, SR^-]$ are fairly readily hydrolysed [23,151], while the anions of strong acids, particularly large anions ($B_{12}H_{12}^{2-}$, PF_6^-), increase the hydrolytic stability of the salts [140,150].

The hydrolytic stability of the cationic boron complexes depends on the magnitude of the positive charge of the cation and decreases as it is diminished [114].

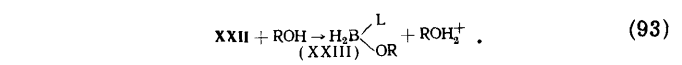
The mechanism of the hydrolysis of boronium salts is still obscure. According to the data of Mikhailov and coworkers [46,183], in the first stage of the solvolysis of the boronium salts $(H_2BL_2)^+Cl^-$ (where L are primary and secondary aliphatic amines) one amine molecule is replaced by water or an alcohol molecule:



(92)

(XXII)

The mixed cation (XXII) formed dissociates at the O–H bond with formation of a neutral complex of the hydroxy- or alkoxy-borane:



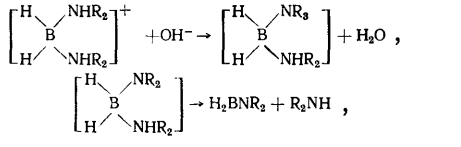
(93)

(XXIII)

Compounds of type (XXIII) are solvolysed at a high rate with evolution of hydrogen.

The mechanism shows that the possibility of the displacement of the ligand in the first stage is determined both by the basicity of the hydrolysing agent and the strength of the boron–ligand bond. On the other hand, the ease of the acid-catalysed dissociation of the cation (XXII) in the second stage depends both on the nature of the amine incorporated in it and on the basicity of the medium. In addition, the rate of alcoholysis decreases with increasing bulk of the alcohol molecule.

In the alkaline hydrolysis of the boronium salts $(H_2BL_2)^+X^-$ (where L are primary or secondary amines), one cannot of course exclude the possibility of the reaction of the hydroxide ion with NH protons:



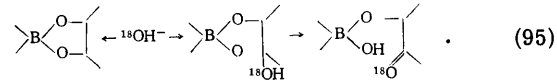
(94)

$H_2B—NR_2 \rightarrow$ hydrolysis .

However, this last mechanism has been questioned by Mikhailov et al. [117]

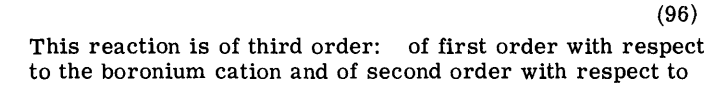
Muetterties [140,150] proposed a different mechanism for the alkaline hydrolysis of boronium salts with the cations $[H_2BL_2]^+$ (where L = PR_3, AsR_3, or SR_2), according to which the initial stages of the process involves the attack by the hydroxide ion on the positively charged heteroatom of the ligand.

It is interesting to note that in certain cases there is a possibility of a nucleophilic attack by the hydroxide ion also on an atom more remote from boron [136,137]. In the alkaline hydrolysis of the boronium cation with tropolone molecules as ligands in a medium containing $H_2^{18}O$, tropolone becomes enriched in oxygen-18 to an extent corresponding to 50% of the possible maximum. On this basis, Muetterties suggests that the initial stage of the hydrolysis consists in the attack by the OH^- ion not on the central boron atom but on the carbon atom linked to oxygen:



(95)

An analogous mechanism of hydrolysis was proposed for the boronium cation $[(CH_3)_3NBH_2O{\leftarrow}P(CH_3)_3]^+$:



(96)

This reaction is of third order: of first order with respect to the boronium cation and of second order with respect to the hydroxide ion [73].

Thus at present it is difficult to imagine a general mechanism for the hydrolysis of boronium salts. Possibly the reaction mechanism varies with the type of hydrolysing agent and the nature of the boronium salt.

c. Effect of Bases on Boronium Salts Containing Amines as Ligands

A number of communications have been published on the preparation of aminoboranes or their polymerisation products by reaction of strong bases with cationic boron complexes. Probably the reactions can be described in all cases by a general mechanism including as the first

stage the elimination by the base A^- of a proton from the amine in the boronium cation:

$$[H_3NBH_2NH_3]^+ + A^- \rightarrow HA + \underset{(XXIV)}{H_3NBH_2NH_2}, \quad (97)$$

where A^- is the base [$C{\equiv}CH^-$, NH_2, H^-, NH_2R (R = H or alkyl)]. The ammine-aminoborane (XXIV) formed dimerises with loss of an ammonia molecule:

$$\underset{\uparrow H_2NBH_2NH_3}{H_3NBH_2NH_2} \rightarrow \underset{(XXV)}{H_2NBH_2NH_2BH_2NH_3} + NH_3. \quad (98)$$

The ammine-aminoborane (XXV) formed or the product of its further condensation may cyclise with elimination of an NH_3 molecule:

$$H_3N(BH_2NH_2)_n \rightarrow (H_2BNH_2)_n + NH_3. \quad (99)$$

Another pathway for the formation of cycloborazanes $(H_2NBH_2)_n$ includes attack on the boron atom in the diammineboronium cation by the ammine-aminoborane (XXIV):

$$\underset{\substack{\uparrow H_2NBH_2\cdot NH_3\\ (XXIV)}}{[H_3N\cdot BH_2NH]_3^+} \rightarrow \underset{(XXVI)}{[H_3NBH_2NH_2BH_2NH_3]^+} + NH_3. \quad (100)$$

The boronium cation (XXVI) can be lengthened by mechanism (98) quoted above with transfer of a proton to the base A^- [reaction (97)] or can cyclise with loss of an ammonia molecule according to reaction (99).

The examples below illustrate the formation of aminoboranes in the reaction of boronium salts with bases. Sodium acetylide reacts with diammineboronium borohydride forming aminoboranes in two different modifications, one of which is cyclotriborazane ($n = 3$): [185]

$$[H_2B(NH_3)_2]^+BH_4^- + NaC{\equiv}CH \xrightarrow{NH_3(liq.)} (H_2BNH_2)_n + NaBH_4 + CH{\equiv}CH{+}NH_3. \quad (101)$$

Cycloborazanes with the composition $(H_2BNH_2)_n$, where $n = 2$, 3, or 5, were synthesised by the reaction of sodamide with diammineboronium borohydride [184]:

$$[H_2B(NH_3)_2]^+BH_4^- + NaNH_2 \xrightarrow{NH_3(liq.)} (H_2BNH_2)_n + NaBH_4 + 2NH_3. \quad (102)$$

The "diammoniate of diborane", which is stable in dry ether at room temperature, decomposes rapidly in the presence of small amounts of ammonia with formation of a polymeric aminoborane [3]:

$$[H_2B(NH_3)_2]^+BH_4^- + NH_3 \xrightarrow{(C_2H_5)_2O} (H_2BNH_2)_n + H_3B\cdot NH_3 + H_2. \quad (103)$$

Probably bis(ethylamine)boronium ethylmercaptide decomposes similarly in ether under the influence of traces of an amine [61]:

$$[H_2B(NH_2C_2H_5)_2]^+SC_2H_5^- \xrightarrow{H_2NC_2H_5} H_2BNHC_2H_5 + C_2H_5SH + C_2H_5NH_2. \quad (104)$$

The reaction of bis(trimethylamine)boronium chloride with sodium hydride [186] and butyl-lithium [164] and also the reactions of a number of boronium salts with metallic sodium [2,50,54] take place with initial elimination of a proton from the nitrogen atom or from the alkyl group of the amine.

The reaction with sodium hydride gives rise to a six-membered boron-containing heterocycle in 5% yield. The formation of this product may be represented by the following mechanism

$$[(CH_3)_3NH_2BN(CH_3)_3]^+Cl^- + NaH \rightarrow NaCl + H_2 + [(CH_3)_3NBH_2N(CH_3)_2\ddot{C}H_2^{\ominus}],$$

$$\left[(CH_3)_3NBH_2N(CH_3)_2\ddot{C}H_2 \rightarrow CH_2(CH_3)_2NH_2BN(CH_3)_3\right] \rightarrow \underset{\substack{BH_2\\ (CH_3)_2N\quad CH_2\\ H_2C\quad N(CH_3)_2\\ BH_2}}{} + 2N(CH_3)_3. \quad (105)$$

In the reaction with butyl-lithium a number of products are formed depending on the proportions of the reactants [71,164]:

$$[(CH_3)_3NBH_2N(CH_3)_3]^+Cl^- \xrightarrow{\leqslant 2\ moles\ C_4H_9Li} LiCl + \underset{(CH_3)_2N-CH_2Li}{H_2B-CH_2N(CH_3)_2} + 2C_4H_{10},$$

$$[(CH_3)_3NBH_2N(CH_3)_3]^+Cl^- \xrightarrow{1.5\ moles\ C_4H_9Li} (CH_3)_3NBH_2\overset{\curvearrowright}{N}(CH_3)_2\ddot{C}H_2 \rightarrow (CH_3)_3NBH_2CH_2N(CH_3)_2,$$

$$[(CH_3)_3NBH_2N(CH_3)_3]^+Cl^- \xrightarrow{\geqslant 1\ mole\ C_4H_9Li} [(CH_3)_2NCH_2BH_2]_2 \quad (106)$$

The reactions of the boronium salts $[H_2B(NH_3)_2]^+X^-$ and $[(CH_3)_2B(NH_3)_2]^+[H_2B(CH_3)_2]^-$ with sodium in liquid ammonia lead to the formation of aminoboranes† [2,49,54]:

$$[H_2B(NH_3)_2]^+X^- + Na \xrightarrow{NH_3(liq.)} H_2NBH_2 + NH_3 + NaX + {}^1/_2H_2,$$

where $X^- = Cl^-$, Br^-, BH_4^-, or $B_3H_8^-$:

$$[(CH_3)_2B(NH_3)_2]^+[H_2B(CH_3)_2]^- + Na \xrightarrow{NH_3(liq.)} Na[H_2B(CH_3)_2] + (CH_3)_2B{-}NH_2 + NH_3 + {}^1/_2H_2. \quad (107)$$

Boronium salts with substituents at the boron atom can also decompose under the influence of amines with formation of aminoboranes [84,86]:

$$[R^1R^2B(NH_2C_4H_9)_2]^+Cl^- + NH_2C_4H_9 \rightarrow \underset{R^2\quad NHC_4H_9}{\overset{R^1\quad NH_2C_4H_9}{B}} + C_4H_9NH_2\cdot HCl,$$

$$\underset{R^2\quad NHC_4H_9}{\overset{R^1\quad NH_2C_4H_9}{B}} \rightarrow \underset{R^2}{\overset{R^1}{B}}{-}NHC_4H_9{-}C_4H_9NH_2, \quad (108)$$

where (1) $R^1 = R^2 = p\text{-}CH_3C_6H_4$ and (2) $R^1 + R^2 = (CH_2)_6$.

It is noteworthy that hexamethylenebis(n-butylamine)-boronium chloride does not react either with CH_3NH_2 or $(C_2H_5)_3N$. Unfortunately there is no explanation in the literature [86] of this phenomenon. At the same time it is known that dichlorobis(dialkylamine)boronium chloride [112] and chlorophenylbis(dimethylamine)boronium chloride [88] decompose smoothly under the influence of $(C_2H_5)_3N$ and $(CH_3)_2NH$:

$$[Cl(X)B(NHR_2')(NHR_2'')]^+Cl^- + 2L \rightarrow XB\overset{NR_2'}{\underset{NR_2''}{}} + 2L\cdot HX, \quad (109)$$

where X = Cl or C_6H_5 and L = $(C_2H_5)_3N$ or $(CH_3)_2NH$.

It is also noteworthy that reactions of a different type, leading to a transformation of the boronium cation, have also been described. Thus the complex $Cl_3B.3NH(CH_3)_2$, which is evidently the divalent cationic boron complex $\{ClB[NH(CH_3)_2]_3\}^{2+}Cl^-$, is converted by triethylamine into the univalent boronium salt $\{Cl_2B[NH(CH_3)_2]_2\}^+Cl^-$. [112]

d. Oxidation of Boronium Salts

Boronium salts containing tertiary amines as ligands are extremely resistant to oxidation. They remain unchanged under the action of oxidising agents such as Ag^+, Cu^{2+}, Hg^+, and Au^{3+} salts, potassium dichromate, and 30% hydrogen peroxide solution. Even "aqua regia" at 100°C does not decompose the cation $[H_2B(NR_3)_2]^+$ but merely converts it into the monochloro-derivative $HB(Cl)B(NR_3)_2$. [58, 140, 150, 164] Cases of the oxidation of boronium salts by potassium permanganate [58, 128] and trimethylamine-*N*-oxide [106] have been described.

† In these reactions the acidic protons of ammonia serve as a source of hydrogen. This was confirmed by Parry and coworkers [6] in a study of the reaction of various deutero-derivatives of the "diammoniate of diborane" with sodium in liquid ammonia.

e. Reduction of Boronium Salts

Very few examples of the reduction of boronium salts are known at present. The preparation of borazanes by the reaction of $LiBH_4$ with $[H_2B(NH_2R)_2]^+Cl^-$ has been reported[4,56,62]. The only product isolated in the reduction of $[(CH_3)_2B(NH_3)_2]^+Br^-$ by hydrogen at 120°C and a pressure of 3200 atm proved to be ammonium bromide[54].

The reduction of a cationic boron complex containing tropolone as a ligand has been described

$$[(C_7H_5O_2)_2B]^+Br^- \xrightarrow{BH_4^-} (C_7H_5O_2)\,B\,(O_2C_7H_5)\ . \qquad (110)$$

Bis-(*NN*-dimethylaminotropolonimine)boronium bromide is reduced similarly by lithium aluminium hydride:

$$[(C_9H_{11}N_2)_2B]^+Br^- \xrightarrow{LiAlH_4} (C_9H_{12}N_2)\,B\,(C_9H_{11}N_2)\ . \qquad (111)$$

Both these boronium cations are resistant to polarographic reduction[136,140].

2. REACTIONS IN THE CATION

a. Ligand Exchange Reactions

The ligands in the boronium cation may be displaced by stronger bases without decomposing the complex. Miller and Muetterties[140,150] quote the following series of bases arranged in order of decreasing ease of exchange of the ligand in boronium salt cations: sulphides ≫ arsines > phosphines > amines > diamine. The electron-donating properties of these bases increase in the same sequence.

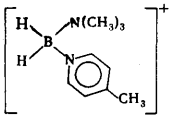
The steric effects of the substituents in the bases also have a significant effect on the possibility of the displacement of ligands from the cation. For example, substitution of dimethyl sulphide in $\{H_2B[S(CH_3)_2]_2\}^{2+}B_{12}H_{12}^{2-}$ by trimethylamine, $\alpha\alpha'$-dipiridyl and *NN*-dimethylpiperazine is rapid at room temperature, while *N*-methylpiperidine and ethyldimethylamine are incapable of displacing dimethyl sulphide. The displacement of tertiary amines by diamines takes place at an elevated temperature (up to about 150°C):

$$\{H_2B[N(CH_3)_3]_2\}_2^{2+}B_{12}H_{12}^{2-} \xrightarrow[(CH_3)_2NCH_2CH_2N(CH_3)_2]{150^\circ} \left[\begin{array}{c}(CH_3)_2\\ N-CH_2\\ H_2B\\ N-CH_2\\ (CH_3)_2\end{array}\right]_2^{+} B_{12}H_{12}^{2-}\ . \qquad (112)$$

Muetterties suggests that the first stage of the reaction is dissociation

$$[H_2B(NR_3)_2]^+ \rightleftarrows [H_2BNR_3]^+ + NR_3\ , \qquad (113)$$

because the formation of the transition state by an S_N2 mechanism is unlikely owing to steric hindrance. However, the absence of the racemisation of the optically active boronium cation



both at room temperature and at 100°C throws doubt on the possibility of the reversible dissociation of one of the ligands at the boron atom[66].

Examples of the substitution of trimethylamine in the cation by pyridine or its derivatives at 100–110°C have been described[58]. A weak base (4-acetylpyridine) proved to be incapable of displacing a molecule of trimethylamine from the cation on refluxing in benzene for 4 h.[58] It is interesting to note that the trimethylamine, a comparatively strong base, does not displace pyridine *N*-oxide from the boronium cation at 50°C.[73]

The exchange of primary and secondary amine ligands in boronium salts with small anions (Cl^-, BH_4^-) takes place under mild conditions[54]. Thus the cations $[H_2B(NH_2CH_3)_2]^+$ and $\{H_2B[NH(CH_3)_2]_2\}^+$ undergo ligand exchange reactions on dissolution in liquid ammonia or liquid amines[23]

$$[H_2B(NH_2CH_3)_2]^+Cl^- \underset{CH_3NH_2\ (liq.)}{\overset{(CH_3)_2NH\ (liq.)}{\rightleftarrows}} \left\{H_2B[HN(CH_3)_2]_2\right\}^+Cl^- \qquad (114)$$

NH_3 (liq.) ↘ ↙ NH_3 (liq.)

$[H_2B(NH_3)_2]^+Cl$

Since in these salts the amine is not dissociated from the boronium cation at a low temperature, one may assume that here the ligand exchange reactions have an S_N2 mechanism.

The attempts to substitute the ligand in di- or trivalent boronium cations by other amines led to the decomposition of the products or the recovery of the initial compounds[114].

b. Hydrogen Substitution Reactions in the Cation $[H_2BL_2]^+$

When chlorine or bromine is allowed to act on solutions of the boronium salts $[H_2BL_2]^+X^-$ in water[138,140,150,154] or methylene chloride[60,66], one hydrogen atom linked to boron is replaced by halogen. However, the chlorination in water is slow even at 90°C:

$$\left[\begin{array}{c}H\\ B\\ H\end{array}\begin{array}{c}L'\\ \\ L''\end{array}\right]^+X^- + Y_2 \rightarrow \left[\begin{array}{c}H\\ B\\ Y\end{array}\begin{array}{c}L'\\ \\ L''\end{array}\right]^+X^- + HY\ , \qquad (115)$$

where X = I or Cl and Y = Cl or Br.

When the boronium salts $[H_2B(NR_3)_2]^+Cl^-$ are acted upon by reactants such as "aqua regia", NCl_3, and SF_5Cl, the monochloro-substituted cations $[H(Cl)B(NR_3)_2]^+$ are formed.

The iodination of boronium salts does not take place either with iodine or iodine monochloride. In the latter case at 80°C both hydrogen atoms are replaced by chlorine:

$$\{H_2B[N(CH_3)_3]_2\}^+Cl^- \xrightarrow{ICl} \{Cl_2B[N(CH_3)_3]_2\}^+\ . \qquad (116)$$

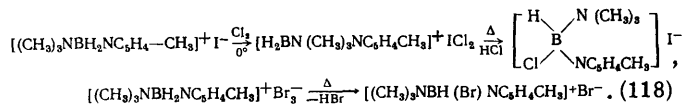
When fluorine in a stream of nitrogen is passed through an aqueous solution of $\{H_2B[N(CH_3)_3]_2\}^+$ at 0°C, the mono- and di-fluorinated cations $\{(F)HB[N(CH_3)_3]_2\}^+$ and $\{F_2B.[N(CH_3)_3]_2\}^+$ are obtained. Fluorination in the presence of chloride ions gives the mixed cation $\{Cl(F)B[N(CH_3)_3]_2\}^+$.

Peroxydisulphuryl fluoride substitutes both hydrogen atoms in the boronium salt cation:

$$\{H_2B[N(CH_3)_3]_2\}^+PF_6^- \xrightarrow{S_2O_6F_2} \{(FSO_3)_2B[N(CH_3)_3]_2\}^+PF_6^-\ . \qquad (117)$$

Miller and Muetterties suggest that the above reactions have a radical mechanism. However, on the basis of data for the chlorination of the boronium salt $[(CH_3)_3NBH_2NC_5.H_4CH_3]^+I^-$ in methylene chloride at a low temperature and in the absence of light, Ryschkewitsch and Garrett[66] suggest that the mechanism of the halogenation of boronium cations consists in the electrophilic attack on the BH bond by a halide molecule.

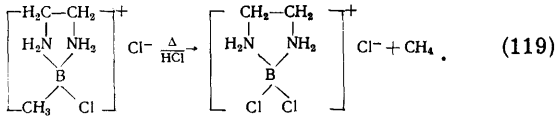
Halogeno-substituted cations are obtained also on heating boronium polyhalide salts[66]:



$$[(CH_3)_3NBH_2NC_5H_4-CH_3]^+I^- \xrightarrow[0^\circ]{Cl_2} [H_2BN(CH_3)_3NC_5H_4CH_3]^+ICl_2 \xrightarrow[HCl]{\Delta} \left[\begin{matrix} H & & N(CH_3)_3 \\ & B & \\ Cl & & NC_5H_4CH_3 \end{matrix}\right] I^-,$$

$$[(CH_3)_3NBH_2NC_5H_4CH_3]^+Br_3^- \xrightarrow[-HBr]{\Delta} [(CH_3)_3NBH(Br)NC_5H_4CH_3]^+Br^-. \quad (118)$$

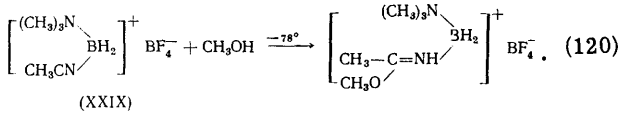
The substitution by chlorine of a methyl group bound to the boron atom in a cationic complex on heating the latter with hydrogen chloride has also been described. However, the reaction conditions and the properties of the final product have not been indicated[148]:



$$\left[\begin{matrix} H_2C-CH_2 \\ H_2N \quad NH_2 \\ B \\ CH_3 \quad Cl \end{matrix}\right]^+ Cl^- \xrightarrow[HCl]{\Delta} \left[\begin{matrix} CH_2-CH_2 \\ H_2N \quad NH_2 \\ B \\ Cl \quad Cl \end{matrix}\right]^+ Cl^- + CH_4. \quad (119)$$

The reaction of $[(CH_3)_3NBH_2N(CH_2)_2CH_2SCH_3]^+$ with hydriodic acid results in the formation of $\{[(CH_3)_3N]_2BH_2\}^+$.[70]

It is noteworthy that the reactions of the cations in boron complexes containing only amine molecules in the cation as ligands have now been described. The sole exception appears to be the reactions with methyl alcohol of the boronium salt (XXIX) containing acetonitrile as a ligand[187]:



$$\left[\begin{matrix} (CH_3)_3N \\ BH_2 \\ CH_3CN \end{matrix}\right]^+ BF_4^- + CH_3OH \xrightarrow{-78^\circ} \left[\begin{matrix} (CH_3)_3N \\ BH_2 \\ CH_3-C=NH \\ CH_3O \end{matrix}\right]^+ BF_4^-. \quad (120)$$

(XXIX)

3. REACTIONS OF BORONIUM SALT ANIONS

Reactions involving the exchange of the anions in boronium salts are widely used to identify these compounds and to modify their properties. Thus when diammineboronium borohydride was treated with ammonium chloride or bromide in liquid ammonia, diammineboronium chloride and bromide were obtained[2]:

$$[H_2B(NH_3)_2]^+BH_4^- + NH_4X \rightarrow [H_2B(NH_3)_2]^+X^- + NH_3BH_3 + H_2, \quad (121)$$

where X = Cl or Br.

When ethereal or aqueous solutions of hydrogen halides (HCl, HBr) react with boronium salts containing the anions BH_4^-,[2,3,22,41] $B_3H_8^-$,[49] and $H_2B(CH_3)_2^-$,[54] the corresponding halides are obtained. The reverse reaction—the replacement of the chloride ion by the borohydride ion—was achieved by allowing sodium borohydride to react with boronium chloride salts in liquid amines[23,158]:

$$[H_2BL_2]^+Cl^- + NaBH_4 \xrightarrow[-45^\circ-(-78^\circ)]{L(liq.)} [H_2BL_2]^+BH_4^- + NaCl, \quad (122)$$

where L = $CH_3NH_2(CH_3)_2NH$;

$$[CH_3NH_2BH_2NHCH_3BH_2NH_2CH_3]^+Cl^- + NaBH_4 \xrightarrow[-30^\circ]{CH_3NH_2}$$

$$\rightarrow [CH_3NH_2BH_2NHCH_3BH_2NH_2CH_3]^+BH_4^- + NaCl.$$

The mercaptide ion is replaced by the chloride ion when boronium mercaptides are treated with hydrogen chloride[61] or benzyl chloride[61,79]. Boronium halides are converted into the corresponding perchlorates on treatment with ammonia or metal (Ag^+, K^+, and Na^+) perchlorates both in water and in organic solvents[67,74-76,90,100,101,103,135]. Hexafluorophosphates[58-60,67,70-73,76,80,114,136,139,141,150,151], hexafluoroarsenite salts[58,66,114], and tetraphenylborate salts[56,58,59,89] are precipitated when aqueous or alcoholic solutions of boronium halides are acted upon by the corresponding ammonium, sodium, and potassium salts.

Boronium chlorides react with the chlorides of iron[56,78,88,115,116,135,143-145,158], aluminium[56,135], tin[1,83,116,135], antimony[63,135], gold[1,150,152], platinum[1,145], zinc, cadmium, and mercury[1,58,66,188], forming salts with complex anions. Treatment of alcoholic solutions of boronium salts containing the anions $FeCl_4^-$ and $SnCl_6^{2-}$ with 70% perchloric acid leads to the formation of the corresponding perchlorates[135] and in reactions of KPF_6 or $NaB(C_6H_5)_4$ with boronium salts having the anions BF_4^- and BH_4^-, the hexafluorophosphates or tetraphenylboronates are formed[40,128].

When ion-exchange resins or the reactions of boronium chlorides with silver oxide in water are employed, the products are cationic complexes of boron containing hydroxide ions and behaving as strong bases. When these complexes were acted upon by acids, boronium salts with different anions were synthesised[89,150,152,155,180]. Boronium salts containing the anions $B_9H_{14}^-$, Br^-, I^-, I_3^-, Br_3^-, N_3^-, $SSP(SH_3)_2^{2-}$, NO_3^-, HSO_4^-, $C(SCN)_4(NH_3)_2^-$, $(NC)_2C-CHC-(CN)_2^-$, etc. have also been obtained by exchange reactions[58,138,150,189]. Several reactions of boronium salts involving transformations in the anion have been described too. When SO_2 is passed through an alcoholic solution of bis-(1,3-diketonato)boronium di-iodoiodate, the corresponding iodide was obtained[135]. A quantitative conversion of boronium salts with the anions I_3^-, Br_3^-, and I_2Cl^- into the corresponding halides takes place when they are treated with $Na_2S_2O_5$, acetone, or an olefin[66]. The reaction of difluoro[tetrakis(dimethylamino)ethylene]boronium tetrafluoroborate with phenylmagnesium bromide results in the formation of the tetraphenylboronate of the cation[40].

REFERENCES

1. W. Diltey, Annalen, 344, 300 (1906).
2. D. R. Schultz and R. W. Parry, J. Amer. Chem. Soc., 80, 4 (1958).
3. S. G. Shore and R. W. Parry, J. Amer. Chem. Soc., 80, 8 (1958).
4. S. G. Shore and R. W. Parry, J. Amer. Chem. Soc., 80, 12 (1958).
5. R. W. Parry and S. G. Shore, J. Amer. Chem. Soc., 80, 15 (1958).
6. S. G. Shore, P. R. Girdrdot, and R. W. Parry, J. Amer. Chem. Soc., 80, 20 (1958).
7. R. W. Parry, G. Kodama, and D. R. Schultz, J. Amer. Chem. Soc., 80, 24 (1958).
8. R. C. Taylor, D. R. Schultz, and A. R. Emery, J. Amer. Chem. Soc., 80, 27 (1958).
9. E. R. Alton, J. C. Carter, C. Cluff, A. R. Emery, C. W. Heitsch, R. W. Parry, R. C. Taylor, C. E. Nordmann, G. Kodama, S. G. Shore, C. R. Peters, C. Reimann, I. R. Weaver, and M. Yamauchi, U. S. Dept. Com., Office Tech. Service, P. R. Rept. 161 080, 1959, p. 178; Chem. Abs., 55, 17 327 (1961).
10. A. Stock, "Hydrides of Boron and Silicon", Cornell Univ. Press., Ithaca, New York, 1933.
11. W. Gerrard, "The Organic Chemistry of Boron" (Translated into Russian), Izd. Khimiya, Moscow, 1966, p. 190.
12. R. W. Adams and A. R. Siedle, "Boron, Metallo-Boron Compounds and Boranes", Interscience Publ., 1964, p. 488.
13. H. Steinberg and A. L. McCloskey, "Progress in Boron Chemistry", Pergamon Press, 1964, Vol. 1, p. 100.

14. K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds" [Vol. 6 of "Anorganische und allgemeine Chemie in Einzeldurstellungen"] (Translated into Russian), Izd. Mir., Moscow, 1968, p. 42.
15. H. Steinberg and R. J. Brotherton, "Organoboron Chemistry", Vol. 2, "Boron-nitrogen and Boron-phosphorus Compounds", Interscience Publ., 1966, p. 458.
16. A. Hajos, "Komplexe Hydride und ihre Anwendung in der organischen Chemie", Deutscher Verl. der Wissensschaften, Berlin, 1966, p. 54.
17. B. M. Mikhailov, "Khimiya Borovodorodov" (The Chemistry of Boranes), Izd. Nauka, Moscow, 1967, p. 243.
18. E. L. Muetterties, "The Chemistry of Boron and Its Compounds", New York, 1967.
19. A. F. Zhigach and D. S. Stasinevich, "Khimiya Gidridov" (The Chemistry of Hydrides), Izd. Khimiya, Leningrad, 1969, p. 219.
20. V. D. Sheludyakov, "Kationnye Kompleksy Bora" (Cationic Boron Complexes), Candidate's Thesis, Institute of General Chemistry, USSR Academy of Sciences, Moscow, 1964.
21. W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin Inc., New York–Amsterdam, 1963.
22. O. T. Beachley, Inorg. Chem., 4, 1823 (1965).
23. M. Inoue and C. Kodama, Inorg. Chem., 7, 430 (1968).
24. S. G. Shore and C. L. Hall, J. Amer. Chem. Soc., 88, 5346 (1966).
25. H. C. Brown, P. F. Stehle, and P. A. Tierney, J. Amer. Chem. Soc., 79, 2020 (1957).
26. J. F. Eastham, J. Amer. Chem. Soc., 89, 2237 (1967).
27. S. G. Shore and C. L. Hall, J. Amer. Chem. Soc., 89, 3947 (1967).
28. A. Stock and E. Kuss, Ber., 56, 789 (1923).
29. S. G. Shore and K. W. Boeddeker, Inorg. Chem., 3, 914 (1964).
30. W. H. Schechter, S. L. Walters, US. P. 2 708 152 (1955); Chem. Abs., 49, 11 969f (1955).
31. E. Wiberg and H. Michaud, Z. Naturforsch., 9b, 497 (1954).
32. J. M. Marhlout, US P. 3 437 456 (1964); Chem. Abs., 71, 4989f (1969).
33. A. Stock and E. Pohland, Ber., 58, 657 (1923).
34. E. Wiberg, Chem. Ber., 69, 2816 (1936).
35. H. I. Schlesinger and A. B. Burg, J. Amer. Chem. Soc., 60, 290 (1938).
36. A. B. Burg, J. Amer. Chem. Soc., 69, 747 (1947).
37. G. W. Schaeffer, M. D. Adams, and F. J. Koeng, J. Amer. Chem. Soc., 78, 725 (1956).
38. S. G. Shore and R. W. Parry, J. Amer. Chem. Soc., 77, 6084 (1955).
39. S. G. Shore, C. W. Hickam, and Y. D. Cowles, J. Amer. Chem. Soc., 87, 2755 (1965).
40. N. Wiberg and J. W. Ruchler, Ber., 96, 3000 (1963).
41. G. E. McAchran and S. G. Shore, Inorg. Chem., 4, 125 (1965).
42. W. L. Jolly and T. Schmitt, J. Amer. Chem. Soc., 88, 4282 (1966).
43. W. L. Jolly and T. Schmitt, Inorg. Chem., 6, 344 (1967).
44. H. C. Brown and W. J. Wallace, "Abstracts of the 142nd Meeting of the American Chemical Society, Atlantic City, September, 1962", p. 9N; from the book by R. M. Adams and A. R. Siedle, "Boron, Metallo-Boron Compounds and Boranes", New York, 1964, p. 489.
45. T. A. Shchegoleva, V. D. Sheludyakov, and B. M. Mikhailov, Dokl. Akad. Nauk SSSR, 152, 888 (1963).
46. B. M. Mikhailov, "Khimiya Borovodorodov" (The Chemistry of Boranes), Izd. Nauka, Moscow, 1967, p. 340.
47. A. Stock, E. Wiberg, and H. Martini, Ber., 63B, 2927 (1930).
48. G. Kodama and R. W. Parry, J. Amer. Chem. Soc., 79, 1007 (1957).
49. G. Kodama and R. W. Parry, J. Amer. Chem. Soc., 82, 6250 (1960).
50. R. Schaeffer, F. Tebbe, and C. Phillips, Inorg. Chem., 3, 1475 (1964).
51. L. J. Edwards, W. V. Hough, and M. D. Ford, "16 Congr. Intern. chim. pure et. appl., Paris, 1957", p. 475; Chem. Abs., 54, 15 062 (1960).
52. R. W. Parry and L. J. Edwards, J. Amer. Chem. Soc., 81, 3554 (1959).
53. W. V. Hough, M. D. Ford, G. T. Hefferan, and L. J. Edwards, U. S. At. Energy Comm., CCC–1024–TR–274; Chem. Abs., 55, 18 414 (1961).
54. P. C. Moews and P. W. Parry, Inorg. Chem., 5, 1552 (1966).
55. H. I. Schlesinger, L. Horvits, and A. Burg, J. Amer. Chem. Soc., 58, 409 (1936).
56. H. Nöth, H. Beyer, and H. J. Vetter, Ber., 97, 110 (1964).
57. G. E. Ryschkewitsch, Adv. Chem. Ser., 42, 54 (1964).
58. K. C. Nainan and G. E. Ryschkewitsch, J. Amer. Chem. Soc., 91, 330 (1969).
59. K. C. Nainan and G. E. Ryschkewitsch, Inorg. Chem., 7, 1316 (1968).
60. G. E. Ryschkewitsch and J. M. Garrett, J. Amer. Chem. Soc., 89, 4240 (1967).
61. V. D. Sheludyakov, T. A. Shchegoleva, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 632 (1964).
62. H. Nöth and H. Beyer, Angew. Chem., 71, 383 (1959).
63. H. Nöth, Angew. Chem., 74, 506 (1962).
64. H. Nöth, Angew. Chem., 72, 638 (1960).
65. H. Nöth and H. Beyer, Ber., 93, 1078 (1960).
66. G. E. Ryschkewitsch and J. M. Garrett, J. Amer. Chem. Soc., 90, 7234 (1968).
67. J. E. Douglass, G. R. Roehrig, and On-Houma, J. Organometall. Chem., 8, 421 (1967).
68. G. E. Ryschkewitsch and W. W. Lochmaier, J. Amer. Chem. Soc., 90, 6260 (1968).
69. R. J. Rowatt and N. E. Miller, J. Amer. Chem. Soc., 89, 5509 (1967).
70. N. E. Miller, D. L. Reznicek, R. J. Rowatt, and K. R. Lundberg, Inorg. Chem., 8, 862 (1969).
71. N. E. Miller and D. L. Reznicek, Inorg. Chem., 8, 275 (1969).
72. G. L. Smith and H. C. Kelly, Inorg. Chem., 8, 2000 (1969).
73. N. E. Miller, Inorg. Chem., 8, 1693 (1969).
74. J. E. Douglass, J. Amer. Chem. Soc., 84, 121 (1962).
75. J. E. Douglass, J. Amer. Chem. Soc., 86, 5431 (1964).
76. G. E. Ryschkewitsch, J. Amer. Chem. Soc., 89, 3145 (1967).
77. T. A. Shchegoleva, E. M. Shashkova, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 366 (1969).
78. B. M. Mikhailov, N. S. Fedotov, T. A. Shchegoleva, and V. D. Sheludyakov, Dokl. Akad. Nauk SSSR, 145, 340 (1962).

79. B. M. Mikhailov, T. A. Shchegoleva, and V. D. Sheludyakov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 816 (1963).
80. K. L. Lundberg, R. J. Rowatt, and N. E. Miller, Inorg. Chem., 8, 1336 (1969).
81. B. M. Mikhailov and N. S. Fedotov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1482 (1959).
82. B. M. Mikhailov and N. S. Fedotov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1590 (1961).
83. B. M. Mikhailov and N. S. Fedotov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1913 (1961).
84. B. M. Mikhailov and N. S. Fedotov, Dokl. Akad. Nauk SSSR, 154, 1128 (1964).
85. T. A. Shchegoleva and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 714 (1965).
86. B. M. Mikhailov, T. K. Kozminskaya, and L. V. Tarasova, Dokl. Akad. Nauk SSSR, 160, 615 (1965).
87. H. Nöth, Z. Naturforsch., 16b, 471 (1961).
88. H. Nöth, S. Lukas, and P. Schweizer, Chem. Ber., 98, 962 (1965).
89. L. Banford and G. E. Coates, J. Chem. Soc., 3564 (1964).
90. H. Holzapfel, P. Nenning, G. Kerns, and C. Tuschick, Z. Chem., 7, 467 (1967).
91. W. Gerrard, M. F. Lappert, and R. Schafferman, J. Chem. Soc., 3828 (1957).
92. P. B. Bridley, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 1540 (1956).
93. S. H. Dandegaonker, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 2893 (1957).
94. S. H Dandegaonker, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 2872 (1957).
95. W. Gerrard, M. F. Lappert, and H. B. Silver, J. Chem. Soc., 3285 (1956).
96. J. D. Edwards, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 1471 (1955).
97. E. W. Abel, J. D. Edwards, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 501 (1957).
98. T. Colclough, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 3006 (1956).
99. M. F. Lappert and G. Srivastava, J. Chem. Soc. (A), 602 (1967).
100. J.M.Davidson and C.M.French, Chem. Ind. (London), 750 (1959).
101. J. M. Davidson and C. M. French, J. Chem. Soc., 3364 (1962).
102. J. M. Davidson and C. M. French, J. Chem. Soc., 114 (1958).
103. R. B. Moodie, B. Ellul, and T. M. Conner, Chem. Ind. (London), 767 (1966).
104. D. R. Armstrong and P. G. Perkins, J. Chem. Soc. (A), 1026 (1966).
105. W. Gerrard, H. R. Hudson, and E. F. Mooney, Chem. Ind. (London), 292 (1958).
106. R. Köster and Y. Morite, Annalen, 704, 70 (1967).
107. W. Gerrard, H. R. Hudson, and E. F. Mooney, J. Chem. Soc., 113 (1962).
108. E. Wiberg, A. Bolz, and P. Buchhoit, Z. anorg. Chem., 256, 285 (1948).
109. E. Wiberg and K. Schuster, Z. anorg. Chem., 213, 77, 89 (1933).
110. E. Wiberg and W. Sutterlin, Z. anorg. Chem., 256, 285 (1948).
111. C. A. Brown and R. C. Osthoff, J. Amer. Chem. Soc., 74, 2340 (1952).
112. H. Nöth, P. Schweizer, and F. Ziegelgaensberger, Chem. Ber., 99, 1089 (1966).
113. J. F. Brown, J. Amer. Chem. Soc., 74, 1219 (1952).
114. C. W. Makosky, G. L. Galloway, and G. E. Ryschkewitsch, Inorg. Chem., 6, 1972 (1967).
115. B. M. Mikhailov, T. A. Shchegoleva, and V. D. Sheludyakov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1698 (1962).
116. B. M. Mikhailov, T. A. Shchegoleva, and V. D. Sheludyakov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2165 (1964).
117. B. M. Mikhailov, T. A. Shchegoleva, N. S. Fedorov, and V. D. Sheludyakov, "Nekotorye Voprosy Organicheskoi Khimii" (Some Problems of Organic Chemistry), Izd. Kazan. Univ., 1964, p. 71.
118. E. L. Muetterties, J. Inorg. Nuclear Chem., 15, 182 (1960).
119. A. Fratiello and R. E. Schuster, Inorg. Chem., 7, 1581 (1968).
120. N. N. Greenwood and B. H. Robinson, J. Chem. Soc. (A), 511 (1967).
121. K. J. Wynne and W. L. Jolly, Inorg. Chem., 6, 107 (1967).
122. A. P. Zuur, J. I. Van Houte, and W. Z. Groeneveld, Rec. Trav. Chim., 87, 755 (1968).
123. C. D. Schmulbach and I. J. Ahmed, Inorg. Chem., 8, 1414 (1969).
124. C. D. Schmulbach and I. J. Ahmed, J. Chem. Soc. (A), 3008 (1969).
125. I. J. Ahmed and C. D. Schmulbach, Inorg. Chem., 8, 1411 (1969).
126. E. L. Muetterties, J. Amer. Chem. Soc., 82, 4163 (1960).
127. E. L. Muetterties and F. N. Tebbe, Inorg. Chem., 7, 2663 (1968).
128. N. Wiberg and I. W. Buchler, J. Amer. Chem. Soc., 85, 243 (1963).
129. S. Lukas, Dissertation, Munich, 1962.
130. J. Goubeau, M. Rahtz, and H. I. Becher, Z. anorg. Chem., 275, 161 (1954).
131. W. Gerrard, H. R. Hudson, and E. F. Mooney, J. Chem. Soc., 5168 (1960).
132. N. N. Greenwood and K. Wade, J. Chem. Soc., 1130 (1960).
133. L. I. Pechalin and G. M. Panchenko, Zhur. Fiz. Khim., 41, 682 (1967) [Russ. J. Phys. Chem., No. 3 (1967)].
134. A. Fratiello, T. P. Onak, and R. E. Schuster, J. Amer. Chem. Soc., 90, 1194 (1968).
135. A. Barabas, E. Isfan, M. Roman, M. Paraschiv, E. Romas, and A. T. Balaban, Tetrahedron, 24, 1133 (1968).
136. E. L. Muetterties and C. W. Wright, J. Amer. Chem. Soc., 86, 5132 (1964).
137. E. L. Muetterties and C. W. Wright, J. Amer. Chem. Soc., 87, 21 (1965).
138. E. L. Muetterties, Angew. Chem., 77, 264 (1965).
139. E. L. Muetterties, US P. 3 177 240 (1963); Chem. Abs., 63, 14 776b (1965).
140. E. L. Muetterties, Pure Appl. Chem., 10, 53 (1965).
141. E. L. Muetterties, H. Roesky, and C. W. Wright, J. Amer. Chem. Soc., 88, 4856 (1966).
142. E. L. Muetterties, US P. 3 336 380 (1963); Chem. Abs., 69, 2582q (1968).
143. H. Nöth, W. A. Dorochov, P. Fritz, and E. Pfab, Z. anorg. Chem., 318, 293 (1962).
144. H. Nöth and S. Lukas, Ber., 95, 1505 (1962).
145. H. Nöth and P. Frifz, Z. anorg. Chem., 322, 297 (1963).
146. H. Nöth and W. Schraegle, Ber., 97, 2218 (1964).
147. H. Nöth and H. Vahrenkamp, Ber., 99, 2757 (1966).
148. J. Goubeau and A. Zappel, Z. anorg. Chem., 279, 38 (1955).

149. J. E. Milks, G. M. Kennerly, and J. H. Polevy, J. Amer. Chem. Soc., 84, 2529 (1962).
150. N. E. Miller and E. L. Muetterties, J. Amer. Chem. Soc., 86, 1033 (1964).
151. H. C. Miller, N. E. Miller, and E. L. Muetterties, J. Amer. Chem. Soc., 85, 3885 (1963).
152. N. E. Miller, US P. 3 217 023 (1962); Chem. Abs., 64, 3103d (1966).
153. N. E. Miller, US P. 3 314 990 (1961); Chem. Abs., 67, 99 645g (1967).
154. N. E. Miller, DBR P. 1 235 912 (1963); Chem. Abs. 67, 218 244 (1967).
155. N. E. Miller, French P. 1 394 178 (1962); Chem. Abs., 63, 15 897a (1965).
156. N. E. Miller, H. C. Miller, and E. L. Muetterties, Inorg. Chem., 3, 866 (1964).
157. O. T. Beachley, Inorg. Chem., 7, 701 (1968).
158. O. T. Beachley, Inorg. Chem., 6, 870 (1967).
159. A. T. Balaban, A. Arsene, I. Bally, A. Barabas, M. Paraschiv, and E. Romas, Tetrahedron Letters, 3917 (1965).
160. A. Barabas and A. T. Balaban, Tetrahedron Letters, 3925 (1965).
161. S. F. Stafiej and D. A. Carvalho, US P. 3 296 274 (1964); Chem. Abs., 66, 85 700p (1967).
162. S. F. Stafiej and E. A. Takas, US P. 3 305 555 (1964); Chem. Abs., 68, 95 705z (1968).
163. M. F. Lappert, H. Pyszora, and M. Rieber, J. Chem. Soc., 4256 (1965).
164. N. E. Miller, J. Amer. Chem. Soc., 88, 4284 (1966).
165. F. J. Sowa, US P. 2 655 524 (1953); Chem. Abs., 48, 13 710f (1954).
166. S. Prasad and N. Prasad Singh, Z. anorg. Chem., 346, 217 (1966).
167. S. Prasad and N. Prasad Singh, J. Proc. Inst. Chemists (India), 38, 22 (1966); Chem. Abs., 64, 17 023a (1966).
168. S. Prasad and N. Prasad Singh, Z. anorg. Chem., 350, 332 (1967).
169. A. R. Johnson, J. Phys. Chem., 16, 1 (1912).
170. C. E. Nordmann and C. R. Peters, J. Amer. Chem. Soc., 81, 3551 (1959).
171. C. E. Nordmann, C. Reimann, and C. R. Peters, Adv. Chem. Ser., 32, 204 (1961).
172. C. R. Peters and C. E. Nordmann, J. Amer. Chem. Soc., 82, 5758 (1958).
173. B. Z. Egan and S. G. Shore, J. Amer. Chem. Soc., 83, 4717 (1961).
174. J. R. Weaver, S. G. Shore, and R. W. Parry, J. Chem. Phys., 29, 1 (1958).
175. G. E. Ryschkewitsch, S. Lawrence, C. Makosky, and G. L. Galloway, Chem. Eng. News, 45, 48 (1967).
176. T. P. Onak and I. Shapiro, J. Chem. Phys., 32, 952 (1960).
177. C. W. Heitsch, Inorg. Chem., 4, 1019 (1965).
178. N. M. D. Brown and P. Pladon, J. Chem. Soc. (A), 526 (1969).
179. A. Arsene, A. T. Balaban, J. Bally, A. Barabas, M. Paraschiv, and C. N. Renea, Spectrochim. Acta A., 23, 1373 (1967).
180. N. E. Miller, B. L. Chamberland, and E. L. Muetterties, Inorg. Chem., 3, 1064 (1964).
181. T. C. Bissot and R. W. Parry, J. Amer. Chem. Soc., 77, 3481 (1955).
182. A. Stock and E. Poland, Ber., 59, 2215 (1926).
183. T. A. Shchegoleva, V. D. Sheludyakov, and B. M. Mikhailov, Zhur. Obshch. Khim., 35, 1066 (1965).
184. K. W. Böddeker, S. Shore, and R. K. Bunting, J. Amer. Chem. Soc., 88, 4396 (1966).
185. S. G. Shore and C. W. Hickam, Inorg. Chem., 2, 638 (1962).
186. N. E. Miller and E. L. Muetterties, Inorg. Chem., 3, 1196 (1964).
187. S. F. Stafiej and E. A. Takas, US P. 3 341 582 (1964); Chem. Abs., 68, 68 486X (1968).
188. G. E. Coates and D. Ridley, J. Chem. Soc., 166 (1964).
189. S. F. Stafiej and E. A. Takas, US P. 3 383 399 (1964); Chem. Abs., 69, 4989t (1968).

Zelinskii Institute of
Organic Chemistry,
USSR Academy of
Sciences, Moscow