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Gas chromatography of homologous esters

XXXIV.[a] Alkyl borate and boronate esters

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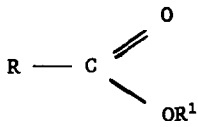
ABSTRACT

The preparation and gas chromatographic behaviour of simple alkyl borate and boronate esters is reported. Difficulties with the gas chromatography of some of these esters, the rearrangements that occur with the boronate esters and the formation of cyclic and acyclic boronates were investigated. The effect of the alkyl substituent on retention when adjacent to a boron or oxygen atom has been considered and the effects are discussed in relation to the behaviour of other ester series.

INTRODUCTION

The retention behaviour of a considerable number of series of homologous esters, including *n*-alkyl [1,2] and *n*-alkenyl [3,4] straight- and branched-chain aliphatic esters [5], keto esters [6], chlorinated aliphatic esters [7,8], aromatic [9], cycloalkyl [9] and phosphorus esters [10] has been studied previously.

The influence of the polar nature of the stationary phase on retention, the effect of the position of a substituent group, either an alkyl group, unsaturation or a chlorine atom, on retention, the increasing contribution with increasing phase polarity of carbonyl and phenyl groups on retention and the relative influence of a substituent when in the alkyl or alcohol chain (R^1) or the acyl or acid chain (R^1) according to the following convention have been reported:



All of the series studied showed the expected increase in retention with increasing phase polarity, while the effect of a structural parameter, *e.g.*, a methylene group, an

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unsaturated linkage, an aromatic ring or chlorine atom, has been shown to exhibit a greater effect on retention when in the alkyl rather than the acyl chain, with the exception of the phosphorus esters, where the reverse effect was evident. The conclusions that have been reached [1–9] have largely been corroborated by subsequent reports using the same esters by other workers [11,12].

With phosphate esters the three substituent groups were equivalent, but the phosphinate esters are comparable to the carbonyl esters with substituents adjacent to both an oxygen atom and the parent atom. The effect with the phosphinate esters was explained on the basis that there are two OR^1 chains, and hence the inductive effect of the P=O group is split between the two and is thus reduced in magnitude. The polarity of the phosphoryl group is lower than that of the carbonyl group owing to the effects of the d electrons in the phosphorus, which tend to neutralize the electron-withdrawing effects of the O atom. The possibility of a similarity with borate and boronate esters was suggested.

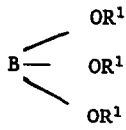
The gas chromatography (GC) of borate esters has received little attention and no publications restricted to the GC of the esters seem to have appeared. The sole work employing GC–mass spectrometry (MS) is apparently that of Wada *et al.* [13], which considered triisopropyl borate. The electron impact (EI) mass spectrum of trimethyl borate was reported in 1956 [14]. Subsequently, EI mass spectra of trimethyl borate and higher trialkyl borates were reported [15–18]. Mass spectrometry has also been used to show that exchange reactions occur between mixtures of trialkyl borates [19,20]. The simple alkyl boronates have similarly attracted little attention. However, several of the acids have been extensively studied in the formation of derivatives for the identification of multifunctional compounds [21].

This paper reports the preparation and GC behaviour of simple alkyl borate and boronate esters. Difficulties with the GC of the borate and acylic boronate esters were investigated, and the effect on retention of the position of the alkyl substituent in the alkyl or acyl chain is discussed in relation to the behaviour of the other ester series reported previously.

Earlier studies of many types of homologous esters [1–10] have been reported and this work allows a study of a wider range of esters to be made using conditions relatively comparable to those in the earlier work.

Borate esters

The borate esters



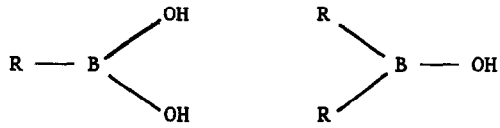
were prepared using a borane–methyl sulphide complex and alkanol under anhydrous conditions:

$$3R^1OH + BH_3S(CH_3)_2 \rightarrow B(OR^1)_3 + S(CH_3)_2 + 3H_2 \quad (1)$$

This minimizes the presence of water and reduces the susceptibility to hydrolysis.

Boronic acid esters

Two types of organoboron acids are formed: the boronic acids (I) and the borinic acids (II) with the following formulae shown below:

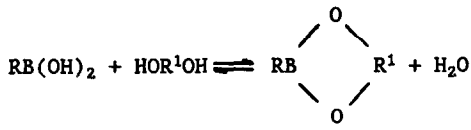


(I) (II)

The borinic acids have not been shown to have any analytical application, although the boronic acids have been extensively used for the formation of derivatives of bifunctional compounds since their introduction by Brooks and Watson [21] in 1967.

Two series of esters of alkyl boronic acid may be prepared by simple esterification. With monofunctional alcohols the acyclic dialkyl boronates are formed, whereas with bifunctional alcohols the cyclic alkyl boronates are formed:

(2a)



(2b)

The dialkyl boronates are of low hydrolytic stability and not usually stable to GC. The cyclic alkyl boronates have good GC properties.

The cyclic *n*-butane [21–23] and methane [24–28] boronates were first used, and subsequently also benzeneboronic acid [29–36], cyclohexaneboronic acid [23,24,26–28], *tert.*-butylboronic acid [27] and *n*-octaneboronic acid. Acylic boronates frequently occur with bifunctional compounds with isolated amino or hydroxy groups. The presence of such species has been attributed to the poor GC behaviour of some carbohydrates [27].

Cyclic boronates containing halogens [37–40] have been introduced to allow electron-capture detection. The use of boronates for derivatization and their mass spectra have been extensively reviewed [41,42].

EXPERIMENTAL

Alkyl borate esters

The esters were prepared [43] from the borane–methyl sulphide complex (10 *M*) (Aldrich, Milwaukee, WI, USA). All reactions were carried out in a dry nitrogen atmosphere, using glassware dried in an oven at 150°C. A special experimental technique was used in handling the air- and moisture-sensitive $BH_3 \cdot S(CH_3)_2$.

A dry 500-ml flask equipped with an injection port, PTFE-covered magnetic stirring bar, pressure-equallized dropping funnel and a reflux condenser connected to

an oil bubbler was purged with nitrogen. Then 7.5 ml of $BH_3 \cdot S(CH_3)_2$ were injected into the flask with a syringe through a rubber septum. While stirring and cooling in a water-bath, the alcohol was added dropwise at 25°C. Quantitative amounts of the alkyl borate esters in dimethyl sulphide were formed. The borate esters were stored under dry nitrogen, as they are extremely sensitive to moisture.

Boronic acid

The boronic acids were prepared by the hydroboronation reaction [44]:

$$RCH=CH_2 + HBr_2 \cdot S(CH_3)_2 \xrightarrow{CH_2Cl_2} RCH_2CH_2Br_2 \cdot S(CH_3)_2$$

$$\xrightarrow{H_2O} RB(OH)_2 + 2HeBr \qquad (3)$$

The *n*-butylboronic acid was obtained from Alltech (Deerfield, IL, USA) and the alkenes, the dibromoborane–dimethyl sulphide complex $HBBr_2 \cdot S(CH_3)_2$ (1 *M* in dichloromethane) and the alcohols were obtained from Aldrich.

The alkene (100 mmol) dissolved in chloromethane (100 ml) was placed in a 500-ml reaction flask. The 1 *M* $HBBr_2 \cdot S(CH_3)_2$ solution (100 ml; 100 mmol) was added slowly, using a syringe. The mixture was heated (40°C) under reflux and stirred for about 3 h. The alkyldibromoboranedimethyl sulphide formed was cooled to 0°C and transferred to a stirred, cold (0°C) mixture of water (18 ml; 1000 mmol) and diethyl ether (100 ml) through a double-ended needle. The stirring was continued for 10 min, then the water layer was separated and discarded. The organic layer was washed with cold water (2 × 30 ml) and saturated brine (1 × 50 ml) and dried over anhydrous magnesium sulphate. After evaporating the solvent, using a water aspirator, white crystals of the boronic acid were formed [45].

Alkylboronate esters

The dialkyl alkylboronate and the alkyl alkylboronate esters were formed by the esterification of the corresponding alkylboronic acids with the respective alcohols in *n*-pentane.

The alkylboronic acid (0.5 g) was suspended in 10 ml of *n*-pentane in a separating funnel. An equivalent amount of the alkanol was added, and the mixture was shaken for a few seconds. The water formed was separated. Another equivalent of the alkanol was added to the mixture and the water layer formed was separated. The pentane layer was dried with anhydrous magnesium sulphate. While the ester formed and the reacting alcohol are soluble in pentane, water and the boronic acid are not. The esters formed in pentane were stored in air-tight vials with silicone seals.

The cyclic alkylboronate esters were prepared in the same manner as outlined above, except that there was no need to add an excess amount of alkanediol.

Gas chromatography

For GC a Shimadzu GC-8A gas chromatograph fitted with a flame ionization detector and a Shimadzu Chromatopac C-RGA data processor was used. The oven temperature was 110°C and the injection port temperature was 220°C. Helium was

used as the carrier gas at a flow-rate of 30 ml/min. Three stationary phases were used: 5% SE-30 on 80–100-mesh Chromosorb W AW DMCS, 4% OV-17 on 80–100-mesh Chromosorb M AW DMCS and 3% XE-60 on 80–100-mesh Gas-Chrom Q11.

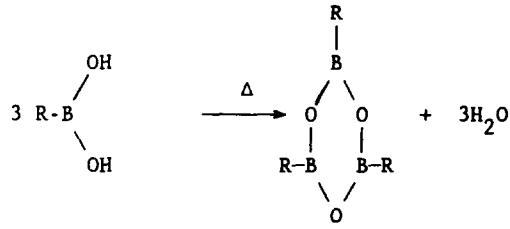
Gas chromatography–mass spectrometry

The gas chromatograph–mass spectrometer used to obtain retention times and chemical ionization mass spectra was a Finnigan 3200 quadropole instrument, interfaced with a TO.2300 Incos computer data system. The ion source was maintained at 110°C by filament emission (100 mA) and the source pressure was 0.8 Torr. Three 1.5 m × 4 mm I.D. glass columns, containing 3% OV-1, OV-17 and OV-225 as stationary phases, were used. The carrier gas was methane at a flow-rate of 20 ml/min. The oven temperature was maintained at 50 and 70°C. In one experiment with a mixture of alkyl borates, temperature programming from 35 at 6°C/min was used. The scan frequency was 1 cycle/s.

RESULTS AND DISCUSSION

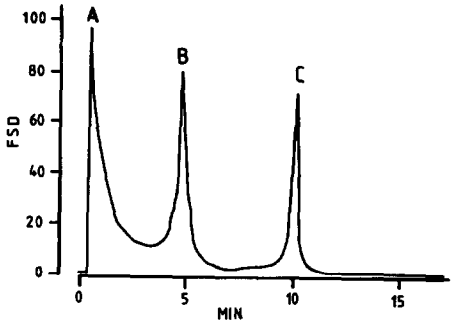
The *n*-alkyl borate esters were not eluted through the gas chromatograph owing to their ease of hydrolysis, evidently assisted by traces of moisture in the carrier gas and no doubt accentuated by their limited thermal stability. This result clearly explains why minimal GC studies of the trialkyl borate esters have been published. The conditions used in the gas chromatograph–mass spectrometer with methane as carrier gas are not usually used for simple GC. However, the esters were eluted through the gas chromatograph–mass spectrometer, the hydrolysis being retarded owing to the use of both ultra-dry methane as the carrier gas and a lower column temperature. The eluted compounds exhibited very broad and unsatisfactory peaks, and the resulting peak areas were not reproducible owing to the varying degree of hydrolysis. Temperature programming when methane was the carrier gas allowed good elution of the alkyl borates. The mass spectra of the esters were readily obtained. However, it was not possible to elute the acyclic alkyl boronates, as they were readily hydrolysed to the corresponding boronic acids, but again with methane as the carrier gas satisfactory peak elution occurred.

At higher temperatures, *i.e.*, 150–200°C, it was shown by mass spectrometry that the boronic acids dehydrated to form boroxines [46]:



(4)

The separation of triethyl, tri-*n*-propyl and tri-*n*-butyl borates on OV-1 with temperature programming from 35°C at 6°C/min is shown in Fig. 1. Figs. 2 and 3 show the separation of the cyclic *n*-alkyl boronates. Fig. 2 shows the alcohol esters (R = C_4–C_7), separated on 3% XE-60, and Fig. 3 the acid esters (R^1 = C_2–C_4) on 3%



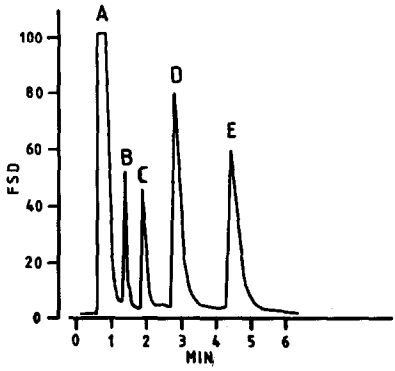


Fig. 1. Chromatogram of separation of (A) triethyl, (B) tri-*n*-propyl and (C) tri-*n*-butyl borates on OV-1 temperature programmed from 35°C at 6°C/min.

Fig. 2. Chromatogram of separation of cyclic *n*-alkyl boronates (alcohol esters, R = C_4–C_7) on XE-60 at 100°C. (A) Solvent; (B) ethyl *n*-butylboronate; (C) ethyl *n*-pentylboronate; (D) ethyl *n*-hexylboronate; (E) ethyl *n*-heptylboronate.

XE-30, with isothermal operation at 110°C in both instances. Tables I–III show retention data for the cyclic and acyclic alkyl boronate esters. Retention index plots for the cyclic alkyl boronates with both the acid (R = C_4–C_7) and alcohol (R^1 = C_2–C_4) chain as the ordinate produced linear plots on all of the stationary phases.

In a study of a sample homologous aliphatic ester series, Ashes and Haken [1] observed linearity for the acid ester series on non-polar, donor and acceptor columns. However, for the alcohol ester series they reported a loss of linearity on the acceptor column and linearity on the non-polar and donor columns. The loss of linearity for the alcohol ester series on the acceptor column was attributed to the transmission of the induced dipole in the acid chain in a geometric progression with the methylene increments, as expressed by the decreasing interaction of the carbonyl group and the

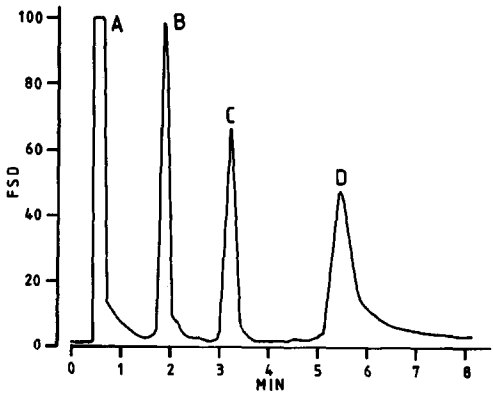


Fig. 3. Chromatogram of separation of cyclic *n*-alkyl boronates (acid esters, R^1 = C_2–C_4) on SE-30 at 110°C. (A) Solvent; (B) ethyl *n*-pentylboronate; (C) *n*-propyl *n*-pentylboronate; (D) *n*-butyl *n*-pentylboronate.

TABLE I

RETENTION DATA FOR CYCLIC *n*-ALKYLBORONATE ESTERS AT 110°C

Conditions: isothermal, 110°C; helium carrier gas at 30 ml/min; 2 m × 1/8 in. I.D. stainless-steel column.

Compound	Mol. wt.	Stationary phase								
		SE-30 (5%)			OV-17 (4%)			XE-60 (3%)		
		t_R[a] (min)	I[a]	ΔI[a] per CH_2	t_R (min)	I	ΔI per CH_2	t_R (min)	I	ΔI per CH_2
Alcohol ester series										
Ethyl *n*-butylboronate	128	1.488	914		1.22	1039		1.233	1131	
Ethyl *n*-pentylboronate	142	2.422	1020	106	1.925	1143	104	1.765	1227	96
Ethyl *n*-hexylboronate	156	4.142	1117	*97*	3.233	1242	*99*	2.697	1324	*97*
Ethyl *n*-heptylboronate	170	7.337	1214	97	5.712	1341	99	4.302	1420	96
Acid ester series										
Ethyl *n*-pentylboronate	142	2.400	1018		1.917	1141	*113*	1.757	1225	*102*
n-Propyl *n*-pentylboronate	156	4.267	1123	*105*	3.475	1254		2.733	1327	145
n-Butyl *n*-pentylboronate	170	7.447	1217	94				5.622	1472	
n-Alkane series										
Decane (C_{10})	140	2.183			1.043			0.845		
Undecane (C_{11})	154	3.745			1.578			1.110		
Dodecane (C_{12})	168	6.728			2.587			1.578		
Tridecane (C_{13})	182	12.358			4.485			2.413		
Tetradecane (C_{14})	196	23.192			8.127			3.900		

[a] t_R = Retention time; I = retention index; ΔI = retention index increment.

TABLE II

RETENTION DATA FOR CYCLIC AND ACYCLIC *n*-ALKYLBORONATE ESTER SERIES AT 70°C

Conditions: isothermal, 70°C; methane flow-rate, 20 ml/min; 1.5 m × 4 mm I.D. glass columns.

Compound	Mol. wt.	Stationary phase									
		OV-1			OV-17				OV-225			
		t_R[a]	I[a]	Δt_R[a] per CH_2	(t_R-50)[a]	t_R[a]	I	Δt_R per CH_2	(t_R-50)	t_R	I	Δt_R per CH_2
Cyclic alcohol ester series												
Ethyl *n*-butylboronate	128								(18)	68	1131	
Ethyl *n*-pentylboronate	142	(34)	1023		(33)	83	1136		(87)	137	1234	103
Ethyl *n*-hexylboronate	156	(129)	1123	*100*	(127)	176	1232	*96*	(227)	277	1332	*98*
Ethyl *n*-heptylboronate	170	(320)	1218	95	(330)	379	1330	98	(513)	563	1429	97
Cyclic acid ester series												
Ethyl *n*-pentylboronate	142	(32)	1019		(34)	84	1137		(86)	136	1233	
n-Propyl *n*-pentylboronate	156	(130)	1124	*105*	(141)	191	1247	*106*	(243)	293	1340	*107*
n-Propyl isopentylboronate	156	(49)[b]	(1044)	[b]								
n-Butyl *n*-pentylboronate	170	(299)	1210	86	(303)	353	1321	78	(568)	618	1441	101
Acyclic alcohol ester series												
Dimethyl *n*-pentylboronate	144	(6)	968									
Dimethyl *n*-hexylboronate	158	(55)	1052	84								
Dimethyl *n*-heptylboronate	172	(162)	1145	*93*								

Acyclic acid ester series									
Diethyl *n*-butylboronate	158	(13)	984						
Di-*n*-propyl isobutylboronate	186	(60)[b]	(1058)[b]						
Di-*n*-propyl *n*-butylboronate	186	(176)	1153	*84.5*					
Di-*n*-butyl *n*-butylboronate	214								
n-Alkane series									
Decane (C_{10})	140	(21)							
Undecane (C_{11})	154	(100)			(13)	63			
Dodecane (C_{12})	168	(274)			(88)	138		(0)	50
Tridecane (C_{13})	182	(640)			(274)	297		(58)	108
Tetradecane (C_{14})	196				(611)	661		(169)	219
Pentadecane (C_{15})	210							(405)	455
Hexadecane (C_{16})	224								

[a] (t_R-50) = retention time as shown on RIC chromatograms which was 50 s after injection; t_R = actual retention time; other abbreviations as in Table I.
[b] These retention times are for the isomers of the corresponding alkylboronates.

TABLE III

RETENTION DATA OF CYCLIC AND ACYCLIC *n*-ALKYLBORONATE AND *n*-ALKYLBORATE ESTER SERIES AT 50°C

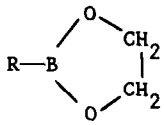
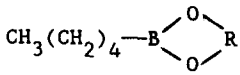
Conditions: isothermal, 50°C; 20 ml/min; 1.5 m × 4 mm I.D. glass columns, 3% OV-17.

Compound	t_R[a]	I^a	ΔI^a per CH_2	Mol.wt.
Cyclic alcohol ester series				
Ethyl *n*-butylboronate	54	1044		128
Ethyl *n*-pentylboronate	196	1146	102	142
Ethyl *n*-hexylboronate	534	1247	*101*	156
Cyclic acid ester series				
Ethyl *n*-pentylboronate	195	1146		142
n-Propyl *n*-pentylboronate	574	1255	*109*	156
n-Butyl *n*-pentylboronate	–	–	–	170
Acyclic alcohol ester series				
Dimethyl *n*-pentylboronate	23	1002		144
Dimethyl *n*-hexylboronate	127	1108	106	158
Dimethyl *n*-heptylboronate	383	1212	*104*	172
Acyclic acid ester series				
Dimethyl *n*-butylboronate	19	995		158
Di-*n*-propyl *n*-butylboronate	285	1182	*94*	186
Di-*n*-butyl *n*-butylboronate	–	–	–	170
n-Alkyl borate esters				
Triethyl borate	2	960		146
Tri-*n*-propyl borate	148	1114	54	188

[a] Abbreviations as in Tables I and II.

TABLE IV

METHYLENE INDEX INCREMENTS FOR THE ACID AND ALCOHOL CHAINS OF THE CYCLIC ALKYLBORONATE ESTERS

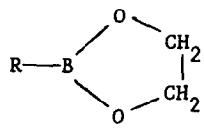
Compound	Stationary phase						
	OV-1 (70°C)	OV-17 (50–70°C)		OV-225 (70°C)	SE-30 (110°C)	OV-17 (110°C)	XE-60 (110°C)
Alcohol series:	100	101	96	98	97	99	97
							
R = C_4–C_7							
Acid series:	105	109	106	107	105	113	102
							
R′ = C_2–C_4							

methyl group, resulting in an uneven relative retention for the lower and higher alcohol ester series. As the methyl group moved further away from the carbonyl group, the increase in retention became smaller, *i.e.*, as the acid chain became longer than three carbon atoms. It was reported that the expected loss of linearity for the acid ester series on the acceptor column did not occur, probably owing to the ether linkage allowing better transmission of the induced dipole, resulting in similar increases in the relative retentions of the lower and higher acid ester series.

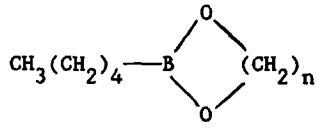
The linear relationships for the cyclic alkylboronate alcohol ester series on the acceptor columns, in contrast to the non-linear relationship for the aliphatic alcohol ester series, may be explained as being due to the boron end of the alcohol ester series being much less polar than the carbonyl end of the aliphatic alcohol ester series. This is expected, owing to the lower polarizability of the cyclic boron–oxygen bond as compared with the carbon–oxygen double bond of the carbonyl group of the aliphatic esters. Also, boron is less electronegative than carbon [9]. Therefore, unlike the aliphatic alcohol ester series, where there was a significant but diminishing interaction between the carbonyl and the methyl groups, there seemed to be no significant interaction between the boron end and the methyl group, owing to weak polarity of the boron end of the alcohol ester. The retention index increments per methylene unit added to the alcohol or acid chain of the cyclic alkylboronate, shown in Table IV, were obtained from the differences in the successive homologous ester series.

Table IV shows that the methylene increments in the alcohol chain have a greater effect on the retention index than in the acid chain for all the stationary phases considered. This behaviour is similar to that previously observed with simple, homologous aliphatic ester series but for slightly different reasons owing to their cyclic configurations. It is also evident that in the alcohol ester series, the magnitude of the retention index increment did not change very much with increase in polarity of the stationary phases. However, with the acid ester series, there was a significant increase for OV-17, indicating a greater interaction. Ashes and Haken [1] reported a decrease in retention index increments for aliphatic esters as the polarity of stationary phase increased.

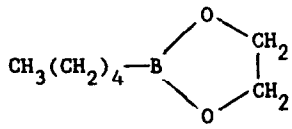
For the aliphatic ester series, Ashes and Haken [1] also reported that the greater effect in the alcohol chain was due to the ether linkage, hindering rotation of the alcohol chain, and hence an incremental change in this chain will have greater effect on molecular shape, maximizing the surface area owing to the lack of rotation and thus increasing the cohesive forces of molecules. The ether linkage was also reported to allow better transmission of the induced dipole, resulting in an increase in retention for the alcohol ester series. The same considerations also seem to explain in part the greater effect of methylene increments on the alcohol chain of the cyclic alkylboronate esters relative to the acid chain. However, the main reason for the greater effect in the alcohol chain seems to be the cyclic configuration of the alkylboronate esters. In the alcohol ester series, there is the usual increase in chain length:



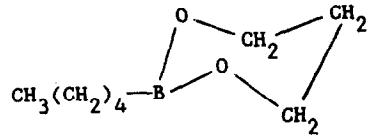
where R = C_4–C_7, without a change in the shape of the molecule. Therefore, the GC behaviour should be conventional.

In the acid ester series, 

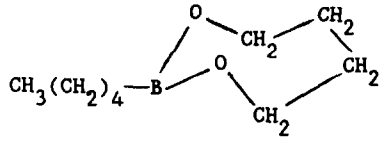
where n = 2–4, the system expands and the ring acquires a different shape. The most probable shapes for the acid ester series [47] are as follows:



almost planar



probably chair



probably distorted chair

Insertion of methylene groups in the alcohol chain varies the shape of the molecule, which in turn affects the retention behaviour of the series. The variation in the ring size seems to be the main reason for the greater effect of the methylene increment in the alcohol chain rather than the acid chain.

The change in the shape of the ring (*i.e.*, steric effects) may also explain why the overall retention index increments are greater for the acid ester series than in the alcohol ester series, indicating greater interaction with the OV-17 stationary phase.

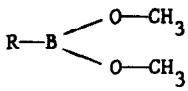
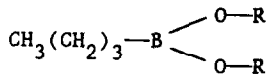
Studies with cyclic alkanes [32] and cyclic alkylboronates [47] have shown significant differences in molecular shapes with increasing size. As the size of the cyclic configuration increases from a five- to a seven-membered ring, the availability of the Pz orbital of the boron and the unpaired electrons of oxygen for interaction with the stationary phases increases.

Retention index plots for the acyclic alkylboronate ester series *versus* the number of carbon atoms in the acid or alcohol chain (retention index *versus* R or R′) were examined. For the alcohol ester series, the retention index plot was linear. However, for the acid ester series, the linear relationship is suspect, as it was only possible to obtain the retention time for two esters, and manipulation of column temperature to obtain retention times for three esters at a particular temperature did not succeed. The operating temperature for the third acid ester series, di-*n*-butyl *n*-butylboronate, was not high enough. However, the assumption that the retention index plot for the acid ester series is linear seems to be reasonable in view of the linearity of the cyclic alkylboronate esters.

Table V shows that the methylene increments in the acid chain have a greater

TABLE V

METHYLENE INCREMENTS FOR THE ACID AND ALCOHOL CHAIN OF THE ACYCLIC ALKYLBORONATE ESTER SERIES

Compound	Stationary phase	
	OV-1 (70°C)	OV-17 (50°C)
Alcohol ester series:		
	93	104
Acid ester series:		
	84	94

effect on the retention index than in the alcohol chain. The differences in retention index, *i.e.*, $\Delta CH_2R' - \Delta CH_2R$, was -10 units on OV-17 and -9 units on OV-1. In a similar study of aliphatic ester series [14], the retention index differences, *i.e.*, $\Delta CH_2R' - \Delta CH_2R$, of $+15$, $+7.5$ and $+11$ units on SE-30, DC-710 ($\equiv$OV-17) and Silar 5CP, respectively, were reported.

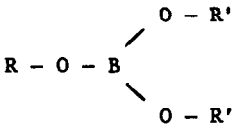
Crank and Haken [10] in a study of alkylphosphonate esters reported retention index differences, *i.e.*, $\Delta CH_2R' - \Delta CH_2R$, of -7 units on OV-17. The retention index differences of the acyclic alkylboronates, *i.e.*, $\Delta CH_2R' - \Delta CH_2R$, are similar in magnitude to those for the alkylphosphonate and aliphatic ester series. The sign is the same as that for the alkylphosphonates and opposite to that for the aliphatic ester series.

The effect with the phosphonate esters was explained on the basis that there are two $-OR'$ chains and, hence, the inductive effect of the $P=O$ group is split between the two and is thus reduced in magnitude. Also, the polarity of the phosphoryl group was reported to be less than that of the carbonyl group, owing to the effects of d electrons in phosphorus, which tend to neutralize the electron-withdrawing effect of the $=O$ atom.

Similar arguments to those for the alkylphosphonates seem also to be applicable to explain why the methylene increment on the acid chain has a greater effect on the retention index than in the alcohol chain. The structures of the acyclic alkylboronate esters in Table V indicate that there are three $-OR'$ ester chains bonded to the boron atom. Boron atoms usually form three bonds, involving their three sp^2 hybrid orbitals. The remaining p_z orbital is empty and accepts a pair of electrons from one of the $-OR'$ ester chains, making the boron–alcohol chain slightly polar. As this polarity effect is divided between the three $-OR'$ groups, the methylene increment on the alcohol chain will have less effect on the retention index relative to the methylene increment in the

acid chain. In addition, as indicated, the boron–alcohol chain is also less polar than the carbonyl chain.

The alkyl borate esters studied could be represented by



where R′ = *n*-alkyl.

Plots for both the alcohol and acid esters of the cyclic alkylboronates are shown in Fig. 4a and b, and similar plots of the acyclic esters are shown in Fig. 5, the data

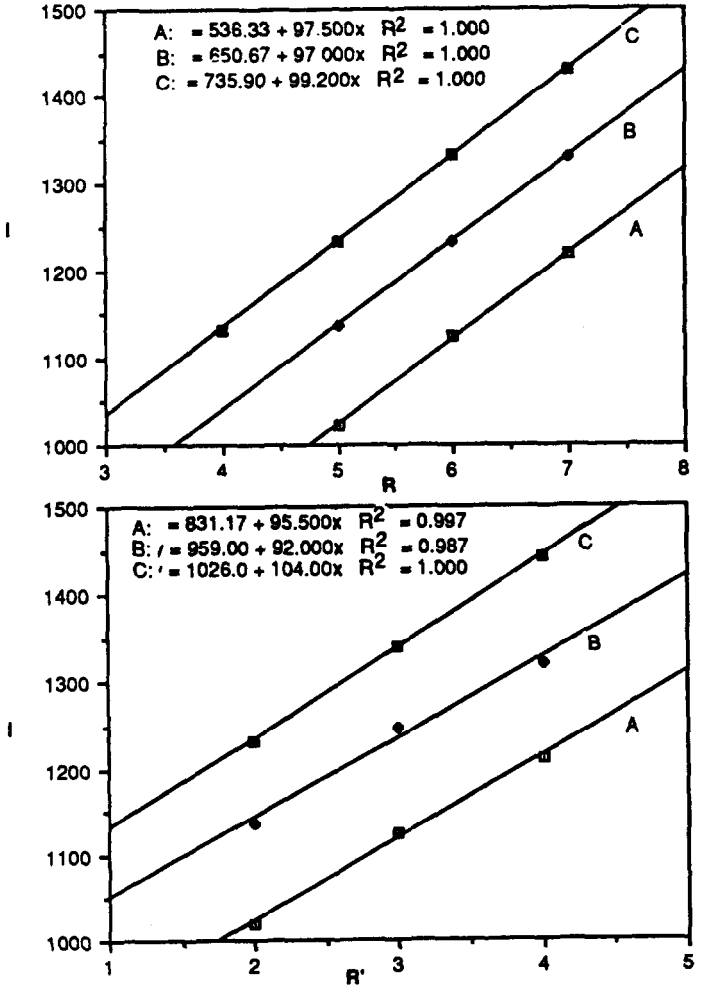


Fig. 4. Retention plots for cyclic alkylboronates: (A) alcohol ester series; (B) acid ester series. □ = OV-1; ● = OV-17; ■ = OV-225.

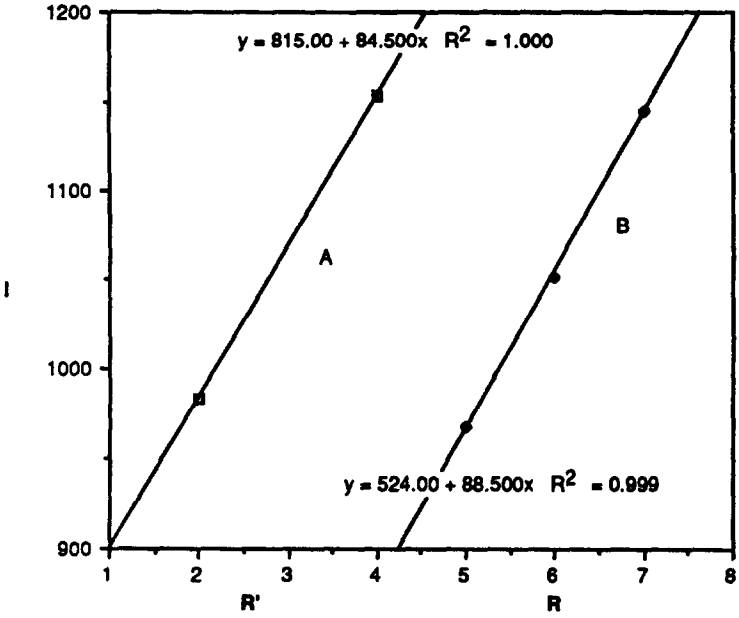


Fig. 5. Retention plots for acyclic alkylboronates: (A) acid and (B) alcohol ester series. □ and ● both OV-1.

being obtained at 70°C in all instances. Equations for the respective data on the various stationary phases are shown, and the linearity is indicated by the correlation coefficients.

The retention times and retention indices at 50°C are shown in Table III. With temperature-programmed operation the retention times are 12, 72 and 316 s for triethyl, tri-*n*-propyl and tri-*n*-butyl borate, respectively. The alkyl borates were found to be extremely sensitive to moisture, which explains the lack of GC reports in the literature. At 50°C, it was possible to achieve GC–MS elution of only two esters, *viz.*, triethyl and tri-*n*-propyl borate. Therefore, it is impossible to draw conclusions regarding the linearity or non-linearity of the data.

The retention index increments, *i.e.*, $\Delta CH_2R'$, per methylene unit in the *n*-alkyl borate ester were 54 index units, as shown in Table III. In a similar study of alkyl phosphate, Crank and Haken [10] reported about 94 retention index units on OV-17. These significant differences in retention index increments seem to be due to the borate esters being more polar than the phosphate esters. The borate esters, being more polar, will be retained less relative to the phosphate on OV-17 as the stationary phase.

The greater polarity of the alkyl borates appears to be due to its coplanar structure with sp^2 bond hybridization and ability of the empty orbital to form a dative bond by accepting the lone pairs of electrons in the OR group. This will have the effect of making the whole molecule more polar owing to the formation of three resonance structures. On the other hand, the phosphoryl group of the phosphates was reported [10] to be less polar owing to the effects of the d electrons in the phosphorus, which tend to neutralize the electron-withdrawing effect of the =O atom.

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