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STUDY OF THE THERMAL REACTIONS OF BORIC ACID WITH POLYOLS

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II. THE INTERACTIONS OF BORIC ACID WITH PENTAERYTHRITOL AND ANALOGOUS COMPOUNDS

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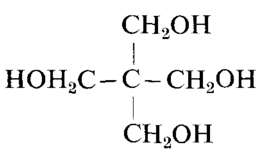
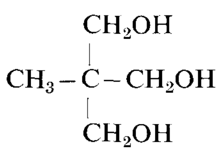
Thermal analysis shows that the interaction of boric acid with pentaerythritol on heating leads to the formation of a polymeric complex acid (1 : 1) and the direction of the interaction does not depend on the molar ratio of the reacting compounds. The interaction of boric acid with methriol and ethriol leads to the formation of two types of esters, depending on the molar ratio of the reactants. The formation of an unstable polyolboric acid is an intermediate stage of each interaction.

This work is devoted to the thermal study of the interactions of boric acid with 1,3-dihydroxy-2,2-dioxymethylpropane (pentraerythritol) (I), 1,3-dihydroxy-2-oxymethyl-2-methyl-propane (methriol) (II), and 1,3-dihydroxy-2-oxymethyl-2-ethyl-propane (ethriol) (III).


I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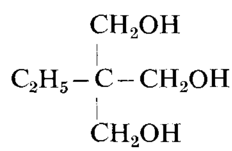

III

The thermal curves of I, II and III have been given earlier [2]. As shown in [1], we can determine the direction of interaction from the weight loss at the end of the dehydration interaction (on the TG curve). Theoretically various reactions can take place on heating boric acid with I:

1a) $H_3BO_3 + C(CH_2OH)_4 \rightarrow 2\,H_2O + C(CH_2OH)_2(CH_2O)_2BOH$

1b) $H_3BO_3 + C(CH_2OH)_4 \rightarrow 2\,H_2O + H[C(CH_2OH)(CH_2O)_3BOH]$

2a) $H_3BO_3 + C(CH_2OH)_4 \rightarrow 3\,H_2O + C(CH_2OH)(CH_2O)_3B$

2b) $n\,H_3BO_3 + nC(CH_2OH)_4 \rightarrow 3n\,H_2O + H_n[C(CH_2O)_4B]_n$

We can assume some other interactions in the case of an excess of polyol in the reaction mixture, e.g.:

3a) $H_3BO_3 + 2\,C(CH_2OH)_4 \rightarrow (CH_2OH)_3C(CH_2O)B(OCH_2)\,C(CH_2OH)_2 + 3H_2O$

3b) $H_3BO_3 + 2\,C(CH_2OH)_4 \rightarrow H[(CH_2O)_2C(CH_2O)_2B(OCH_2)_2C(CH_2OH)] +$
$+\,3\,H_2O$

4a) $2\,H_3BO_3 + C(CH_2OH)_4 \rightarrow HOB(OCH_2)_2C(CH_2O)_2BOH + 4\,H_2O$

4b) $2\,H_3BO_3 + C(CH_2OH)_4 \rightarrow H_2[(HO)_2B(CH_2O)_2C(CH_2O)_2B(OH)_2] + 2\,H_2O$

5) $8\,CH_3C(CH_2OH)_3 + 8\,H_3BO_3 \rightarrow H(C_5H_9O_3B)_8OH + 23\,H_2O$

6) $8\,C_2H_5C(CH_2OH)_3 + 8\,H_3BO_3 \rightarrow H(C_6H_{11}O_3B)_8OH + 23\,H_2O$

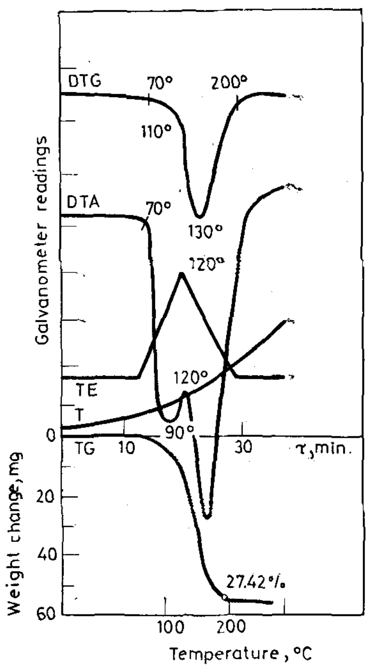


Fig. 1. DTA, TG, DTG and TE curves of a 1 : 1 mixture of boric acid and pentaerythritol (I)

In the case of interactions 1(a,b) the calculated weight loss is 18.2%, in 2(a,b) it is 27.3%, in 3(a,b) 16.3%, in 4a 27.7% and in 4b 18.2%.

The formation of esters (cases a) or complex acids with tetra-co-ordinated boron (cases b) can be demonstrated by the presence or absence of electrical conductivity on melting. As shown by Fig. 1, when an equimolar mixture of boric acid and pentaerythritol is heated, reaction 2 takes place in the temperature range 70 – 130 –

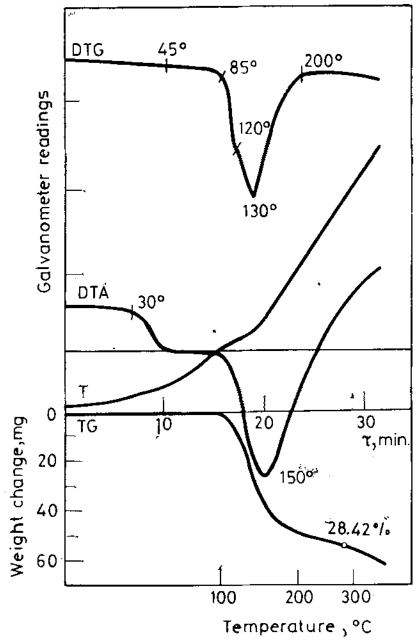


Fig. 2. DTA, TG, DTG curves of an equimolar mixture of boric acid and methriol (II)

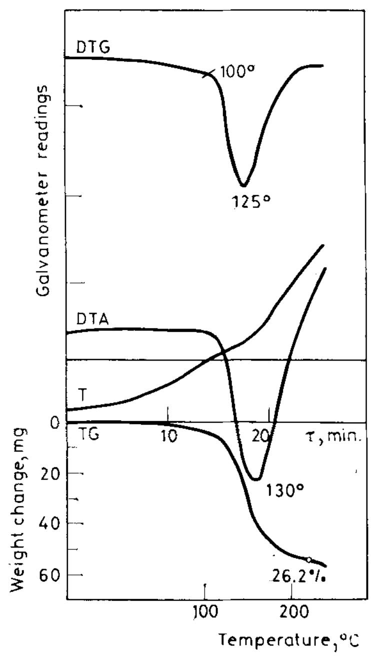


Fig. 3. DTA, TG, DTG curves of an equimolar mixture of boric acid and ethriol (III)

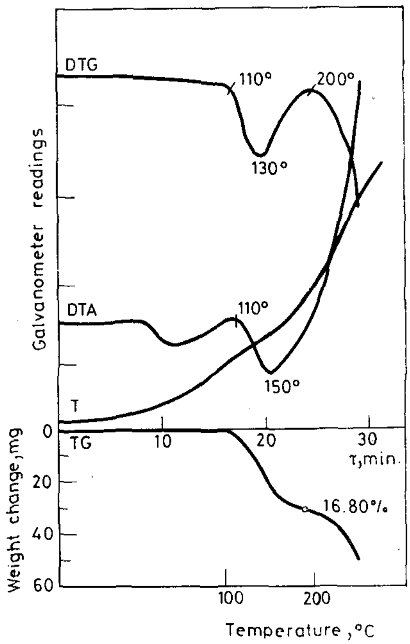


Fig. 4. DTA. TG, DTG curves of a 1 : 2 mixture of boric acid and methriol

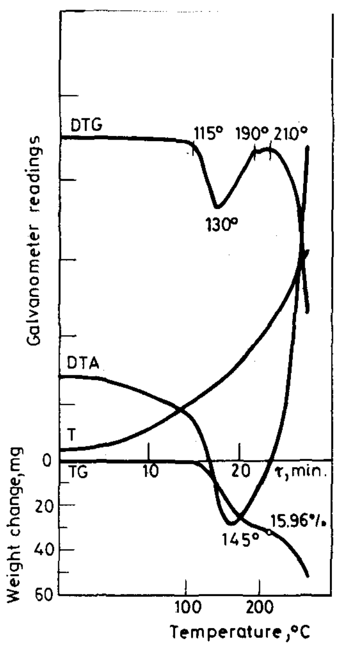


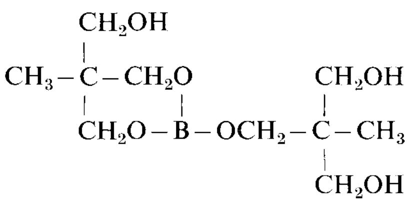
Fig. 5. DTA, TG, DTG curves of a 1 : 2 mixture of boric acid and ethriol

200° (heating rate 10°/min). The rise of electrical conductivity in this temperature range indicates the formation of complex acid (case 2b). The acid, a crystalline compound, is isolated after interrupting the heating when the reaction is finished (controlled on the TG and DTG curves). The IR spectra show that boron is tetra-co-ordinated in this compound [3]. The excess of pentaerythritol in the reaction mixture does not change the direction of the interaction (Table 1). The DTA curve of the mixture of boric acid with excess pentaerythritol shows two endothermic minima, at 180° and 260°, which are due to the polymorphous transformation and melting of the excess of pentaerythritol.

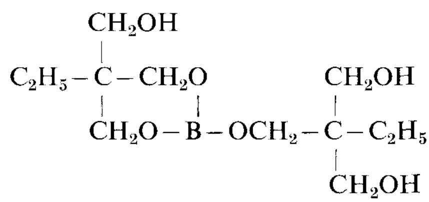
Compounds II and III differ from pentaerythritol only by the substitution of one OH group by a methyl or ethyl group, respectively. However, the interaction with boric acid occurs in this cases in a different manner. The glassy polymeric esters are formed by heating an equimolar mixture of the components (Figs 2 and 3). The average number of monomer in the polymer, as calculated according to [1], is ~ 8. The weight loss (Table 1) shows that in this case reactions 5 and 6 take place. The polymers were isolated by interrupting the heating at the end of interaction. They contain tri-co-ordinated boron (IR absorption bands in the region of 1300 – 1500 cm^{-1}).

If an excess of II or III is taken, crystalline monomeric esters (IV and V) with a boron to II or III ratio of 1 : 2 are formed by interaction.

The d/n of IV and V respectively, are:
4.44(4), 4.75(5) and 5.54(3); and 5.04(3), 5.36(5), 5.73(5) and 6.27(3).



IV



V

As is seen from Table 1 and Figs 4 and 5, the interaction in this case can be described by equations 7 and 8:

(7) $2\ CH_3C(CH_2OH)_3 + H_3BO_3 \rightarrow C_{13}H_{21}O_6B + 3\ H_2O$
(8) $2\ C_2H_5C(CH_2OH)_3 + H_3BO_3 \rightarrow C_{15}H_{25}O_6B + 3\ H_2O$

A further excess of polyol does not change the direction of the interaction. The melting point of ethriol is seen on the DTA curve of a 1 : 4 mixture of boric acid with ethriol.

As seen from Figs 3 – 5, the thermal curves taken at a heating rate of 10°/min, with Al_2O_3 as reference material, and a sample of 100 – 200 mg in a small platinum crucible, do not enable the intermediate stages of interaction to be identified.

However, DTA curves taken with simultaneous measurement of electrical conductivity by an NTR-64 apparatus, which has more sensitive galvanometers, show that the interaction of boric acid with II or III occurs in two stages (Figs 6 and 7). The first stage, stage at 110 – 120 – 140° in the case of ethriol (III) and at 70 – 120 – 130° in the case of methriol (II), is accompanied by a rise of electrical conductivity. The maximum electrical conductivity is at 120°, and it then falls to zero. The second stage of interaction takes place in the temperature range 140 – 160 – 275° in the

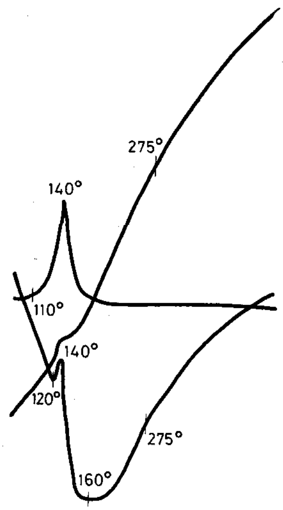


Fig. 6. DTA and TE curves of an equimolar mixture of boric acid and methriol (II), taken on the NTR-64 instrument

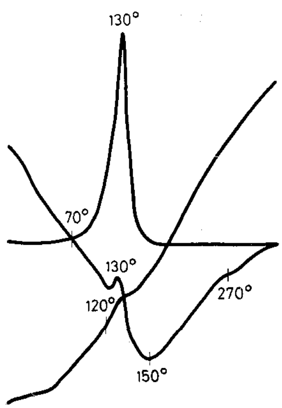


Fig. 7. DTA and TE curves of an equimolar mixture of boric acid and ethriol (III), taken on the NTR-64 instrument

Table 1

Weight losses in the interactions of boric acid with pentaerythritol, methriol and ethriol

Molar ratio H_3BO_3 : polyol	$H_3BO_3 + C(CH_2OH)_4$ (I)		$H_3BO_3 + CH_3C(CH_2OH)_3$(II)		$H_3BO_3 + C_2H_5C(CH_2OH)_3$(III)	
	Found %	Calculated %	Found %	Calculated %	Found %	Calculated %
1 : 1	27.4	27.3*	28.4	28.42**	26.2	26.23**
1 : 2	17.90	16.3*	16.8	16.80***	15.96	15.46***
1 : 4	8.7	8.9*	9.45	9.27***	8.3	8.46***

* Calculated from Eq. 2
** Calculated from Eqs 5 and 6, respectively
*** Calculated from Eqs 7 and 8, respectively

case of II, and at 130 – 150 – 270° in the case of III, and is not accompanied by a rise of electrical conductivity. This shows that the intermediate stage of interaction of boric acid with methriol (II) and ethriol (III) is the formation of an unstable complex acid, which decomposes to form the ester.

References

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2. E. M. SCHWARTZ, V. V. GRUNDSTEIN, A. F. IEVINS, A. A. TERAUDA and A. A. VEGNERE, J. Thermal. Anal., 5 (1973) 665.
3. E. M. SCHWARTZ, V. V. GRUNDSTEIN and A. F. IEVINS, Zh. Neorgan. Khim., 16 (1971) 351.

RÉSUMÉ — On montre par analyse thermique que l'acide borique réagit par chauffage avec le penta-érythritol et qu'il se forme un acide complexe polymère (1 : 1). Le sens de la réaction est indépendant du rapport molaire des composés réagissant. Au contraire, l'interaction de l'acide borique avec le méthriol et l'éthriol donne deux types d'esters suivant le rapport molaire des corps réagissant. La formation d'un acide polyol-boıique instable constitue une étape intermédiaire de chaque interaction.

ZUSAMMENFASSUNG — Durch die Thermoanalyse kann bewiesen werden, daß die bei der Erhitzung auftretende Reaktion von Borsäure mit Pentaerythrit zur Bildung einer polymeren Komplexsäure im Verhältnis (1 : 1) führt und daß die Richtung der Einwirkung nicht von dem molaren Verhältnis der Reaktionskomponenten abhängt. Umgekehrt führt die Reaktion von Borsäure mit Methriol und Äthriol in Abhängigkeit von dem molaren Verhältnis der Reaktionspartner zur Bildung zweier Typen von Estern. Die Bildung einer unbeständigen Polyolborsäure ist eine Zwischenstufe beider Reaktionen.

Резюме — Применением метода термического анализа показано, что взаимодействие борной кислоты с пентаэритритом ведет к образованию полимерной пентаэритритборной кислоты 1:1. Направление реакции не зависит от относительных количеств реагирующих веществ. В противоположность этому при взаимодействии борной кислоты с метриолом и этриолом образуются два типа эфиров: 1:1 и 1:2 в зависимости от молярного отношения реагирующих веществ. Образование нестабильных полиолборных кислот является промежуточной стадией взаимодействия.