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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC SEPARATIONS OF SOME BORANES AND THEIR DERIVATIVES

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SUMMARY

The high-performance liquid chromatographic conditions required for the liquid–solid separation of about 20 higher boranes, heteroboranes and their derivatives were established. The separations were carried out on silica gel using *n*-heptane and methylene chloride as mobile phases. Except for several *closo*-boranes, spectrophotometric detection at 254 nm was used for borane compounds. Instead of water, acetonitrile and in some instances isopropanol were used as silica gel modifiers.

INTRODUCTION

The rapid development of high-performance liquid chromatography (HPLC) has greatly extended the range of chemical systems in which this technique, using micro-particles of diameter $< 15\ \mu m$, has proved its high separating efficiency and adaptability. While HPLC has been applied to a wide range of organic compounds, little attention has so far been paid to organometallic species.

The chemistry of boron compounds has expanded in recent years, especially in the field of metalloboranes, heteroboranes and borane anions. A wide variety of closely related species has been synthesized and the application of an efficient separation technique became necessary. A few reported HPLC studies in this area include those Kindsvater *et al.*[1] on the reversed-phase separation of a series of 1,2-dicarba-*closo*-dodecaborane derivatives, Evans and Hawthorne[2], who resolved cobalt metalloboranes, and Čoupek *et al.*[3], who investigated the separation of 1,2-dicarba-*closo*-dodecaborane derivatives using styrene–divinylbenzene gel as adsorbent. This lack of application of HPLC is in contrast to the wide use of classical low-pressure liquid chromatography[4], dry column chromatography[5] and thin-layer chromatography (TLC)[6] in boron chemistry. In order to provide a means of separating different low-volatility boron cage compounds, which are susceptible to both thermal reactions and hydrolysis, we investigated a high-performance liquid–solid chromatographic technique.

EXPERIMENTAL

Home-built apparatus, assembled partly from commercially available components, was used. The pumping system was either a membrane pump (Model VCM 150, Development Works of Czechoslovak Academy of Sciences, Prague, Czechoslovakia) with a damping device[7] operating at pressures up to 30 MPa and a flow-rate 6 ml/min or a pneumatic pump of our own construction made of stainless-steel tubing (length 2 m, I.D. 24 mm) and an appropriate valve system, operating at pressures up to 15 MPa.

For sample injection a Waters U6K injector (Waters Assoc., Milford, Mass., U.S.A.) or a septumless injector of our own construction[7] was used. The column was assembled from stainless-steel tubing (length 300 mm, I.D. 3.3 mm) with a 2-μm stainless-steel frit (Ugine Carbone, Grenoble, France) at the bottom and a PTFE frit (Hamilton, Reno, Nev., U.S.A.) at the top. The column was connected by a stainless-steel capillary (length 7 cm, I.D. 0.23 mm) with a spectrophotometric detector (Developments Works of Czechoslovak Adademy of Sciences) operating at 254 nm (cell volume 10 μl) or a differential refractometer (Model 2025/50, Knauer, Oberursel, G.F.R.).

The columns were packed with silica gel prepared from Kieselgel H for TLC (Merck, Darmstadt, G.F.R.) by sorting with an Alpine MZR 100 air classifier. A fraction with an average particle diameter of 13 μm (standard deviation 4.8 μm) was used. The specific surface area of this material (400 m^2/g) was determined by the nitrogen desorption method. The balanced-slurry packing technique, using an apparatus described by Coq *et al.*[8], was used for this adsorbent. Columns with a plate height of 90–100 μm (sample, diphenyl; capacity factor, 2.5; linear flow velocity, 0.5 cm/sec; eluent, *n*-heptane) were obtained. From values of the pressure drop and flow-rate, a particle diameter (d_p) of 8.4 μm was calculated according to an equation presented by Halász[9] for defining d_p. For some separations and for the guard column[10] (length 5 cm, I.D. 3.3 mm) Corasil II (Waters Assoc.) was used as the sorbent, the dry packing procedure being used for packing the columns.

TLC was carried out in glass tanks ($10 \times 15 \times 25$ cm) with the walls covered with filter-paper and well saturated with the vapour of a solvent. Silufol plates (Kavalier, Sázava, Czechoslovakia) were used and spots were detected with iodine vapour or by spraying with aqueous silver nitrate solution stabilized with ethylenediamine.

All solvents were filtered through a column of activated silica and alumina[11], dried with molecular sieve 4A, degassed and distilled on a rotary evaporator under reduced pressure before use.

All samples were obtained from laboratory stocks; their purities were checked by TLC. The methods of preparation of the boron compounds are cited in the tables of results. Sample sizes of 2–40 μl of fresh 0.5% solutions in the mobile phase were injected and the capacity factor (k') was calculated from the equation $k' = (t_r - t_0)/t_0$, where t_r is the retention time of the sample and t_0 is the hold-up time. Tetrachloroethylene was injected into the mobile phase to determine the hold-up time of each column.

RESULTS AND DISCUSSION

The optimal chromatographic conditions that would provide a satisfactory

separation in a reasonable time were determined by changing the polarity of the mobile phase to obtain k' values within the range 1–10. The chromatographic conditions, k' values and TLC data for some rigid boron compounds are summarized in Tables I, II and III. In order to ensure that the peaks would correspond to the species chromatographed, the fractions were collected and analysed by TLC with selective detection. In some instances, the qualitative integrity of the eluates was established after evaporation by high-resolution mass spectrometry.

Except for some *closo* compounds, most borane compounds absorb at 200–350 nm and therefore spectrophotometric detectors operating at 254 nm can be used for their detection. In Table IV, the minimal detectable amounts of some boron

TABLE I

CHROMATOGRAPHIC DATA FOR SOME HETEROBORANES

Compound	*k' (HPLC)* **	*R_F (TLC)* ***	*Reference to method of preparation*
1,6-$(Me_2S)_2B_{10}H_8$	2.8	0.34***	12
1,10-$(Me_2S)_2B_{10}H_8$	0.6	0.48***	12
5-Me_2S-7,8-$C_2B_9H_{11}$	6.1	0.41	13
10-Me_2S-7,8-$C_2B_9H_{11}$	12.9	0.30	14
9-SH-1,2-$C_2B_{10}H_{11}$	3.6	0.45	15
4-Me_2S-B_9H_{13}	6.6	0.37	16

* HPLC: Column, length 300 mm, I.D. 3.3 mm; sorbent, silica gel, 13 μm; eluent, 79.6% *n*-heptane–20% CH_2Cl_2–0.4% acetonitrile; flow-rate, 1.3 ml/min; pressure drop, 4.0 MPa; detection, UV at 254 nm.

** TLC: Silufol plates developed in benzene; detection with iodine vapour and spraying with $AgNO_3$ solution.

*** Developed in dichloromethane.

TABLE II

CHROMATOGRAPHIC DATA FOR SOME FURTHER HETEROBORANES

Compound	*k' (HPLC)* **		*R_F (TLC)* ***	*Reference to method of preparation*
	System I	*System II*		
5,6-$C_2B_8H_{12}$	1.2	1.1	0.42	17
6,8-$C_2B_7H_{13}$		5.6	0.16	18
5-(3-F-$C_6H_4CH_2$)$B_{10}H_{13}$	19.9	1.9	0.09	19
6-(3-F-$C_6H_4CH_2$)$B_{10}H_{13}$	25.0	2.3	0.09	19
6,9-$C_2B_8H_{14}$		5.5	0.10	20
6,8-SCB_7H_{11}	1.2	1.0	0.42	21
6,8-$S_2B_7H_9$	0.3		0.71	21
1-$SB_{11}H_{11}$	0.7		0.56	22

* HPLC System I: Column, length 300 mm, I.D. 3.3 mm; sorbent, silica gel, 13 μm; guard column, length 60 mm, I.D. 3.3 mm; sorbent, Corasil II; eluent, *n*-heptane; flow-rate, 0.89 ml/min; pressure drop, 42 MPa; detector UV at 254 nm (except for 1-$SB_{11}H_{11}$: refractive index detector. System II: eluent, *n*-heptane + 0.4% acetonitrile; other parameters as in system I.

** TLC: Silufol plates developed with *n*-hexane; detection with iodine vapour and spraying with $AgNO_3$ solution.

TABLE III

CHROMATOGRAPHIC DATA FOR BORANE LIGAND DERIVATIVES

Compound	*k' (HPLC)* *		*R_f (TLC)* **	*Reference to method of preparation*
	System I	*System II*		
9-Me_2S-7,8-$C_2B_9H_{11}$	2.2	5.7	0.21	14
10-Me_2S-7,8-$C_2B_9H_{11}$	1.8	3.7	0.30	14
4-Me_2S-B_9H_{13}	0.8	1.9	0.37	16
6,9-$(Me_2S)_2B_{10}H_{12}$	4.4		0.08	23
7-MeO-4-Me_2S-B_9H_{12}		3.6	0.23	24

* HPLC. System I: column, length 300 mm, I.D. 3.3 mm; sorbent, silica gel, 13 μm; guard column, length 60 mm, I.D. 3.3 mm; sorbent, Corasil II; eluent, 59.6% *n*-heptane–40% CH_2Cl_2–0.4% acetonitrile; flow-rate, 1.28 ml/min; pressure drop, 5.0 MPa; detection, UV at 254 nm. System II: eluent, 69.6% *n*-heptane–30% CH_2Cl_2–0.4% acetonitrile; flow-rate, 0.97 ml/min; pressure drop, 5.2 MPa; other parameters as in system I.

** TLC: Silufol plates developed in benzene; detection with iodine vapour and spraying with $AgNO_3$ solution.

TABLE IV

MINIMAL DETECTABLE AMOUNTS (W_{min}) OF SOME BORON COMPOUNDS

Column: length 300 mm, I.D. 3.3 mm; sorbent, silica gel, 13 μm; eluent, *n*-heptane; flow-rate, 0.91 ml/min; pressure drop, 5.0 MPa.

Compound	*W_{min} (g)*	*Detector*
1,7-$C_2B_{10}H_{12}$	1.4×10^{-6}	RI
1-$SB_{11}H_{11}$	7.5×10^{-7}	RI
5,6-$C_2B_8H_{12}$	8.6×10^{-7}	RI
	5.3×10^{-8}	UV
6,8-SCB_7H_{11}	1.1×10^{-6}	RI
	9.0×10^{-8}	UV

compounds, defined as the amount of solute that causes a detector signal of double the noise intensity, are presented. For poorly soluble compounds, the concentration of a sample in the effluent approaches the minimal detectable concentration of the differential refractometer used.

Fig. 1 shows a chromatogram obtained on a mixture resulting from the bromination of decaborane-(14) to form 1- and 2-bromodecaborane isomers, and Fig. 2 shows the separation of 5- and 6-(3-fluorobenzyl)decaboranes. An attempt to separate the latter mixture by classical liquid chromatography was unsuccessful[19]. These results, together with those in Tables I–III, demonstrate the capability of liquid–solid chromatography on columns with an efficiency of *ca.* 3000 theoretical plates to separate even rigid isomeric boron compounds in less then 25 min. The short time of analysis is a great advantage of HPLC because, in some instances, the reactivity of hydride compounds with water, some solvents and oxygen is a problem. Efforts to prevent evolution of hydrogen and destruction of the adsorbent column in classical liquid chromatography were not completely successful[4].

Rigid borane compounds, *e.g.*, decaborane-(14), behave as Brönsted and Lewis acids[25] and have a high permanent dipole moment (*e.g.*, 3.52 for decaborane-(14)[26].

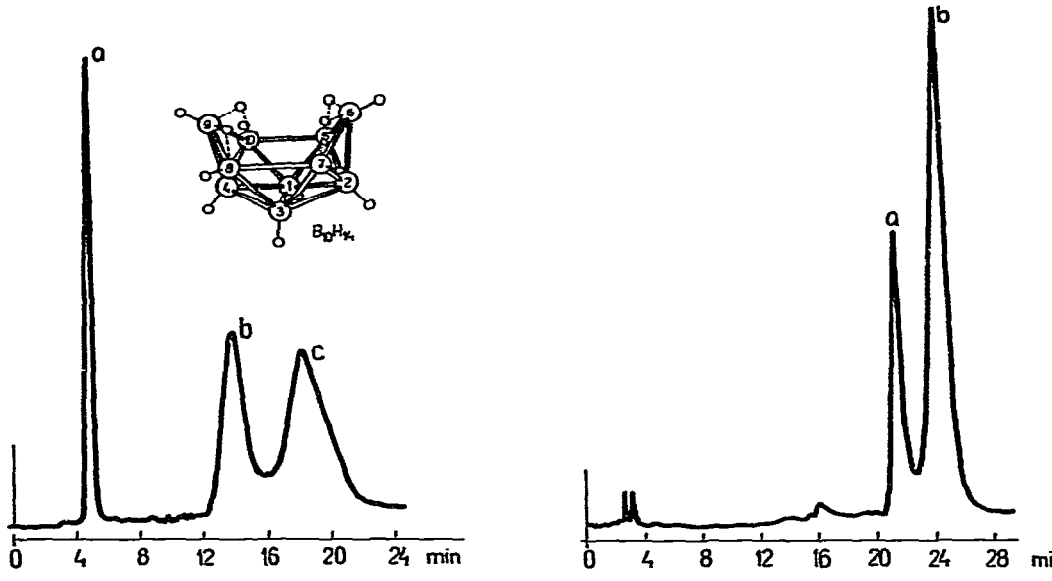

Fig. 1. Separation of boranes: (a) decaborane; (b) 1-bromodecaborane; (c) 2-bromodecaborane. Column: length 50 cm, I.D. 3.3 mm; sorbent, Corasil I; flow-rate, 0.69 ml/min; inlet pressure, 0.7 MPa; eluent, *n*-heptane + 0.1% isopropanol; sample size, 5 μl; detection, UV; sensitivity, 0.25 absorbance unit.

Fig. 2. Separation of substituted benzyldecaboranes: (a) 5-(3-F-$C_6H_4CH_2$)$B_{10}H_{13}$; (b) 6-(3-F-$C_6H_4CH_2$)$B_{10}H_{13}$. Column: length 30 cm, I.D. 3.3 mm; sorbent, silica gel, 13 μm; flow-rate, 1.18 ml/min; inlet pressure, 40 MPa; eluent, *n*-heptane + 0.4% acetonitrile; sample size, 15 μl; detection, UV; sensitivity, 0.12 absorbance unit.

It was found that for icosahedral carborane derivatives it is mainly the dipole moment that determines the retention behaviour of these compounds[3]. However, in general, it is difficult to predict the retention of borane compounds in liquid–solid chromatographic systems and therefore TLC was used to establish the retention behaviour and to permit a suitable solvent system to be chosen. TLC, as a complementary technique to HPLC, proved to be both an effective tool for the identification of eluted samples and a source of information on the retention behaviour of all of the components of a mixture. Owing to the dependence of k' values on the composition of the mobile phase in column chromatography, some solutes are not eluted from the column within the time of analysis.

Quantitative methods dealing with the transfer of TLC data to conditions of column chromatography have been published[27,28]. In practice, however, it is difficult to meet even fundamental assumptions of this relationship, *e.g.*, identical adsorbents in both TLC and HPLC. For this reason, a trial and error approach was used to choose the appropriate solvent composition for HPLC after preliminary TLC separation bearing in mind that a slightly less polar solvent should generally be used in a corresponding separation by HPLC[29].

In liquid-solid chromatography, water is usually added to the asorbent in order to optimize the linear capacity and column efficiency. The capacity factors (k') are significantly affected by changing the concentration of water in a solvent

and so, in order to achieve reproducible separations, the amount of water in the stationary and mobile phases must be carefully controlled. Instead of water, another type of polar compound such as lower alcohols[30], *e.g.*, isopropanol, has been recommended as a modifier in non-polar mobile phases. As all of these compounds react with boron hydrides, acetonitrile at a concentration of 0.1–0.4% was used as a modifier for the separations in our study. In some instances, even isopropanol at the same concentration gave good and reproducible results also. No change in the peak shapes was observed with these modifiers when the peaks of test organic compounds and boron compounds were compared. The column activity was tested periodically with a test mixture consisting of, *e.g.*, tetrachloroethylene, diphenyl, *o*-terphenyl and nitrobenzene with *n*-heptane as the eluent.

During this study, a paper by Saunders[31] was published dealing with the deactivation of silica gel by acetonitrile when *n*-hexane is used as a mobile phase. It was shown that acetonitrile is equal to or better than water with respect to sample capacity, plate height, convenience and equilibration time. Our experience with this solvent as a silica gel modifier with solvents of low polarity is in agreement with this result.

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