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STUDIES ON BORATE ESTERS II *

STRUCTURE AND STABILITY OF BORATE ESTERS OF POLYHYDROXYCARBOXYLATES AND RELATED POLYOLS IN AQUEOUS ALKALINE MEDIA AS STUDIED BY ^{11}B NMR

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ABSTRACT - ^{11}B NMR data are presented for borate esters of a series of polyols and polyhydroxycarboxylates in aqueous alkaline solution. For each compound the prevailing borate mono- and diesters were identified. ^{11}B chemical shifts and line widths together with the corresponding association constants have been determined. Empirical rules are put forward for predicting the ^{11}B chemical shift, the relative stability and the structure of borate esters in aqueous media.

INTRODUCTION

Borate esters of polyhydroxy compounds and their potential for separation and protection are being explored for a long time. In this laboratory Böeseken and coworkers studied the stability of esters of boric acid and borate using conductometry and polarimetry from 1910 to 1940.[1] The results served as a tool in the configurational analysis of carbohydrates. More recently, Makkee[2] has utilized borate to enhance the selectivity of the hydrogenation of fructose towards mannitol. Further interest in borate esters is derived from our complexation studies of calcium(II) and lanthanide(III) cations with polyoxygen ligands[3,4] together with the fact that mixtures of borate and gluconic acid or glucaric acid in aqueous alkaline solution are disclosed in the patent literature[5,6] as triphosphate substitutes in detergent formulations.

In order to understand the calcium sequestering ability of borate esters of sugar acids first their structures have to be determined and the factors governing their relative stability should be understood. Then in a next stage the effect of cation addition to the borate polyol system should be investigated. In the present paper the usefulness of ^{11}B NMR as an experimental technique for the analysis of borate esters of sugar acids and related polyols will be demonstrated. Some general rules for both the assignment of ^{11}B resonances and the estimation of the relative stability of borate esters will be put forward and discussed. The influences of the vicinity (α,β or α,γ), the configuration (threo or erythro and syn or anti), and the number of hydroxyl groups (2-5) as well as the presence of substituents have been studied.

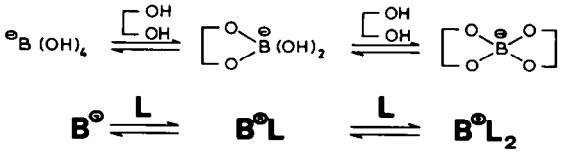

Fig. 1. Equilibria between borate (B^-) and a diol function (L) at pH > 10.

* For part I see reference 7.

In this study we confine ourselves to the high pH area (pH = 11.0) where borate and borate esters of aliphatic diol functions occur predominantly (Fig. 1) and the concentrations of boric acid, boric acid esters and borate esters of α-hydroxycarboxylic acid functions are negligible.[7] In addition, it should be noted that the line width of the borate signal at -17.6 ppm is small (10 Hz) and therefore no interference occurs with most of the other signals of borate esters.

RESULTS AND DISCUSSION

General

The exchange rate between borate, its monoesters and diesters at room temperature is slow on the ^{11}B NMR time scale. This enabled the determination of the chemical shifts, line widths and intensities of the signals of the various borate esters (Table 1) for a series of sugar acids and related polyols (Fig. 2). The assignment of the signals will be discussed in the next section.

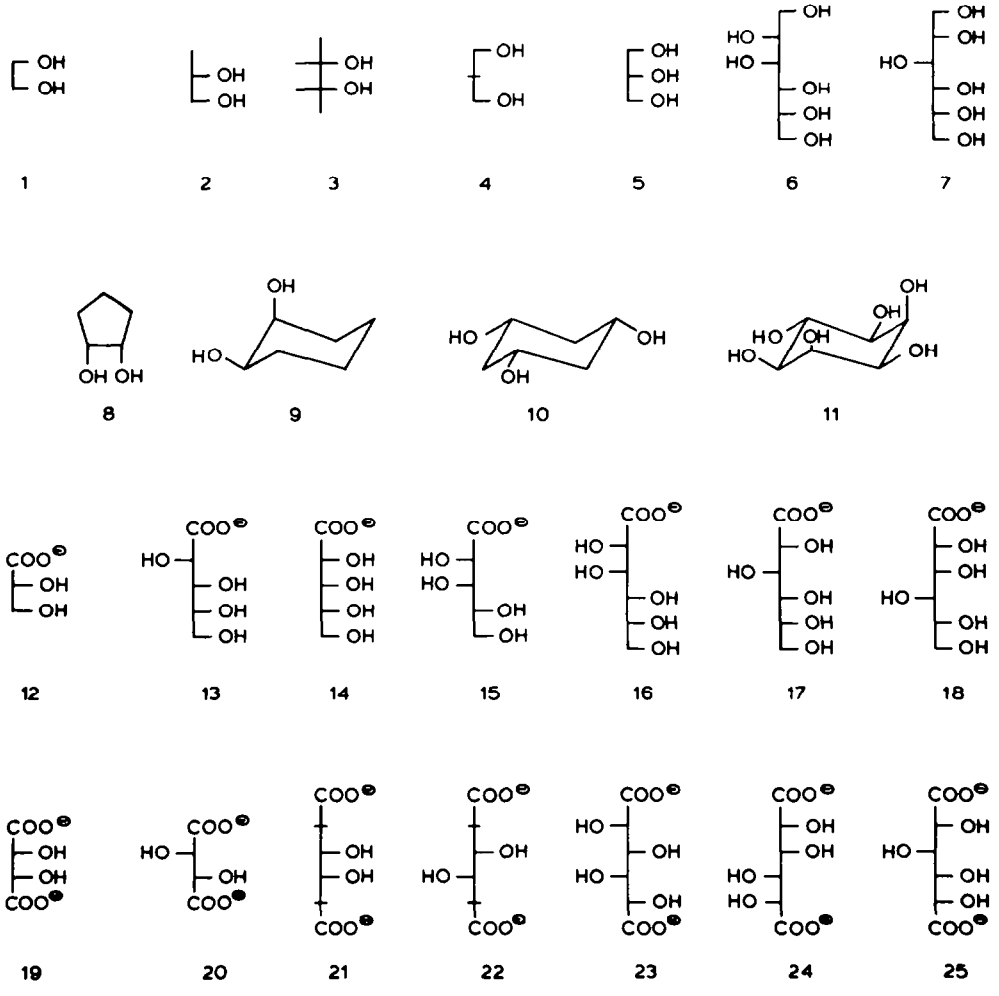

Fig. 2. Structures of polyols and polyhydroxycarboxylates.

Table 1. ^{11}B chemical shifts, line widths and association constants for borate esters (25 °C; D_2O, pD = 11).

		ester type	chemical shift[a] (ppm)		line width (Hz)		association constant (1/mole)	
			B^-L	B^-L_2	B^-L	B^-L_2	B^-L	B^-L_2
1	glycol[8,b]	1,2	-13.9	-10.1	13	16	1.0	0.1
2	1,2-propanediol[8,b]	1,2	-14.0	-10.2	12	26	1.8	1.5
3	pinacol[8,b]	2,3	-14.8	-11.9	14	45	3.5	8.5
4	1,3-propanediol[8,b]	1,3	-18.3	-18.9	9	—	1.2	0.05
5	glycerol	1,2	-13.6	-9.6	18	30	25	3.0
		1,3	-18.5	-19.0	9	—	3.7	0.05
		1,2 + 1,3		-14.2		16		0.18[c]
6	mannitol[9]	erythro-2,3	-14.7					
		threo-3,4	-13.7	-9.6				
7	glucitol[9]	threo	-13.6	-9.5				
		erythro-4,5	-14.6					
8	cis-1,2-cyclo-pentanediol[9]	1,2	-13.6	-9.4				
9	cis-1,2-cyclo-hexanediol[9]	1,2	-14.2	-10.7				
10	all-cis-cyclohexane-1,3,5-triol	1,3,5	-18.1		13		14	
11	epi-inositol	1,3,5	-19.4		—		10000	
12	glycerate	2,3	-13.1	-8.7	23	—	6.2	0.62
13	arabinonate	threo-2,3	-13.2	-9.3	26	78	44	13
		erythro-3,4	-14.2		38		10	
		4,5	-13.5		24		18	
		2,4/3,5	-18.1		16		0.31	
14	ribonate	erythro-2,3	-13.8	-9.9	29	95	13	4.3
		eryhtro-3,4	-14.4		49		6.6	
		4,5	-13.3	-9.3	41	47	10	0.98
		2,4	-18.0		19		14	
15	lyxonate	erythro-2,3	-14.9		—		6.9	
		threo-3,4	-13.6	-9.7	20	58	230	27
		2,4/3,5	-18.2		11		5.1	
16	mannonate	threo-3,4	-13.4	-9.2	42	111	1200	48
		erythro-4,5	-14.5		35		140	
		2,4/3,5/4,6	-18.3		34		54	
17	gluconate	threo	-13.4	-9.4	35	85	240	31
		erythro-4,5	-14.2		36		72	
		2,4	-18.2		21		19	
18	gulonate	erythro-2,3	-14.6		30		65	
		threo	-13.5	-9.5	39	81	540	79
		3,5	-18.2		21		17	
19	meso-tartrate	erythro-2,3	-13.0	-8.7	55	120	2.2	0.36
20	(S,S)-tartrate	threo-2,3	-12.6	-7.7	58	160	11	17
21	meso-3,4-dihydroxy-adipate	erythro-3,4	-13.9	-10.4	31	74	3.3	0.42
22	rac. 3,4-dihydroxy-adipate	threo-3,4	-13.8	-10.1	27	87	15	3.2

Table 1 - continued

23 idarate	threo	-13.2	-9.1	57	120	120	20
	2,4	-18.0	-18.4	10	18	—	--
24 galactarate	threo-2,3	-13.3	-9.1	32	93	260	7.7
	erythro-3,4	-14.4		26		42	
25 glucarate	threo	-13.2	-9.0	59	168	180	31
	erythro-4,5	-14.0		--		20	
	2,4	-17.9		—		11	

[a] Relative to 0.1 M boric acid as external reference.

[b] Corrected for $\delta_{B^-} = -17.1$ ppm.

[c] $K_2 = [B^-(L_{1,2})(L_{1,3})]/[B^-(L_{1,2})] * [L]$.

The association constants for the borate mono- and diesters, defined as

$$K^{B^-}_{B^-L} = [B^-L]/[B^-] * [L] = K_1 \qquad (I)$$

$$K^{B^-L}_{B^-L_2} = [B^-L_2]/[B^-L] * [L] = K_2 \qquad (II)$$

are mean values (Table 1) determined over a range of total borate (C_B = 0-0.15 M) and polyol concentrations (C_L = 0-1 M). They were calculated using equations (I) and (II) together with the material balance equations for borate and the polyol.

$$C_B = [B^-] + \Sigma [B^-L] + \Sigma [B^-L_2] \qquad (III)$$

$$C_L = [L] + \Sigma [B^-L] + 2 * \Sigma [B^-L_2] \qquad (IV)$$

Chemical shifts

The chemical shifts of the borate esters of the diols 1-4, 8, 9, 12, and 19-22 can be assigned in a straightforward fashion since these compounds can bind borate just in a single way. The ^1H NMR spectrum of the borate ester of all-cis-cyclohexane-1,3,5-triol (10) unambiguously shows that this compound forms a tridentate borate ester, which is in agreement with the results observed for epi-inositol (11).[10] In both cases borate diesters could not be detected. On the basis of the assignments of the borate esters of these 13 compounds some general rules were derived which served for the further assignment of the other borate esters in Table 1. Firstly, borate esters can be divided into groups with a characteristic range of chemical shifts, depending upon the type of ester involved (Table 2) as was noted before by Henderson et al.[8] and by us.[7] The substantial difference in chemical shifts between borate esters of α,β- and α,γ-diols should be traced back to differences in the geometry of the borate ester ring (Fig. 3).

Table 2. Characteristic chemical shift ranges for various types of borate esters.

ester type	δ_{B^-L} (ppm)	$\delta_{B^-L_2}$ (ppm)
α,β-bidentate	-12.6 to -14.9	-7.7 to -11.9
α,γ-bidentate	-17.9 to -18.5	-18.4 to -19.0
α,γ,ε-tridentate	-18.1 to -19.4	

ϕ	104° (± 2)	110° (± 3)
B–O	1.47 Å (± 0.05)	1.50 Å (± 0.05)
ring geometry	half chair/envelope	chair

Fig. 3. Mean O–B–O valence angles and B–O bond distances for borate esters of α,β- and α,γ-diols (standard deviations between brackets)[11].

Secondly it may be noted that for α,β-diols the difference in ^{11}B chemical shift between the borate monoester and borate (Δ_1) roughly equals that between the borate diester and the monoester (Δ_2), as shown in Fig. 4.

$$\Delta_1 \approx \Delta_2 \qquad \text{(V)}$$

$$\Delta_1 = \delta_{B^-L} - \delta_{B^-} \qquad \text{(VI)}$$

$$\Delta_2 = \delta_{B^-L_2} - \delta_{B^-L} \qquad \text{(VII)}$$

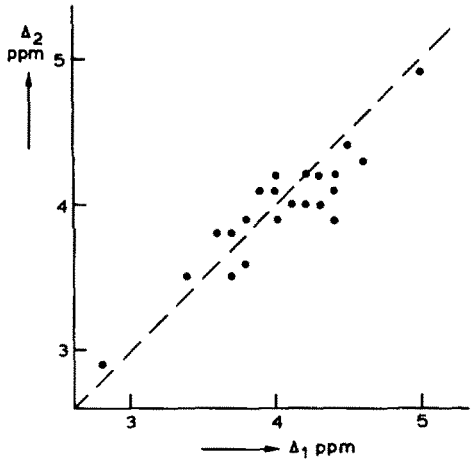

Fig. 4. Δ_2 as a function of Δ_1 for α,β-diol type borate esters.

Equation (V) does not hold for borate esters of α-hydroxycarboxylic acids[7] which is probably due to resonance effects. Although for borate esters of α,γ-diols only a few experimental data are available and Δ_1 and Δ_2 are small, equation V seems to be applicable here too.

Thirdly, borate esters of threo-diols have chemical shifts which are more downfield than those of erythro diols (cf. compounds 19–22). With the aid of these three general rules ^{11}B NMR signals of the borate esters of 5–7, 15–18, and 23–25 were assigned. A comparison of the chemical shifts enabled us to determine characteristic shift ranges for borate esters of threo-, erythro- and terminal α,β-diols. In this way the signals of the borate esters of arabinonate (13) and ribonate (14) were fully assigned.

The regularities observed in the ^{11}B chemical shifts of borate esters of α,β-diols ($\delta_{B^-L_n}$) can be summarized by the following empirical equation:

$$\delta_{B^-L_n} = \delta_{B^-} + n * (\Delta + i) \qquad \text{(VIII)}$$

in which δ_{B^-} is the chemical shift of borate (δ_{B^-} = -17.6 ppm), n the number of diols bound by the borate anion (n = 1 or 2), Δ the shift induced by one bound glycol molecule (Δ = 3.7 ppm) and i an increment depending upon substituents on the glycol moiety and their configuration. The use of equation (VIII) and the increments i given in Table 3 allows the prediction of ^{11}B chemical shifts of α,β-diol borate esters with an accuracy of ± 0.2 ppm (± 0.6 ppm for borate esters of erythro-α,β-dihydroxycarboxylic acids). This additivity is also valid for mixed borate diesters such as B^-(1,2-glycerol)(1,3-glycerol) and B^-(glycol)(1,3-propanediol).[10] Mixed borate diester formation is also plausible for ribonate (14) because of the rather broad borate diester signal as shown in Fig. 5.

Table 3. Configuration and substituent increments in ppm (equation VIII).

Configuration		Substituents				
X-CHOH-CHOH-Y	X/Y =	CH_2/CH_2	CHOH/CHOH	COO^-/COO^-	$CHOH/COO^-$	CHOH/CHOH and $CHOH/COO^-$
threo		0.1	0.3	1.3	0.5	0.5
erythro		-0.1	-0.6	0.8	-0.2	—
X-CHOH-CH_2OH	X =	CH_2	CHOH	COO^-		
		0.0	0.4	0.8		

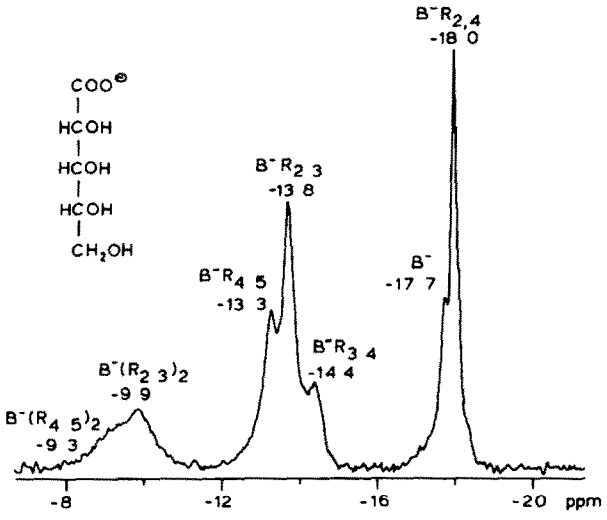

Fig. 5. 64.19 MHz ^{11}B NMR spectrum of ribonate (R, 0.2 M) and borate (0.1 M) in D_2O (pD = 11.0) at 25 °C.

In this respect it has to be noted that borate esters of threo-α,β-diols are more stable than those of erythro-α,β-diols.[12-15] The same holds for borate esters of syn-α,γ-diols in comparison with those of anti-α,γ-diols.[15] The relative intensities of the various ^{11}B signals gave a further confirmation of the assignments made. Since ^{11}B NMR is not adequate to distinguish between the borate esters of different threo diol functions in a given polyol, complete assignment requires additional techniques such as ^1H and ^{13}C NMR.[16]

Although more research is necessary for the further refinement of equation (VIII), Fig. 5 once again demonstrates the versatility of ^{11}B NMR as a tool for the structural analysis of borate esters.

Line widths

The line width of the ^{11}B signal is dominated by the quadrupolar relaxation.[17] The quadrupolar relaxation rate in the case of rapid tumbling can be approximated by

$$1/T_2 = \frac{3(2I+3)}{40I^2(2I-1)} (2\pi e^2 qQ/h)^2 (1+\eta^{2/3}) \frac{4\pi r^3 \eta_s}{3kT} \qquad (IX)^{18}$$

in which $2\pi e^2 qQ/h$ is the quadrupole coupling constant, η the field gradient asymmetry, η_s the solution viscosity and in which the molecule under study is regarded as a rigid sphere with radius r. The other symbols have their usual meaning.

Borate itself gives rise to a sharp line (10 Hz), as should be expected since this ion possesses a strictly regular tetrahedral structure and, therefore, a near zero field gradient. The line widths of borate esters are larger, viz. 10–170 Hz (Table 1) and are independent of C_B and C_L, i.e. the influence of exchange between free borate and its mono- and diesters is negligible. One exception is observed, viz. epi-inositol (11). The line widths of the borate monoesters of the α,β-diol type vary between 10 and 60 Hz and those of the α,γ-diol type between 10 and 30 Hz. The line widths of the borate diesters vary between 20 and 170 Hz. An increase of line width with a factor of about 1.5 should be expected as a result of the increase of the molecular radius. Overlap of signals of parent borate diesters is caused by signals of mixed borate diesters (Fig. 5). The temperature dependence of the line widths was demonstrated for a sample with C_B = 0 1 and C_L = 0.2 (L = galactarate, 24). Two signals were observed, viz. the borate mono- and diester of the threo-2,3-diol function. Increasing the temperature from 20 to 95 °C results in a decrease in the line widths from 28 to 17 Hz and from 90 to 30 Hz, respectively.

Association constants

The effects which determine the stability of the various borate esters will be discussed in the order of decreasing importance. Tridentate borate esters are known to exist[10,19] but require polyols with specific configurations. All-cis-cyclohexane-1,3,5-triol (10) forms a tridentate ester with a relatively low association constant compared with epi-inositol (11). This phenomenon can be understood by redefining K_1 as

$$K_1 = \frac{[\bar{B}L]}{[\bar{B}] * [L]} = \frac{[L']}{[L]} * \frac{[\bar{B}L]}{[\bar{B}] * [L']} = K^L_{L'} * K_{1'} \qquad (X)$$

all-cis-1 3 5-trihydroxycyclohexane epi-inositol

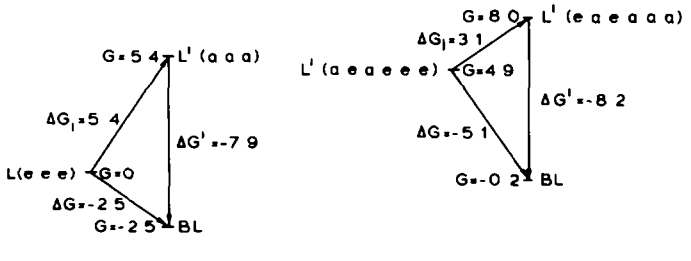

Fig. 6. Free energy diagrams for tridentate borate ester formation of all-cis-1,3,5-trihydroxycyclohexane (10) and epi-inositol (11) (kcal/mole).

in which L' is the ring-inversed form of L. Using the data of Angyal et al.[19] for the calculation of ΔG and ΔG' (Fig. 6), $K_{1'}$ appears to be nearly constant and thus K_1 depends solely on $K^L_{L'}$, the equilibrium constant for the cyclohexane ring inversion. The calculated difference in ΔG of −2.6 kcal/mole between epi-inositol and all-cis-1,3,5-trihydroxycyclohexane is close to the experimental value of −3.8 kcal/mole.

Although there has been some dispute concerning the relative stability of borate esters of glycol (1) and 1,3-propanediol[20] (4) it is now well established that these esters are about equally stable.[8] One of the causes of the dispute has been the fact that both substituted compounds and configurational isomers were used in the comparison, which may change the picture dramatically. As monodentate borate esters are unstable in aqueous media (log $K_1 < 0$), chelating effects seem to be a major factor determining cyclic borate ester stability.

The stability of α,β-bidentate type of esters of the aldonates and aldarates is enhanced upon increasing the number of hydroxyl groups (n_{OH}). To a lesser extent the same holds for borate esters of the α,γ-type. It may be noted that for $n_{OH} > 2$ borate esters of α,β-diols generally are more stable than those of α,γ-diols. Choosing the adequate experimental conditions ($C_B > C_L$) we have ascertained that no esters were formed with 2 borate anions bound to the sugar acids ($(B^-)_2L$). Although such esters exist for mannitol[9,21,22] the presence of the carboxylate groups in combination with the smaller n_{OH} hinders the formation of $(B^-)_2L$ esters of sugar acids.

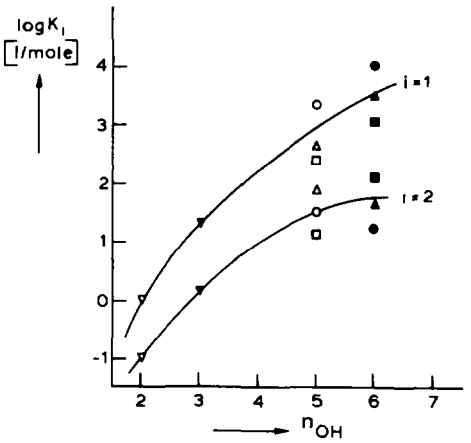

Fig. 7. log K_1 as a function of n_{OH} for borate ester formation of alditols (▽ glycol, ▼ glycerol, ○ xylitol, ▲ arabinitol, □ adonitol, ● sorbitol, ▲ galactitol, ■ mannitol).

For the alditol series with n_{OH} varying from 2 to 6 the overall association constants (glycol,[8] glycerol,[23] ribitol,[14] xylitol,[14] arabinitol,[14] mannitol,[13] glucitol[14] and galactitol[14]) increase upon increasing n_{OH} (Fig. 7). Statistically the number of possibilities for a borate anion to bind an alditol as an α,β-diol increases with n_{OH}. In glycol there is just one mode, in glycerol two, etc. Introducing the statistical effect in the entropy term of the Gibbs' equation[24] the increase in stability going from glycol to glycerol would only be log $\frac{2}{1}$ = 0.3 log K unit. Because this statistical effect is too small to explain the observed increase in log K an extra effect upon borate ester dissociation, the stepwise hydrolysis of the 2 B-O ester bonds,[7] might be operative a chelation-migration effect. After hydrolysis of the first B-O bond, formation of another B-O bond, resulting in a new borate ester, competes with total hydrolysis. The escape difficulties of a borate anion upon hydrolysis might be translated into a stabilizing factor. It possibly also explains the difference in borate ester stability between α,β- and α,γ-diols when $n_{OH} > 2$. As suggested by Pâal[25] intramolecular hydrogen bonding might be an additional stabilizing factor for borate esters of polyols. In the case of borate diesters steric constraints will hinder the formation of these intramolecular hydrogen bridges. The effects discussed above, together with a small substituent effect are responsible for the influence of n_{OH} upon borate ester stability.

Statistical and steric considerations will be used to explain the observed increase in Δ log K as a function of n_{OH}

$$\Delta \log K = \log K_1 - \log K_2 \qquad \text{(XI)}$$

Twelve possibilities exist for binding a diol by a borate anion but only two for binding a diol by a borate monoester. For glycol Δ log K = 1.0, close to the predicted value of log $\frac{12}{2}$ = 0.8. With increasing n_{OH}, Δ log K increases which might be due to the relatively large enhancement of steric hindrance in the borate diesters.

The configuration of the α,β-diol (threo-erythro) and α,γ-diol (syn-anti) moiety is also of importance. The diastereomeric tartrates (19, 20) and 3,4-dihydroxyadipates (21, 22) clearly show that threo-α,β-diols form more stable borate monoesters than erythro-α,β-diols. This is in agreement with results for borate esters of (S,S)- and meso-2,3-butanediols,[13] of ribitol, arabinitol and xylitol,[12,14] of galactitol,[14] glucitol[14] and mannitol[13] and of 1,6-dideoxy-1,6-dibromogalactitol and -mannitol.[20] In addition syn-α,γ-diols are known to form more stable borate esters than anti-α,γ-diols.[15]

These differences in stability are mainly caused by differences in steric interaction between the substituents R and R' in both the free diol and in the borate ester (Fig. 8), which are estimated to be 1 and 2.5 kcal/mole for the borate esters of the diastereomeric α,β- and α,γ-diols, respectively. Thus $K_{threo}/K_{erythro} \approx 6.5$. This value agrees with experimental ratios varying from 3.4 to 14. Although the reaction enthalpy for the borate ester formation of terminal diols probably is somewhat smaller than that of threo diols, loss of entropy will be more substantial and therefore $K_{threo} > K_{terminal} > K_{erythro}$ as is demonstrated for arabinonate (13) and ribonate (14).

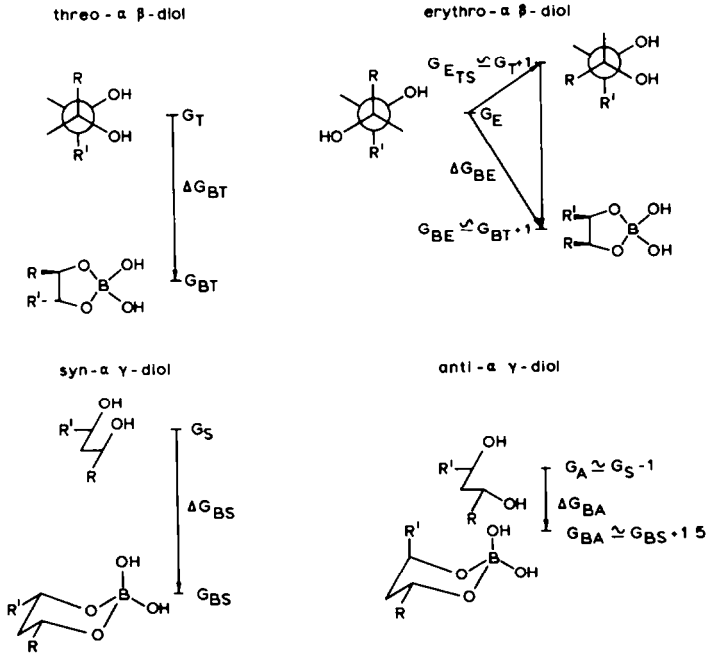

Fig. 8. Free energy diagrams for borate ester formation of threo- and erythro-α,β-diols and of syn- and anti-α,γ-diols (kcal/mole).

Introduction of alkyl substituents increases the stability of the borate esters as appears from the association constants for glycol (1), 1,2-propanediol (2) and pinacol (3). This is not only caused by inductive effects, as was suggested by Pšal,[25] because similar stabilities are observed for glycerate, 3-methoxy-1,2-propanediol[26] and 3-chloro-1,2-propanediol.[20] Furthermore the decrease of reaction enthalpy in the series glycol, 1,2-propanediol, 2,3-butanediol, 2-methyl-2,3-butanediol and pinacol does not parallel log K_1 because of entropy effects.[13] So the variation of K_1 (2-20) and K_2 (0.5-2.5) for substituted glycols will be due to both inductive and steric effects. We have started a series of valence force field calculations for

both free diols and the corresponding borate monoesters using Allinger's MM2 force field to quantify the substituent effects as well as some of the other effects dealt with in this paper.[29]

A special substituent effect that plays a secondary role in the overall picture is observed upon introduction of negatively charged carboxylate groups. Generally a decrease of the stability of a borate ester is observed as a result of electronic repulsion between the negatively charged COO and BO_4 moieties. Thus, the stabilities of the borate esters of the threo-α,β type of arabinonate (13) and gluconate (17) are lower than those of lyxonate (15) and gulonate (18), respectively, because of smaller distances between the charged groups. The same holds for borate esters of the tartrates compared with those of the 2,3-butanediols (K_1 = 37 and 2.7 and K_2 = 4.4 and 1.7,[13] respectively). Exceptions are the borate esters of erythro-2,3- and erythro-3,4-ribonate (14). This again asks for extensive force field calculations.

The effect of temperature on the stability of borate esters was studied for the formation of the borate diester of galactarate (24): ΔH_2 = -3 kcal/mole and ΔS_2 = -6 kcal/mole.K were obtained. These values are in the same region as those reported by Conner and Bulgrin[13] for other diols and result in lower borate ester stability with increasing temperature which is in agreement with early results of Coops.[30]

CONCLUSIONS

^{11}B NMR enables the distinction and direct identification of a variety of borate esters and simultaneously the determination of the corresponding association constants. This technique, therefore, has definite advantages over the commonly used techniques such as potentiometry and polarimetry. The present results together with data from the literature allow the formulation of empirical rules as is shown in Tables 2 and 3 and equation (VIII) for the ^{11}B chemical shifts of borate esters. With respect to the relative stabilities of borate esters these can be summarized as follows.

tridentate > bidentate > monodentate

increase n_{OH} ⟶ more stable

threo > terminal > erythro-α,β-diol

syn > anti-α,γ-diol

Coulomb repulsion ⟶ less stable

$\log K_1 - \log K_2 > 0{,}8$

These general rules will be helpful in the study of the interaction of borate with polyhydroxy compounds. It allowed us, for instance, to tackle some of the problems when dealing with the calcium(II) sequestering abilities of borate-polyhydroxycarboxylate mixtures.[16]

EXPERIMENTAL

All ^{11}B NMR spectra were recorded at room temperature on a Nicolet NT-200 WB spectrometer at 64.19 MHz using a 12 mm sample tube and a 0.1 M boric acid solution as external reference. Base line correction was applied to suppress the broad signal of the boron incorporated in the glass sample tube and in the insert. Sometimes it was necessary to use a deconvolution program to obtain all the signal characteristics. C_B and C_L were varied from 0 to 0.15 M and from 0 to 1.0 M, respectively. Measurements were performed with D_2O as solvent at pD = 11.0. The total volume of each sample was 5 ml. Potassium lyxonate (15) and racemic and meso-3,4-dihydroxyadipic acid (21, 22) were synthesized according to Moore and Link,[31] Posternak and Susz,[32] and Linstead et al.,[33] respectively. Iditol, obtained by the reduction of sorbose[34] followed by removal of glucitol with pyridine[35] was converted into idaric acid (23) using the procedure for the preparation of mannaric acid.[33]

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