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STUDY OF THE THERMAL REACTIONS OF BORIC ACID WITH POLYOLS

I. THE INTERACTIONS OF BORIC ACID WITH HEXITOLS AND PENTITOLS

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The possibility of detecting the direction of reaction of boric acid with polyol and its intermediate stages by means of the data obtained with a Derivatograph is shown. An equation is given for determining the average monomer number in polymers with terminal H and OH groups from weight loss data. In the interaction of boric acid with hexitols and pentitols, polymeric esters are formed. It is found that formation of complex polyolboric acid is the intermediate stage of each interaction.

Thermal analysis can be applied very successfully in the detection of the direction and mechanism of chemical reactions, e.g. in the investigation of the interactions of boric acid with polyols on heating. The most convenient instruments for this purpose are the Derivatograph and a DTA apparatus with simultaneous recording of electrical conductivity.

The existence of some new effects, different from those of boric acid and polyol, on the DTA curve of the mixture indicates that interaction takes place. (The TG, DTG and DTA curves of hexitols and pentitols have been published earlier [1].) TG gives the quantity of water evolved, and allows the direction of the interaction to be determined. The peaks on the curve of electric conductivity vs. temperature enable indirect conclusions to be drawn about the nature of the liquid phases, e.g. the presence of ions, or non-conducting molecules. The possibility of interrupting heating at any point and examining the contents of the crucible allows identification of the products of the interaction. Various reactions can take place on heating boric acid with polyols, e.g.:

1) $H_3BO_3 + CH_2OH(CHOH)_nCH_2OH \rightarrow H_2O +$

$$+ \begin{cases} CH_2OHCHOB(OH)_2(CHOH)_{n-1}CH_2OH \\ H[CH_2OHCHB(OH)_2CHO(CHOH)_{n-2}CH_2OH] \end{cases}$$

2) $H_3BO_3 + CH_2OH(CHOH)_nCH_2OH \rightarrow$

$$\rightarrow 2H_2O + CH_2OHCHOBCHO(CHOH)_{n-2}CH_2OH$$

$$\qquad\qquad\qquad\qquad\qquad\quad |$$

$$\qquad\qquad\qquad\qquad\qquad\quad OH$$

3) $mH_3BO_3 + mCH_2OH(CHOH)_nCH_2OH \rightarrow$

$$\rightarrow 3mH_2O + [CH_2OHCHOBOCH(CHOH)_{n-3}CHOCH_2OH]_m$$

$n = 3$ or 4.

The above reactions can be distinguished by the amount of water evolved. In the case of interactions 1, 2, 3 for hexitols ($n = 4$) the calculated weight loss is 7.38, 14.78 and 22.15%, and for pentitols is 8.41, 16.81 and 25.20%, respectively.

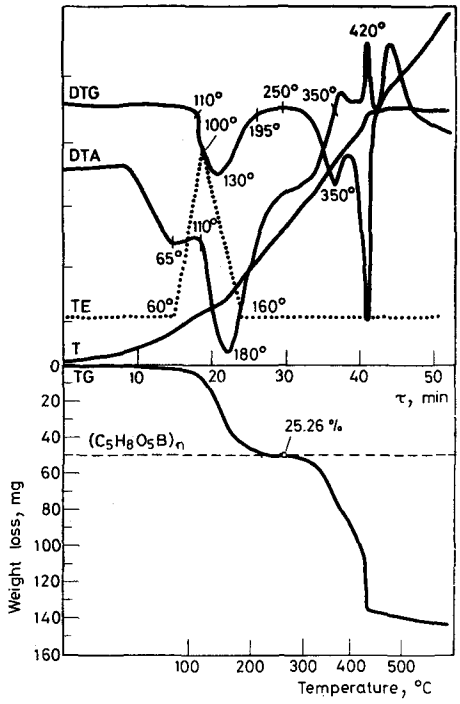

Fig. 1. DTA, TG, DTG and TE curves of an equimolar mixture of H_3BO_3 and L-arabitol

In reaction 3 a polymer is formed. If 3m moles of water are evolved, the polymer consists of infinite-lenght chains. Actually the number of monomer units m in the polymer is limited and the polymer has two terminal groups – H and OH. Formally they can be attributed to the formation of one mole of water per mole of polymer. This leads to the conclusion that in fact the amount of water evolved is

less than 3m. We can therefore calculate the average number of monomer units in the polymer from the weight loss data:

$$m = \frac{q}{N - N_1}$$

where q is the number of similar terminal groups, N is the theoretical weight loss in mole H_2O when infinite-length chains are formed, and N_1 is the practical weight loss in mole H_2O at each stage of dehydration.

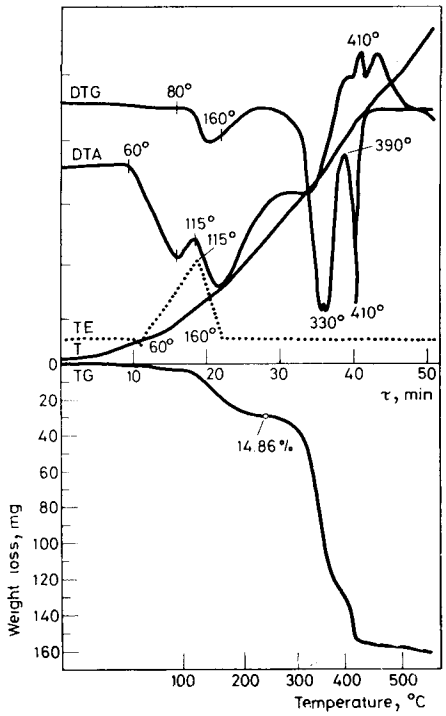

Fig. 2. DTA, TG, DTG, and TE curves of a 1 : 2 mixture of H_3BO_3 and L-arabitol

In reaction 1 the interaction can lead to an ester or a complex acid. In the latter case the electrical conductivity rises on melting. As can be seen from Table 1, the interaction of boric acid with hexitols or pentitols in a molar ratio of 1 : 1 proceeds in two steps. The first step is characterized by one irreversible endothermic minimum on the DTA curve (Fig. 1) at 40 – 100 – 110°, which is accompanied by an increase of electrical conductivity and a negligible weight loss. This is the result of an incongruent melting of the reaction mixture and formation of an intermediate complex acid in the solution, according to reaction 1. The weight loss is due only to

the evaporation of some water. In most cases the acids I are not stable and do not exist in the solid state. Only adonitolboric acid can be isolated in the crystalline state by evaporating to dryness an aqueous solution of an equimolar mixture of boric acid and adonitol [2]. The IR spectra show that boron in adonitolboric acid is tetraco-ordinated.

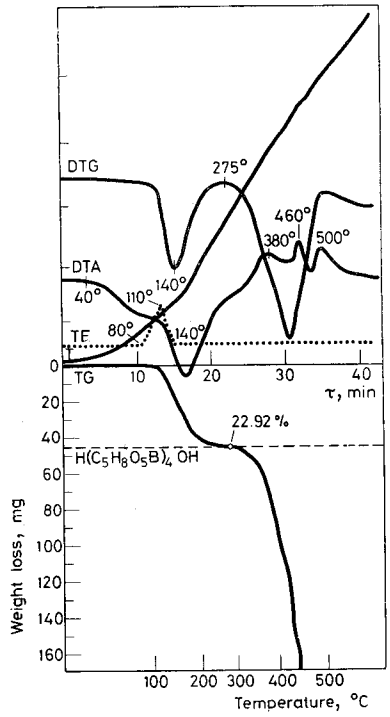

Fig. 3. DTA, TG, DTG and TE curves of a 1 : 1 mixture of H_3BO_3 and adonitol

In the second stage of interaction we observe the evaporation and splitting-off of the water from the complex acid. In this way polymeric esters are formed. The degree of polymerization depends on the constitution and chain length of the polyol. In the cases of adonitol and xylitol, tetramers are formed. In the cases of L-arabitol and D-sorbitol, polymers with long chains are obtained. In the cases of dulcitol and D-mannitol, the average number of monomer units is eight.

All hydroxy groups of boric acid react with polyol already at a molar ratio of 1 : 1, and therefore increase of the amount of polyol does not change the direction of the interaction. This can be seen from the data in Table 2.

All the polymeric esters were isolated by interrupting the heating at the end of interaction. They are hygroscopic, glassy substances with tri-co-ordinated boron

Table 1

The interaction of boric acid with polyols (1 : 1) as indicated by the data of thermal analysis

Reactants	Stage I of interaction			Stage II of interaction					n (number of monomers)
	temp. of endothermic minima, °C	temp. of electric conductivity, °C	Weight loss	temp. of endothermic minima, °C	temp. of electric conductivity, °C	Weight loss found %	Weight loss found mole H_2O%	Weight loss calculated %	
H_3BO_3 + adonitol	40—110	80—110—140	practically none	110—190—250	no	22.98	2.75	23.10	4
H_3BO_3 + xylitol	40—115	60—110—140	practically none	110—150—275	no	22.90	2.75	23.10	4
H_3BO_3 + L-arabitol	40— 65—110	60—110—160	practically none	110—140—250	no	25.35	3	25.20	great
H_3BO_3 + dulcitol	90—110	90—100—110	practically none	110—125—255	no	21.59	2.875	21.6	8
H_3BO_3 + D-sorbitol (anhydrous)	60—100	—	practically none	100—110—230	no	22.20	3	22.15	great
H_3BO_3 + D-mannitol	60—100—110	60—100—130	practically none	110—130—230	no	21.56	2.875	21.6	8

* Heating rate 10°/min, reference substance Al_2O_3, sample 100—200 mg in small platinum crucible, the temperature is measured in the sample.

Table 2

Weight loss (230—250 °C) in the interaction of boric acid with polyols

Molar ratio	H_3BO_3-D-mannitol		H_3BO_3-dulcitol		H_3BO_3-D-sorbitol		H_3BO_3-L-arabitol		H_3BO_3-adonitol		H_3BO_3-xylitol	
	Found %	Calculated*** %	Found %	Calculated*** %	Found %	Calculated,* %	Found %	Calculated,* %	Found %	Calculated,** %	Found %	Calculated,** %
1 : 1	21.56	21.6	21.59	21.6	22.20	22.15	25.26	25.20	22.92	23.10	22.9	23.10
1 : 2	12.0	12.12	12.25	12.12	13.25	12.68	14.86	14.74	13.53	13.20	12.9	13.20
1 : 4	6.25	6.56	6.13	6.56	—	6.84	7.80	8.07	6.64	7.17	6.47	7.17

* Calculated from Eq. 3.
** Calculated for the case where tetramer is formed
*** Calculated for the case where octamer is formed

(detected by IR). If the amount of polyol is greater than that corresponding to equimolar, an excess of polyol is always found in the reaction products (detected by X-ray analysis and via the thermal curves). (see Fig. 2). If the amount of boric

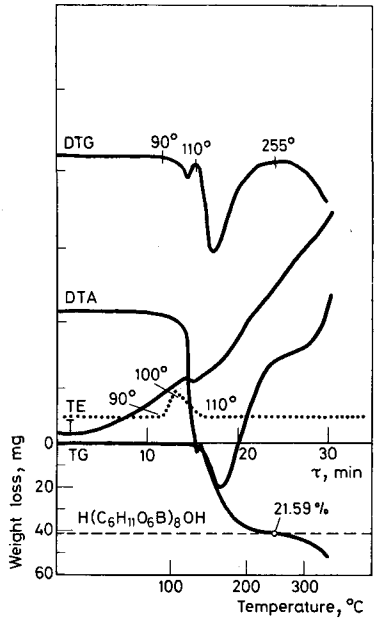

Fig. 4. DTA, TG, DTG and TE curves of a 1 : 1 mixture of H_3BO_3 and dulcitol 1 : 1

acid is greater than equimolar, a more complicated interaction takes place, resulting in the formation of esters which contain two boron atoms per mole of polyol.

References

1. E. M. SCHWARTZ, V. V. GRUNDSTEIN and A. F. IEVINS, J. Thermal. Anal., 4 (1972) 331.
2. V. V. GRUNDSTEIN, E. M. SCHWARTZ and A. F. IEVINS, Izv. AN Latv. SSR., Ser. Khim., (1973) 267.

RÉSUMÉ — On montre qu'il est possible de détecter le sens de la réaction de l'acide borique avec les polyols ainsi que les étapes intermédiaires à partir des données obtenues à l'aide d'un "Derivatograph". On donne une équation qui permet de calculer à partir des pertes de poids le nombre moyen de monomères dans les polymères avec H et OH comme groupes terminaux. L'interaction de l'acide borique avec les hexitols et pentitols donne des esters polymères. On trouve que la formation du complexe polyol-acide borique constitue l'étape intermédiaire de toutes les interactions.

ZUSAMMENFASSUNG — Es wird gezeigt wie mit Hilfe eines Derivatographen die Richtung der Reaktion von Borsäure mit Polyolen sowie die Zwischenstufen bestimmt werden können. Eine Gleichung zur Bestimmung der durchschnittlichen Monomerenzahl in Polymeren mit H- und OH-Endgruppen aus Gewichtsverlust-Daten wird gegeben. Bei der Reaktion von Borsäure mit Hexitolen oder Pentitolen werden polymere Ester gebildet. Es wurde gefunden, daß die Bildung von komplexer Polyolborsäure die Zwischenstufe jeder Reaktion ist.

Резюме —Показана возможность определения направления реакции и ее промежуточных стадий в системах борная кислота-полиол из дериватографических данных. Предложена формула для приблизительного подсчета числа мономеров в полимерах, конечными группами которых являются H и OH. Показано, что при взаимодействии борной кислоты с гекситами и пентитами образуются полимерные эфиры, но промежуточный этап каждого взаимодействия составляет образование комплексных полиолборных кислот.