Short Communications

THERMAL ANALYSIS OF BORON COMPLEXES CONTAINING LIGANDS OF THE TYPE $R-C(CH_2OH)_3$

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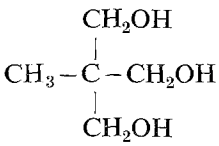
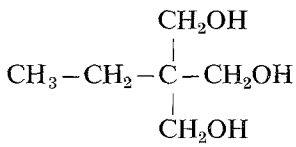
The thermal behaviours of certain salts of the complex "ethriol-" and "methriolboric" acids have been investigated by means of Derivatograph and IR spectra.

It is shown that compounds of this type decompose in three main stages on heating: 1) the crystallization water is lost, 2) the condensation water is lost and dimers are formed containing bridge bonds B_4-O-B_4; 3) up to 600–700° all the organic matter is lost; the residue is the corresponding borate (1 : 1). The possibility of performing a fast full analysis by means of the TG and DTG curves has been demonstrated.

A number of salts have been prepared of the complex acids formed by boric acid and methriol (2-methyl-2-hydroxymethylpropanediol-1,3) (I) or ethriol (2-ethyl-2-hydroxymethylpropanediol-1,3 (II) [1, 2].

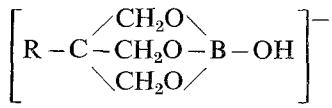


I



II

These salts are crystal-hydrates containing the complex "methriol-" or "ethriolborate" anion (III).



III

Experimental

The thermal behaviour of these compounds was studied with a Paulik–Paulik–Erdey Derivatograph. The following conditions were used: 0.1–0.2 g samples in a small platinum crucible; heating rate 12°/min; air atmosphere; the tempera-

ture was measured inside the sample; reference substance: Al_2O_3. IR spectra has been taken with a IKS – 14A apparatus, between 3000 – 3800 cm^{-1}, the sample suspended in paraffin oil.

Results

Some of the TG, DTG and DTA curves are presented in Figs. 1 – 4. The weight-loss data are listed in Table 1.

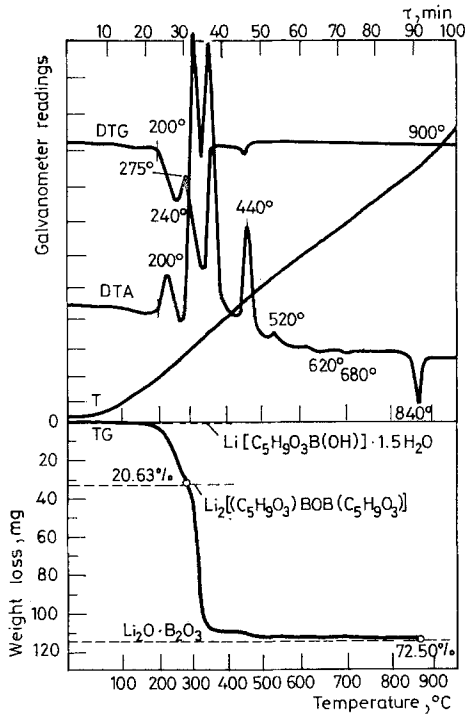


Fig. 1. TG, DTG and DTA of lithium methriolborate $Li[CH_3C(CH_2O)_3B(OH)] \cdot 1.5H_2O$

The compounds under investigation exhibit three main stages of thermal decomposition. The first is the loss of crystallization water by heating from 60° up to 200°; the second process is the loss of one molecule of water due to dimerization:

$$2M[R-C(CH_2O)_3B(OH)] \rightarrow H_2O + M_2[R-C(CH_2O)_3BOB(OCH_2)C-R]$$

The dimers have been isolated and named "dimethriol-" and "diethrioldiborates".

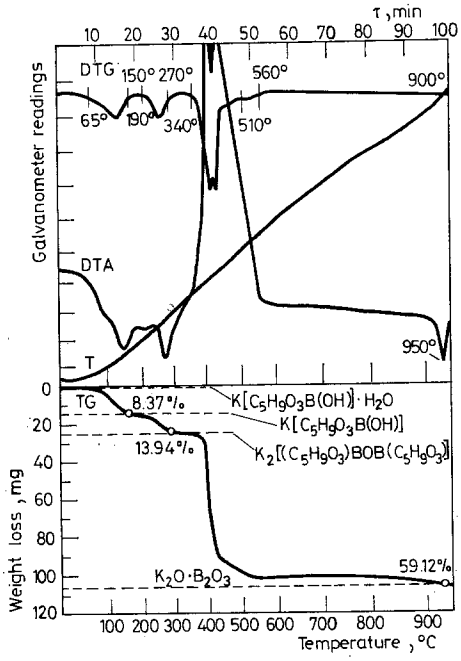


Fig. 2. TG, DTG and DTA of potassium methriolborate $K[CH_3C(CH_2O)_3B(OH)]\ 2H_2O$

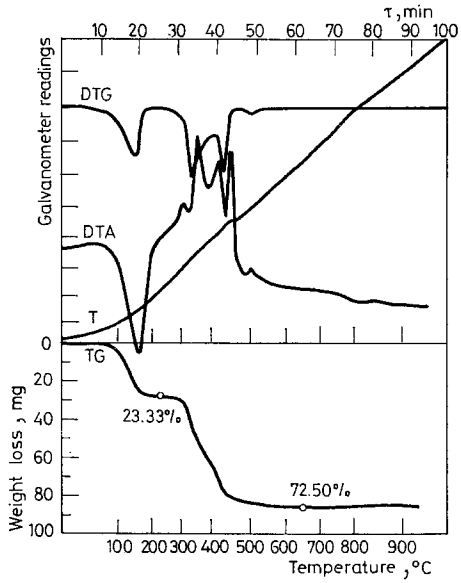


Fig. 3. TG, DTG and DTA of sodium ethriolborate $Na[C_2H_5C(CH_2O)_3B(OH)] \cdot 3H_2O$

Table 1

The thermal behaviour of methriol-

Formula	Stage I of weight loss		
	t°	Obtained %	Calculated % according to 1
$Li[CH_3C(CH_2O)_3B(OH)] \cdot 1.5H_2O$	—	—	—
$Na[CH_3C(CH_2O)B(OH)] \cdot 3H_2O$	60—180	24.38	24.35
$K[CH_3C(CH_2O)_3B(OH)] \cdot 2H_2O$	45—210	15.59	16.37
$NH_4[CH_3C(CH_2O)_3B(OH)] \cdot 0.5H_2O$	100—180	20.91	20.24*
$Ba[CH_3C(CH_2O)_3B(OH)]_2 \cdot 4H_2O$	60—160	15.40	14.49
$Sr[CH_3C(CH_2O)_3B(OH)]_2 \cdot 4H_2O$	—	—	—
$Li[C_2H_5C(CH_2O)_3B(OH)] \cdot 1.5H_2O$	170—180	14.27	14.02
$Na[C_2H_5C(CH_2O)_3B(OH)] \cdot 3H_2O$	60—180	23.33	22.81
$K[C_2H_3C(CH_2O)_3B(OH)] \cdot 0.5H_2O$	190—260	5.13	4.32
$NH_4[C_2H_5C(CH_2O)_3B(OH)] \cdot 0.5H_2O$	90—180	19.42	18.87*
$Sr[C_2H_5C(CH_2O)_3B(OH)]_2 \cdot 4H_2O$	—	—	—
$Ba[C_2H_5C(CH_2O)_3B(OH)]_2 \cdot 2H_2O$	—	—	—

1) $M[R-C(CH_2O)_3BOH] \cdot nH_2O \rightarrow M[R-C(CH_2O)_3BOH] + nH_2O$

2) $2M[R-C(CH_2O)_3BOH] \cdot nH_2O \rightarrow M_2[R-C(CH_2O)_3BOB(OCH_2)_3C-R] + (n+1)H_2O$

3) $2M[R-C(CH_2O)_3BOH] \cdot nH_2O \xrightarrow{O_2} M_2O \cdot B_2O_3(MO \cdot B_2O_3) + mCO_2 + q(H_2O)$

Unambiguous evidence for this process was provided by IR absorption spectra taken immediately after the isolation of the product (the heating was stopped at the endpoint of the corresponding decomposition stage on the DTG (Fig. 5). If only the anhydrous salts are formed, the OH-group bound to boron (B—OH) remains, and the IR spectra show the corresponding absorption band at 3360 cm^{-1}. If the dimer is formed this OH-group is lost, and there is no band at 3360 cm^{-1} organic matter. The third stage of the thermal decomposition is due to oxidation and loss of organic matter. This loss is complete at 600—700°; the process is accompanied by exothermic peaks on the DTA. The residue is the corresponding borate.

The endothermic minima on the DTA, due to melting of the residue, are in agreement with the literature data for the borates $M_2O \cdot B_2O_3$ [3] (Table 2).

In the case of the ammonium compounds, ammonia is split off together with the crystallization water; after the oxidation of the organic matter only boron oxide remains.

In some cases one or an other stage of the dehydration is absent: e.g. the ethriolborates of lithium, sodium and potassium and the methriolborate of sodium do not form dimers on heating (Fig. 3). This is proved by the IR spectra of the isolated intermediates, the OH-stretching absorption band being present. In the

and ethriolborates

Stage II of weight loss			Stage III of weight loss		
t°	Obtained %	Calculated % according to 2	t°	Obtained %	Calculated % according to 3
200—275	20.63	20.13	275—520	72.50	72.19
—	—	—	240—690	70.23	70.46
210—300	20.21	20.46	300—580	62.36	63.59
—	—	—	300—450	79.56	79.76**
160—200	19.24	18.04	200—580	55.80	55.35
50—210	20.55	20.04	218—880	62.73	61.46
—	—	—	280—580	73.98	74.22
—	—	—	280—485	72.50	72.12
—	—	—	300—600	60.39	60.45
—	—	—	340—540	83.58	81.29**
110—250	18.53	18.87	250—620	62.78	63.74
190—280	12.00	10.99	280—620	54.88	54.63

*) Calculated according to $NH_4[RC(CH_2O)_3B(OH)] \cdot nH_2O \rightarrow$
$\rightarrow NH_3 + nH_2O + H[RC(CH_2O)_3B(OH)]$

**) Calculated according to $NH_4[RC(CH_2O)_3B(OH)] \cdot nH_2O \rightarrow$
$\rightarrow 2NH_3 + mCO_2 + (2n + q)H_2O + B_2O_3$

Table 2

Melting points of the residues after heating of the boron complexes containing methriol and ethriol

Cation	t° of the endothermic minima		Melting point of the 1 : 1 borates [3], °C
	Methriol-borates	Ethriolborates	
Li	850	850	849
Na	970	970	967
K	950	955	950

case of lithium methriolborate and strontium methriol- and ethriolborate, the first stage of the thermal decomposition is missing (Fig. 1). The crystallization water is split off together with the condensation water. This fact is confirmed by the IR spectra: the absorption band of the OH-group does not appear in the IR spectrum of the product isolated after heating.

In the case of potassium methriolborate and barium methriol- and ethriolborate all three stages of decomposition mentioned above are present (Figs 2 and 4).

Table 3

Analysis of boron complexes with triols

Formula	C %			
	Obtained		calculated	error %
	from the Ta curve	micro-analytically		
$Na[C_2H_5C(CH_2O)_3B(OH)] \cdot 3H_2O$	30.7	30.41	30.53	+0.56
$Li[C_2H_5C(CH_2O)_3B(OH)] \cdot 1.5H_2O$	37.2	37.76	37.35	−0.40
$K[C_2H_5C(CH_2O)_3B(OH)] \cdot 0.5H_2O$	34.7	35.14	34.79	−0.25
$Sr[C_2H_5C(CH_2O)_3B(OH)]_2 \cdot 4H_2O$	29.17	30.20	30.17	−1.56
$Ba[C_2H_5C(CH_2O)_3B(OH)]_2 \cdot 2H_2O$	29.40	29.60	29.33	+0.24
$Li[CH_3C(CH_2O)_3B(OH)] \cdot 1.5H_2O$	33.36	33.45	33.57	−0.63
$Na[CH_3C(CH_2O)_3B(OH)] \cdot 3H_2O$	27.00	27.26	27.05	−0.19
$K[CH_3C(CH_2O)_3B(OH)] \cdot 2H_2O$	27.59	27.44	27.29	+1.47
$Sr[CH_3C(CH_2O)_3B(OH)]_2 \cdot 4H_2O$	26.62	26.62	26 71	−0.37

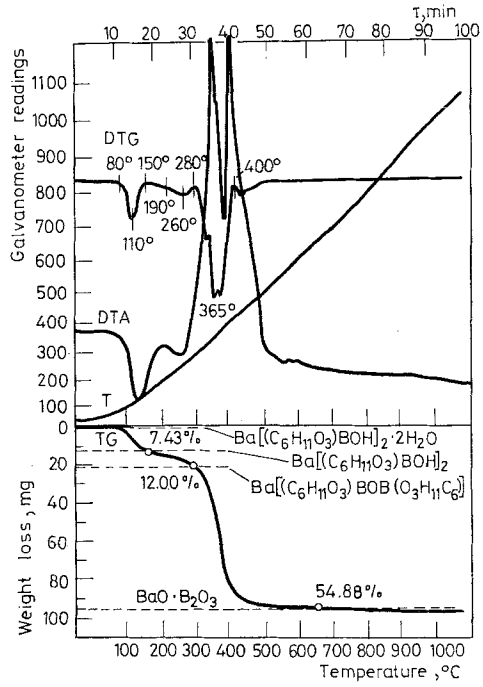


Fig. 4. TG, DTG and DTA of barium ethriolborate $Ba[C_2H_5C(CH_2O)_3BOH] \cdot 2H_2O$

	Residue after heating, %			
	Obtained		calculated $B_2O_3+M_2O$ (MO)	error %
	from the Ta curve	titration* B_2O_3 and M_2O (MO)		
$Na[C_2H_5C(CH_2O)_3B(OH)] \cdot 3H_2O$	27.50	27.99	27.83	−1.36
$Li[C_2H_5C(CH_2O)_3B(OH)] \cdot 1.5H_2O$	26.02	26.00	26.17	−0.37
$K[C_2H_5C(CH_2O)_3B(OH)] \cdot 0.5H_2O$	39.61	39.51	39.55	+0.15
$Sr[C_2H_5C(CH_2O)_3B(OH)]_2 \cdot 4H_2O$	37.22	36.99	36.26	+2.15
$Ba[C_2H_5C(CH_2O)_3B(OH)]_2 \cdot 2H_2O$	45.12	44.73	45.37	−0.55
$Li[CH_3C(CH_2O)_3B(OH)] \cdot 1.5H_2O$	27.50	27.70	27.81	−1.12
$Na[CH_3C(CH_2O)_3B(OH)] \cdot 3H_2O$	29.77	29.65	29.64	+0.44
$K[CH_3C(CH_2O)_3B(OH)] \cdot 2H_2O$	37.64	37.16	37.22	+1.13
$Sr[CH_3C(CH_2O)B(OH)]_2 \cdot 4H_2O$	38.35	—	38.54	−0.49

* B_2O_3 and $MO(M_2O)$ were determined separately by titration.

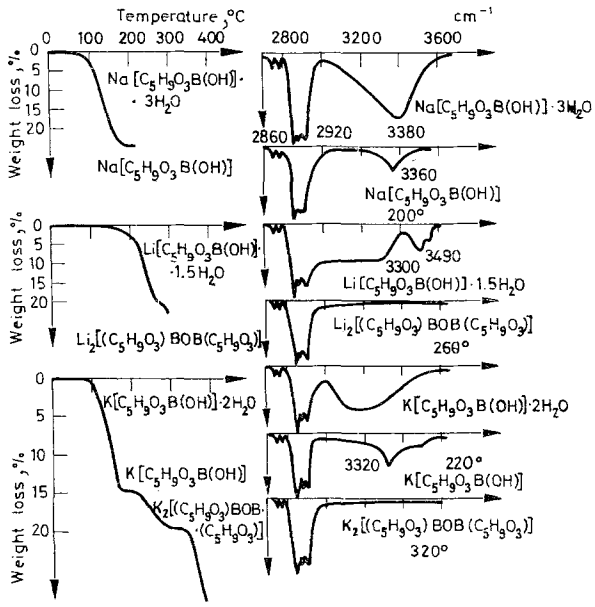
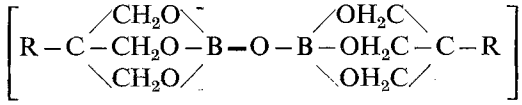


Fig. 5. Dehydration of methriolborates and the IR spectra of the dehydrated products

The dehydrated products can be isolated, together with the dimers (IV), after heating. The probable structure of the dimeric anion is the following (IV):



IV

It was mentioned above that the salts of the complex methriol- and ethriolboric acids decompose to borates on heating, although the dissociation temperatures of the corresponding carbonates are higher than those attainable by means of the derivatograph. However, the less volatile boric acid evolves CO_2 from the carbonates [4].

The TG, DTG and DTA curves of compounds of this type allow a fast full analysis of the compound:

1) The weight loss in the first stage gives the crystallization water content.

2) The difference between the full weight loss and the weight loss in the first stage gives the organic content, from which the carbon content may be calculated.

3) The residue gives the sum of metal oxide and boron oxide contents.

The results of the analysis calculated from thermal analysis are listed in Table 3 and are in good agreement with the theoretical values.

References

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