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THE THERMAL DECOMPOSITION OF SALTS OF BORONIC ACIDS

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ABSTRACT

Salts with the formula $M[RB(OH)_3]$ (where M is Li, Na or K, and R is C_6H_5 or C_6H_{11}) and $M[C_6H_5B(OH)_3]_2$ (where M is Ca, Sr or Ba) were prepared. The thermal decomposition in air and in nitrogen proceeded through a series of intermediate compounds to the respective anhydrous metaborate salt. The possible nature of these intermediate compounds is considered.

INTRODUCTION

The neutralization reaction of group IA and IIA metal hydroxides with organoboron acids has been known for many years[1]. In the case of boronic acids the reaction may be represented by the following equation:

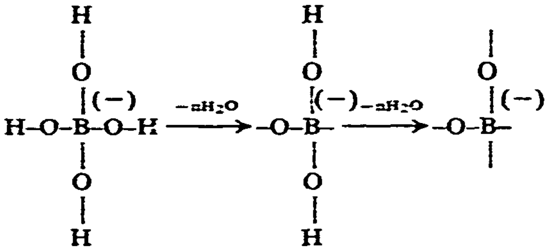
$$MOH + RB(OH)_2 \longrightarrow M[RB(OH)_3] \qquad (1)$$

An investigation of the thermal decomposition of the salts produced in eqn. (1) was initiated as a part of a study of some polymeric materials containing boron–oxygen bonds. This paper will report on our thermogravimetric studies of the group IA and IIA salts produced from phenyl and cyclohexylboronic acids. Subsequent reports will deal with the preparation and thermogravimetry of other salts containing the $[R_2B(OH)_2]^-$ and $[R_3B(OH)]^-$ anions.

The chemistry of hydrated borates has been extensively studied and a number of excellent reviews have been written[2–5]. Various authors have made attempts to systematize the structural chemistry of borates. These schemes fall into two classes: those dealing with anhydrous borates[6,7] and those dealing with hydrated borates[2–5,8]. Two of the four rules formulated by Christ[5] are directly related to the explanation of the thermogravimetric curves observed for salts of boronic acids. These rules may be summarized as follows:

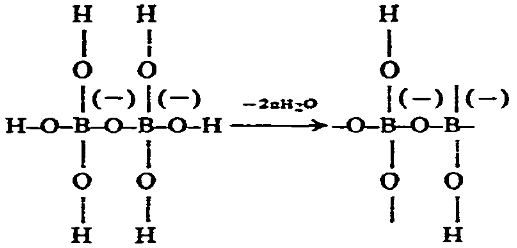
1. *In polyanions of hydrated borates, those oxygens not shared by two borons always attach a proton and exist as hydroxyl groups.* One exception to this rule has been found in the mineral Hambergite, $4BeO \cdot B_2O_3 \cdot H_2O$[9]. Here the OH group is attached to beryllium, probably due to its stronger Lewis acid character.

2. *The insular groups may polymerize in various ways by splitting out water. The insular groups may polymerize, either to infinite chains, or possibly to dimers, but probably rarely or never polymers of a degree between these two extremes.* Heller has proposed a very extensive scheme to systematize borate structures[2]. In this scheme he has proposed the following sequence of reactions which incorporate the two rules listed above.



$$\mathrm{H{-}O{-}B(OH)_2^{(-)}{-}O{-}H \xrightarrow{-nH_2O} {-}O{-}B(OH)_2^{(-)}{-} \xrightarrow{-nH_2O} {-}O{-}B(O{-})^{(-)}{-}} \quad (2)$$

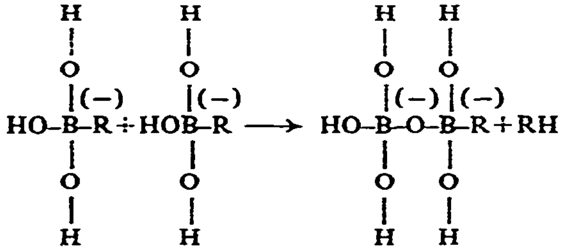
$n[B(OH)_4]^-$ $\{BO(OH)_2\}_n^{n-}$ $\{BO_2\}_n^{n-}$



$$\mathrm{H{-}O{-}B(OH)_2^{(-)}{-}O{-}B(OH)_2^{(-)}{-}O{-}H \xrightarrow{-2nH_2O} {-}O{-}B(OH)(O{-})^{(-)}{-}O{-}B(OH)^{(-)}{-}} \quad (3)$$

$n[B_2O(OH)_6]^{2-}$ $\{B_2O_3(OH)_2\}_n^{2n-}$

Since $[B(OH)_4]^-$ and $[RB(OH)_3]^-$ are structurally and chemically analogous, the thermal decomposition of the $[RB(OH)_3]^-$ anion may follow a scheme similar to that above. In addition to linking together by dehydration, the salts of boronic acids can also link by losing the organic group as shown in eqn. (4):



$$\mathrm{HO{-}B(OH)_2^{(-)}{-}R + HOB(OH)_2^{(-)}{-}R \longrightarrow HO{-}B(OH)_2^{(-)}{-}O{-}B(OH)_2^{(-)}{-}R + RH} \quad (4)$$

EXPERIMENTAL

Materials

The boronic acids and their anhydrides were prepared by a previously described method[10]. All other chemicals were reagent grade.

Trihydroxyphenylborate salts

The following general procedure was used to prepare the salts of phenylboronic acid. Specific quantities of starting materials and solvents are given in Table 1.

A mixture of phenylboronic anhydride, and the appropriate metal hydroxide in a 1:3 ratio for group IA metals and a 2:3 ratio for group IIA metals was dissolved in water on a steam bath. Isopropyl alcohol was added to the hot solution and on cooling to room temperature, the trihydroxyphenylborate salt precipitated in the form of crystalline platelets. The crude product (usually better than 98% pure) was separated by filtration under a nitrogen atmosphere. The product was washed with two 25 ml portions of isopropyl alcohol, then 25 ml of anhydrous ether and finally dried over phosphorus pentoxide in a vacuum desiccator.

The crude product was dissolved in a minimum volume of ether on a steam bath, then isopropyl alcohol was introduced slowly until the hot solution became turbid. The solution was quickly filtered and placed in a refrigerator (4°) to crystallize. The product was isolated as before. Yields and analyses are summarized in Table 1.

Sodium trihydroxy(cyclohexyl)borate

A mixture of 5.00 g of cyclohexylboronic acid and 1.57 g of sodium hydroxide was dissolved in 15 ml of water. The crude product was isolated upon adding 150 ml of isopropyl alcohol and recrystallized from a mixture containing 5 ml of water and 100 ml of isopropyl alcohol. The yield was 4.23 g, 64.4%.

Calculated results for $NaC_6H_{14}BO_3$: C, 42.90; H, 8.40; B, 6.44; Na, 13.69; found: C, 43.40; H, 8.72; B, 6.10; Na, 13.71.

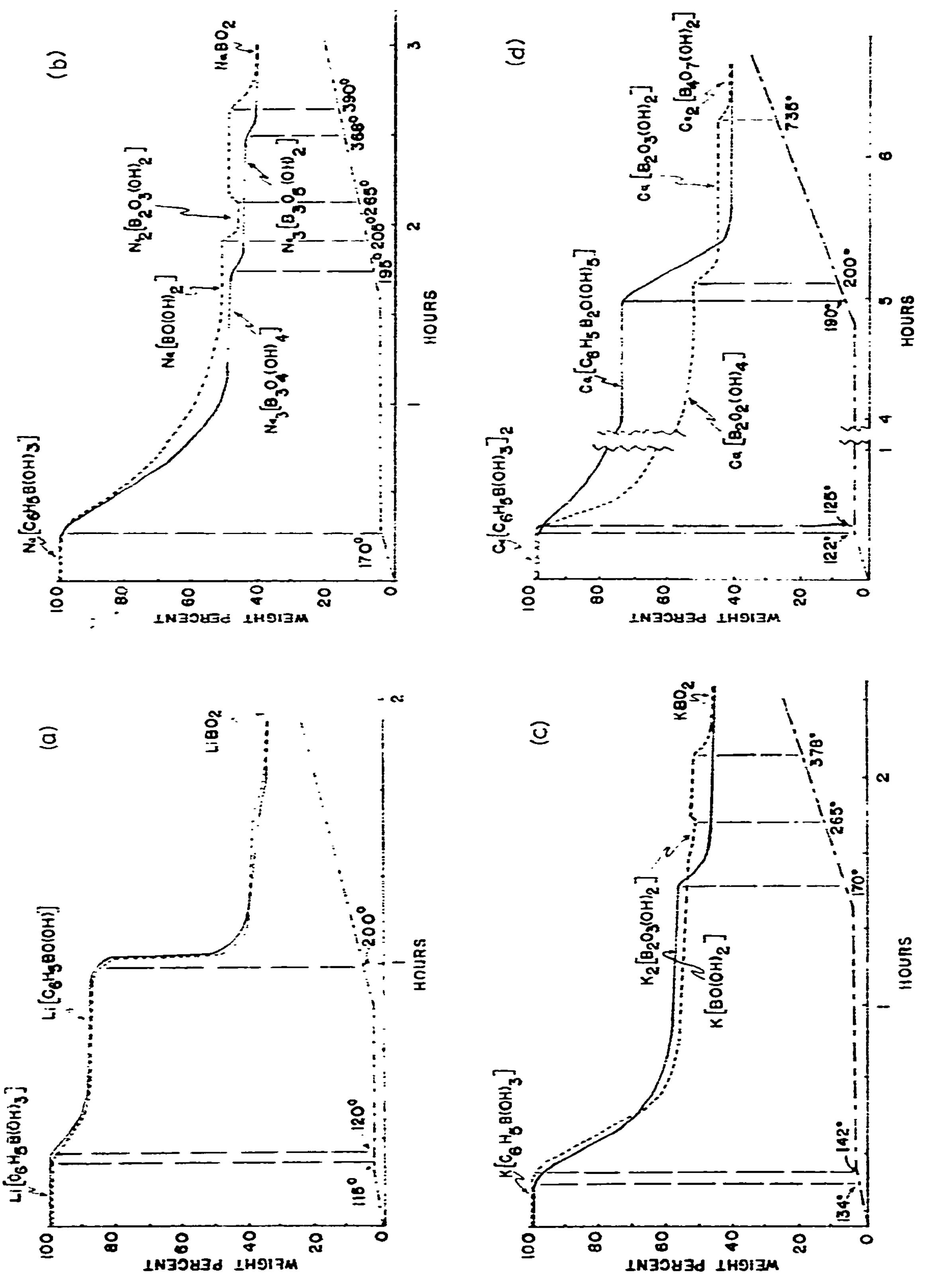
Analytical procedure

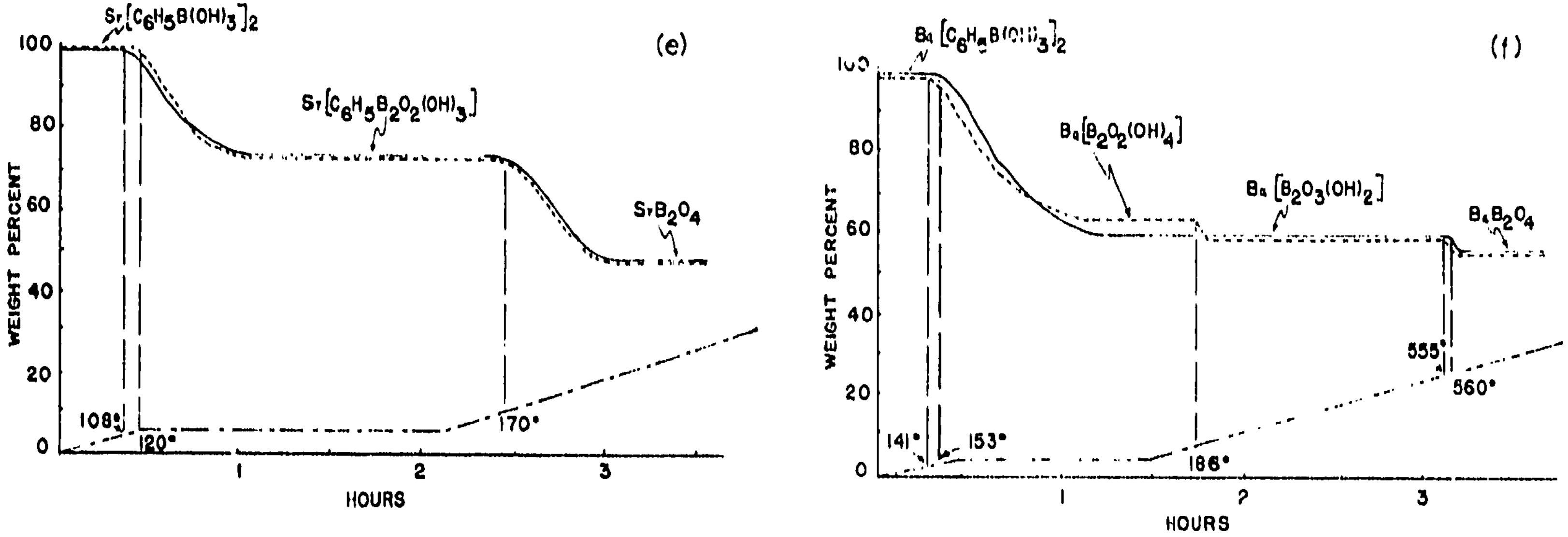
A standard semimicro combustion method was utilized to determine carbon and hydrogen content in each sample, with the exception that each sample was mixed with copper oxide and sodium bisulfate to facilitate combustion.

Metal content was determined by titration with standard hydrochloric acid in the presence of methyl red indicator. Boron was determined by addition of mannitol to the solution at the methyl red endpoint and the resulting boron complex was then titrated with standard sodium hydroxide in the presence of phenolphthalein. Methylene blue was used in the boron determination to make the endpoint more pronounced.

Thermogravimetric analyses

A recording thermobalance, patterned after specifications given by Mauer[11], was employed to study the thermal decomposition of the borate salts. Each sample was treated in the following manner. A 50 mg sample was weighed into an open platinum crucible, which was then suspended from the balance beam and positioned in the center of the furnace, just below the thermocouple. The sample was then heated at a rate of one degree per minute until weight loss was observed and at that point the temperature was held constant until the sample reached constant weight. It was then


(a)
Li[C6H5B(OH)3]
Li[C6H5BO(OH)]
LiBO2
118°
120°
200°
WEIGHT PERCENT
100
80
60
40
20
0
HOURS
1
2
(b)
Na[C6H5B(OH)3]
Na[BO(OH)2]
Na2[B2O3(OH)2]
Na3[B3O4(OH)4]
Na3[B3O5(OH)2]
NaBO2
170°
195°
205°
265°
368°
390°
WEIGHT PERCENT
100
80
60
40
20
0
HOURS
1
2
3
(c)
K[C6H5B(OH)3]
K2[B2O3(OH)2]
K[BO(OH)2]
KBO2
134°
142°
170°
265°
378°
WEIGHT PERCENT
100
80
60
40
20
0
HOURS
1
2
(d)
Ca[C6H5B(OH)3]2
Ca[C6H5B2O(OH)5]
Ca[B2O2(OH)4]
Ca[B2O3(OH)2]
Ca2[B4O7(OH)2]
122°
125°
190°
200°
735°
WEIGHT PERCENT
100
80
60
40
20
0
HOURS
1
4
5
6



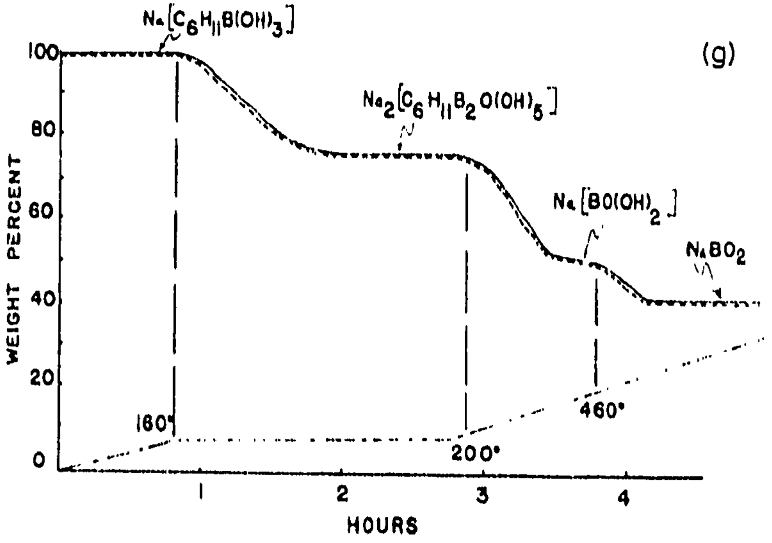


Fig. 1. Thermogravimetric curves of (a) lithium trihydroxyphenylborate, (b) sodium trihydroxyphenylborate, (c) potassium trihydroxyphenylborate, (d) calcium trihydroxyphenylborate, (e) strontium trihydroxyphenylborate, (f) barium trihydroxyphenylborate, and (g) sodium trihydroxy (cyclohexyl)borate. (———) nitrogen, (– – – –) air and (—·—·) temperature.

heated at a rate of three degrees per minute until complete decomposition to the respective metaborate had occurred, except for calcium trihydroxyphenylborate, which did not completely dehydrate below 1000°C.

All samples were analyzed at atmospheric pressure in air and also in an atmosphere of nitrogen. The composition of the intermediate compounds was calculated from the weight losses and final decomposition products were determined from X-ray diffraction data. See Fig. 1. The theoretical composition agreed with that calculated from weight loss for the intermediate compounds within 2% in all cases.

X-ray diffraction data

Samples were exposed to filtered copper Kα radiation in a 114.6 mm diameter Debye–Scherrer powder camera. The *d* spacings, in Angstrom units were recorded directly from the film by means of a set of *d* value templates. These values were then compared with those recorded in the ASTM files[12].

DISCUSSION

Preparation of trihydroxyphenylborate salts

Trihydroxyphenylborate salts were prepared from an aqueous solution of phenylboroxine and the proper metal hydroxide. To effect recrystallization, the impure salts were dissolved in a minimum amount of water, then isopropyl alcohol was added to cause reprecipitation. Analytical data indicated that the formula for the lithium, sodium, and potassium salts was $M[C_6H_5B(OH)_3]$ and the formula for the calcium, strontium and barium salts was $M[C_6H_5B(OH)_3]_2$ (see Table 1).

The yield varied from 23.4% for $Li[C_6H_5B(OH)_3]$ to 80.6% for $Na[C_6H_5B(OH)_3]$. There are a number of factors which affect the yield and purity of these salts. The principle factor which determines the yield, is the quantity of water used to dissolve the reactants. The yields of sodium and potassium salts are particularly affected by this, and no product is obtained if a large amount of water is used. The lithium, calcium, strontium and barium salts behave in the same manner as the sodium and potassium salts, although the yields are not quite so sensitive to the quantity of solvent. Therefore, only the minimum amount of water needed to dissolve the reactants should be used. Solutions of these salts are strongly basic and consequently absorb carbon dioxide. For this reason, the manipulation of solutions of these salts was carried out in a nitrogen atmosphere. Another factor, which affected the purity of these salts, was the amount of metal hydroxide in the starting material. If an excess amount of metal hydroxide was used, the sample was difficult to purify. Consequently, only stoichiometric quantities of starting materials should be used.

Thermal decomposition

The salts were found to decompose through a series of intermediate phases to benzene or cyclohexane, water and the respective metaborate salt, except for $Ca[C_6H_5B(OH)_3]_2$ which did not reach the weight loss calculated to correspond to $Ca(BO_2)_2$ below 1000°C. It was found that holding the temperature constant during the initial decomposition step resulted in a more sharply defined decomposition curve.

TABLE 1

PREPARATIVE DETAILS, ANALYSES, AND YIELDS OF TRIHYDROXYPHENYLBORATE SALTS

Salt	*Analysis (%)*[a]				*Preparative details*				*Yield*	
	Metal	*Boron*	*Carbon*	*Hydrogen*	*Water (ml)*	*Alcohol (ml)*	*Boroxine (g)*	*Metal hydroxide (g)*	*Grams*	*Percent*
Lithium	4.76 4.73	7.42 7.41	49.3 47.16	5.48 5.59	11.5	80	1.039	0.240	0.300	23.43
Sodium	14.20 14.25	6.68 6.65	44.4 43.82	4.97 5.26	5.0	100	1.039	0.400	1.160	80.61
Potassium	21.96 21.76	6.08 6.10	40.4 38.90	4.53 4.74	1.5	200	1.039	0.561	0.685	42.80
Calcium	12.60 12.36	6.80 6.86	45.2 45.51	5.07 5.36	100	100	1.039	0.371	0.732	52.29
Strontium	23.97 23.87	5.92 5.75	39.5 38.46	4.43 4.68	40	100	1.039	1.329	1.273	77.22
Barium	33.08 32.66	5.21 5.26	34.7 34.71	3.89 3.83	30	100	1.039	1.578	1.390	73.31

[a] Calculated values are reported above the experimental values.

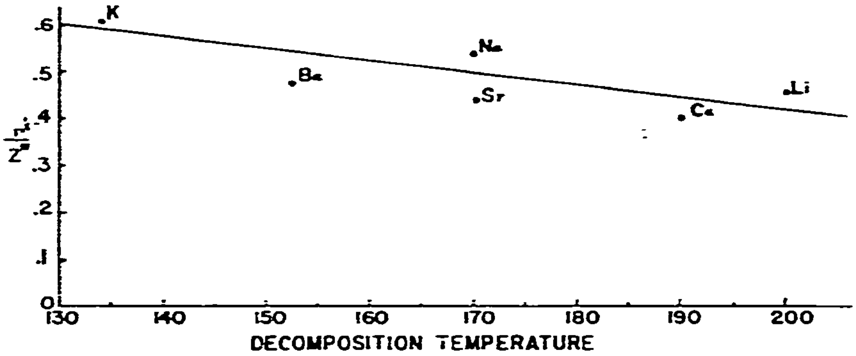
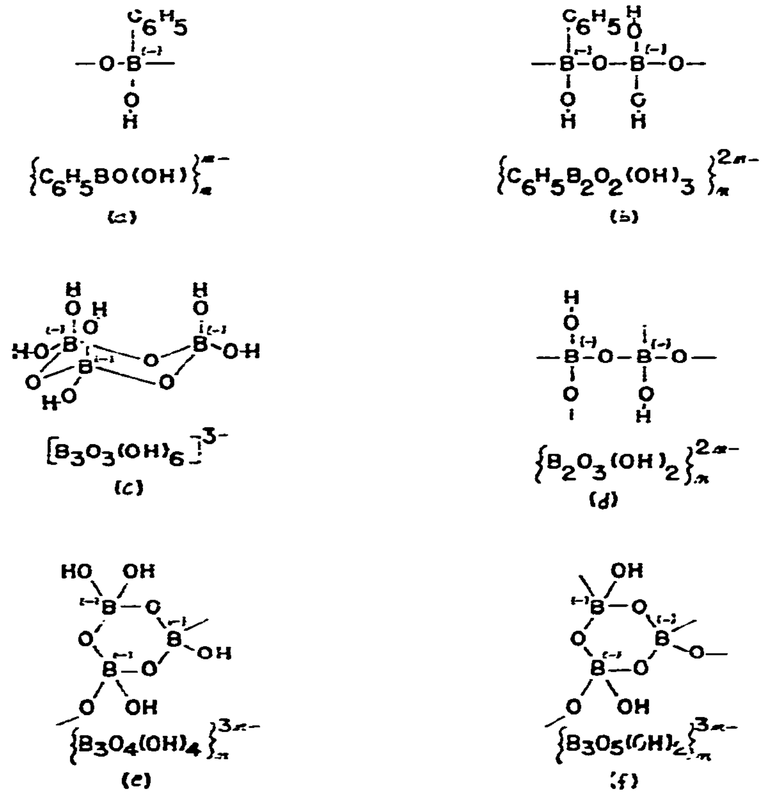


Fig. 2. Correlation of size to effective charge ratio and the temperature at which final loss of benzene occurred. Z* is effective nuclear charge.

There was no general relationship between the size/effective charge ratio of the cation and initial decomposition temperature of the salts as predicted by Sterns[13]. As may be seen in Fig. 2 there was, however, a correlation between the size/effective charge ratio of the cation and the temperature at which the final loss of benzene occurred.

The sodium and potassium trihydroxyphenylborate salts exhibited a weight gain at 265 °C. This weight gain was not reproducible and was due to incorporation



$\{C_6H_5BO(OH)\}_n^{n-}$
(a)

$\{C_6H_5B_2O_2(OH)_3\}_n^{2n-}$
(b)

$[B_3O_3(OH)_6]^{3-}$
(c)

$\{B_2O_3(OH)_2\}_n^{2n-}$
(d)

$\{B_3O_4(OH)_4\}_n^{3n-}$
(e)

$\{B_3O_5(OH)_2\}_n^{3n-}$
(f)

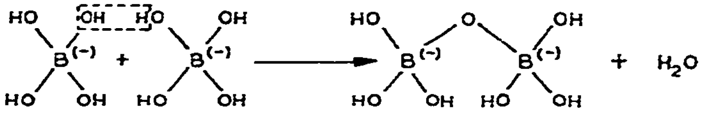
Fig. 3. Postulated structures of thermal decomposition products.

of water into the sample from the air. Under anhydrous conditions this did not occur.

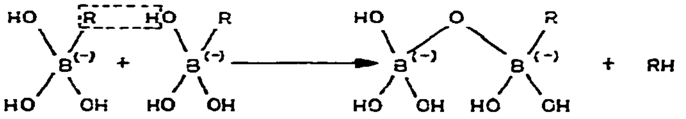
Since each salt exhibited its own unique decomposition curve the thermogravimetric data will be discussed in terms of successive steps in the removal of water from the samples in general. Possible structures are proposed based upon the structural schemes for hydrated borates referred to in the Introduction. These structures are tabulated in Figs. 3a–3f.

1. *Loss of one molecule of benzene or cyclohexane per two [RB(OH)$_3$] units*

The insular borate $[(HO)_3BOB(OH)_3]^{2-}$ exists in the mineral Pinnoit, $MgO \cdot B_2O_3 \cdot 3H_2O$[14]. Its formation can be represented by eqn. (5) in which one molecule of water is removed from a pair of $[B(OH)_4]^-$ tetrahedra.


(5)

A similar reaction has been observed in the thermogravimetric curves of $Na[C_6H_{11}B(OH)_3]$ and $Ca[C_6H_5B(OH)_3]_2$. However, these two salts lose one molecule of cyclohexane and benzene respectively instead of water as represented by eqn. (6) to form salts containing the anion $[RB_2O(OH)_5]^{2-}$.


(6)

2. *Loss of one molecule of water, benzene or cyclohexane per [RB(OH)$_3$]$^-$ unit*

The removal of water from $[B(OH)_4]^-$ units to form chain-like polymers having the formula $\{BO(OH)_2\}_n^{n-}$ and chain structure as shown in eqn. (2) has been demonstrated[15,16]. Each of the $[RB(OH)_3]^-$ salts display a plateau on the thermogravimetric curve which corresponds to the loss of one molecule of either water, benzene or cyclohexane from the $[RB(OH)_3]^-$ anion. The sodium, potassium, calcium and barium salts lose benzene or cyclohexane to form the above chain structures. The lithium salt, however, loses water to form a salt having the formula $Li[C_6H_5BO(OH)]$ which may also be a chain type structure (Fig. 3a). Also the strontium salt has a stable phase with the composition $Sr[C_6H_5B_2O_2(OH)_3]$ which may exhibit chains of the type shown in Fig. 3b, or possibly a mixture of $\{BO(OH)_2\}_n^{n-}$ and $\{C_6H_5BO(OH)\}_n^{n-}$ chains.

It is not very likely that these compounds exist in a six membered ring structure of three tetracoordinate boron atoms as illustrated in Fig. 3c. No compounds having this ion have been found. Furthermore Dale[8] has proposed that this structure is unstable due to repulsion of the axial OH groups.

3. *Crosslinked structures which are the result of removal of more water*

The dehydration of $[B_2O(OH)_6]^{2-}$ according to Heller[2] should produce a borate with the formula $\{B_2O_3(OH)_2\}_n^{2n-}$ and structure shown in Fig. 3d. Borates having this formula and structure are, however, unknown. The sodium, potassium, calcium and barium salts do display a stable phase with this formula and very well may have the structure predicted by Heller.

Finally, the $Na[C_6H_5B(OH)_3]$ salt decomposes in N_2 to yield two compounds $Na_3[B_3O_4(OH)_4]$ and $Na_3[B_3O_5(OH)_2]$. These may be analogous to those found in $\{[K(H_2O)]_3[B_3O_5(OH)_2]\}_n$ and $\{K_3[B_3O_5(OH)_2]\}_n$[17]. The proposed structures for these compounds are illustrated in Figs. 3e and 3f.

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