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GEL CHROMATOGRAPHY OF POLAR MOLECULES

ELUTION BEHAVIOUR OF DICARBA-*closo*-DODECABORANES AND THEIR DERIVATIVES

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SUMMARY

The gel chromatographic behaviour of dicarba-*closo*-dodecaboranes (carboranes) and their derivatives was investigated during elution with tetrahydrofuran and benzene with styrene-divinylbenzene gel as the column packing. The separation of molecules that have identical molecular weights and shapes has been explained by the formation of a solvation complex of the solute with the solvent. The stability of the complex is defined by the polarity, type of the substituent and its position in the molecule of carborane, which can be recommended as a suitable model compound for the study of polar interactions in gel chromatographic systems.

INTRODUCTION

It has often been observed while studying the behaviour of compounds of low molecular weight in gel chromatography that molecules containing certain functional groups seem to be much larger than would be expected from their molecular dimensions. Hendrickson and Moore¹ assigned this effect to the formation of hydrogen bonds between the analyzed compound and the eluent. When chloroform was used as eluent, it was found by Hendrickson² that it behaved as an electron acceptor, in contrast with tetrahydrofuran, which exhibits electron donor properties. Benzene may be classified as a compound that is not able to form hydrogen bonds; if used for gel chromatographic elution, it yields different elution volumes compared with those obtained when using tetrahydrofuran or chloroform³. The observed delays in the elution of aromatic hydrocarbons and oxygen-containing compounds are assigned to an interaction with the polystyrene gel. Edwards and Ng⁴ also found anomalous be-

haviour with certain types of compounds in tetrahydrofuran among about 100 model compounds investigated; they explained this behaviour by solvation of molecules and sorption on the gel packing.

From the gel chromatographic behaviour of phenols and bisphenols⁵⁻⁷, one may deduce that there exists an obvious effect not only of the shape and size of the molecule on its elution volume, but also a distinct dependence on the polarity of the molecule.

An attempt to change the polarity of the molecule by substitution or addition reactions, with the aim of obtaining model compounds for the investigation of the effect of the dipole moment of compounds on their elution behaviour, very often leads to unavoidable changes in the size and shape of the molecule. In order to prevent the effect of the geometrical shape of the molecule and its flexibility caused by rotation of the molecular segments about single bonds in the elution volume measurements, dicarba-*closo*-dodecaboranes (carboranes) and their derivatives were used for the investigation of the effect of the polarity of the molecule on its gel chromatographic behaviour. The spherical molecules of these model compounds are sufficiently rigid and their polarity is determined by the position of the carbon atoms in the molecule, as well as by the position of the substituent. A change in the mutual position of the carbon atoms on which the value of the dipole moment depends, or in the position of the substituent, does not lead to any changes in the size or shape of the molecule. Moreover, dipole moments have been measured for a number of carboranes⁸⁻¹⁰ and found to be in good agreement with the suggested structures.



The possibility of the gel chromatographic separation of organic boron compounds is also interesting from the analytical and preparative viewpoints. For the chromatographic separation and identification of carboranes and their derivatives, column and flat-bed liquid chromatography¹¹⁻¹⁵ on silica gel or alumina as sorbent and gas-liquid chromatography^{16,17} have been used almost exclusively. The advantages of gel chromatography for the separation of carboranes consist in a 100% recovery of all compounds injected into the column, excellent qualitative and quantitative reproducibility of the elution data and considerable durability of the columns.

EXPERIMENTAL

Chemicals

Carboranes and their derivatives were prepared as described in the literature. The purity of all compounds used as models was verified by determination of their physical constants and by gel and thin-layer chromatography. The structure of the molecules of the model compounds was confirmed by mass spectrometry.

Dipole moments

The dipole moments of the compounds investigated were determined from their dielectric constants measured in benzene by the heterodyne beat method at 25° and a frequency of 1 MHz, and also from the densities of solutions of model compounds in benzene for a concentration range from $5 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ M. The calculations were carried out by using a procedure suggested by Halverstadt and Kumler¹⁸ with a 5% correction of molar refraction, R_D , for atomic polarization.

Gel chromatography

The gel chromatography of model compounds was performed with an apparatus developed in the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, using a Waters Associates R-403 differential refractometer and a UV analyzer (Development Works, Czechoslovak Academy of Sciences) as detectors connected in series. The detector response was recorded by means of a two-channel Philips PM 8010 recorder. The separation was carried out in five stainless-steel columns connected in series, 8×1200 mm, efficiency *ca.* 8000 theoretical plates/m, filled with the styrene-divinylbenzene copolymer S-GEL-832 (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences), particle size 32–40 μ m, molecular weight exclusion limit 1000. Tetrahydrofuran (THF) and benzene were used as eluents; the flow-rate was 35 ml/h.

After a preliminary purity check, the model compounds were dissolved to yield a *ca.* 2% solution in the eluent taken directly from the storage tank of the solvent in the gel chromatograph, and injected with an accuracy of ± 0.05 ml into the first column. The elution volume was measured by means of a siphon integral flow-meter and expressed in counts (1 count = 2.72 ml (THF) or 2.14 ml (benzene)). The free volume of the whole system was 49.0 counts (THF) or 55.0 counts (benzene).

RESULTS AND DISCUSSION

Gel chromatographic measurements gave symmetrical peaks in all instances. The responses of the detectors were perfectly reproducible both qualitatively and quantitatively. The separation of a mixture of *o*-, *m*- and *p*-carboranes with tetrahydrofuran and benzene as eluents on the same column system using a differential refractometer detector is illustrated in Fig. 1. *o*-Carborane was completely separated from the mixture of isomeric *m*- and *p*-carboranes, the separation of the latter two being incomplete under the experimental conditions used. The elution volumes of all three compounds could be read off with precision in tetrahydrofuran only.

Table I gives the elution data for isomeric carboranes for measurements carried out in both eluents together with their dipole moments. The elution volumes of carboranes increase with increasing dipole moments in benzene and decrease in tetrahydrofuran. The structure of carboranes allows a dislocation of electrons along the whole molecule in a similar manner to aromatic compounds. The electron density in the carborane molecule is lowest in the close proximity of carbon atoms, which is confirmed by the experimental finding that the electrophilic substitution of an *o*-carborane molecule is most difficult in positions 3 and 6. For *m*-carboranes, a decrease in the electron density on boron atoms in positions 2 and 3 can also be proved. The highest electron density may be observed on boron atoms lying opposite carbon

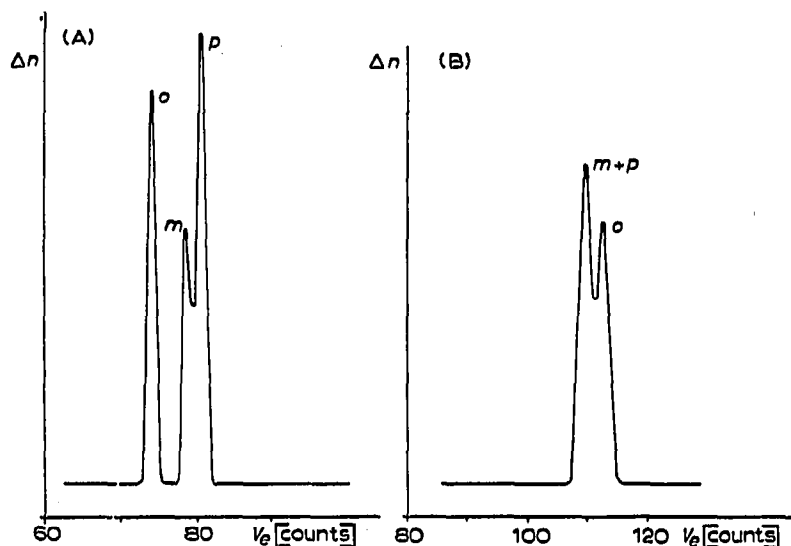


Fig. 1. Gel chromatograms of the separation of a mixture of *o*-, *m*- and *p*-carboranes. A, in tetrahydrofuran; B, in benzene. Detection with a differential refractometer.

TABLE I

GEL CHROMATOGRAPHIC BEHAVIOUR OF CARBORANES IN THF AND BENZENE

V_0 (THF) = 49.0 counts; V_0 (benzene) = 55 counts; V_0/V_e = relative zone velocity.

Compound	M.p. (°C)	THF		Benzene		$\mu(D)$
		V_e (counts)	V_0/V_e	V_e (counts)	V_0/V_e	
<i>o</i> -Carborane	295–206	75.5	0.649	113	0.487	4.53 (ref. 8) 4.31 (ref. 9) 4.42
<i>m</i> -Carborane	272–273	79.3	0.618	111	0.495	2.85 (ref. 8) 2.78 (ref. 9) 2.80
<i>p</i> -Carborane	259.5–261	81.1	0.604	110	0.500	0.00 (ref. 8)

atoms; the lowest density and thus also electron acceptor properties are found in the vicinity of carbon atoms. As *o*-carborane in positions 1 and 2 will exhibit the strongest acceptor properties in contrast with *m*-carborane with a weaker acceptor effect in positions 2 and 3 and a negligible acceptor effect of the *p*-carborane molecule, where all boron atoms are equal, the differences in the elution volumes (V_e) of carboranes in tetrahydrofuran may be explained by a donor–acceptor interaction of the solute with the solvent, leading to the formation of a solvation complex that has the character of a hydrogen bond. According to the measured V_e , the stability of the carborane–tetrahydrofuran complex depends on the polarity of carborane.

In benzene solution, the smaller differences in elution volumes directly depending on the dipole moment are assigned to a stronger tendency to solvation with a non-polar solvent observed for isomers with a lower polarity, such as *m*- and *p*-carboranes.

TABLE II

GEL CHROMATOGRAPHIC BEHAVIOUR OF SUBSTITUTED *o*-CARBORANES IN THF
 V_0 (THF) = 49.0 counts.

Compound	M.p. ($^{\circ}$ C)	V_e (counts)	V_e/V_0	μ (D)
1-Bromo- <i>o</i> -carborane	180	76.2	0.643	3.34 (ref. 10)
3-Bromo- <i>o</i> -carborane	122 -123	74.3	0.659	3.69 (ref. 10)
4-Bromo- <i>o</i> -carborane	142	73.7	0.665	4.47 (ref. 10)
8-Bromo- <i>o</i> -carborane	185 -186	73.0	0.671	5.48 (ref. 10)
9-Bromo- <i>o</i> -carborane	191.5	72.3	0.678	5.98 (ref. 10)
1,2-Dibromo- <i>o</i> -carborane	228	74.9	0.654	2.82 (ref. 9) 2.78
9,12-Dibromo- <i>o</i> -carborane	220 -221	70.9	0.691	7.21 (ref. 9)
1-Phenyl- <i>o</i> -carborane	69 -70	74.8	0.655	4.79
3-Phenyl- <i>o</i> -carborane	108 -109	72.3	0.678	4.57
1,2-Diphenyl- <i>o</i> -carborane	148 -149	74.2	0.660	5.46
1-Ethoxy- <i>o</i> -carborane	48	75.2	0.652	3.68
3-Ethoxy- <i>o</i> -carborane	39.5- 40.5	72.8	0.673	4.35
1-Hydroxy- <i>o</i> -carborane	308 -310	73.7	0.665	4.22
3-Hydroxy- <i>o</i> -carborane	356 -358	72.0	0.681	4.08

The situation observed for substituted carboranes is more complex: here, the donor-acceptor properties of substituents and their positions in the molecule also contribute to the dipole moment, together with the carbon atoms. The gel chromatographic data of substituted *o*-carboranes obtained for elution with tetrahydrofuran are summarized in Table II. The linear dependence of the elution volumes of monobromo derivatives of *o*-carboranes substituted in positions 3, 4, 8 and 9 on their dipole moments (Fig. 2) is in accordance with the dependence of the retention times in TLC and GLC observed earlier¹⁵. The exception to the above is 1-bromo-*o*-carborane, in the molecule of which the polar effect is reduced by substitution on the

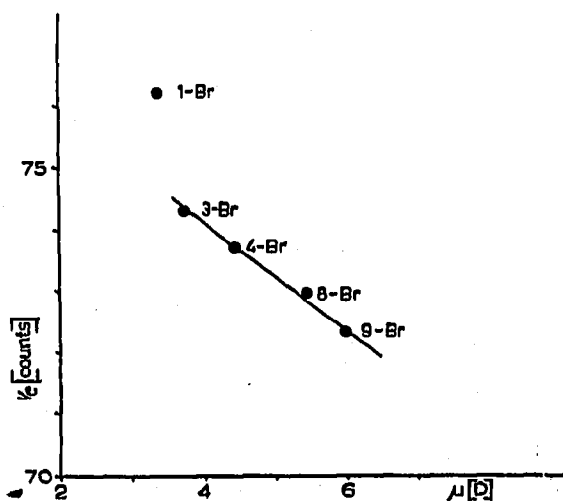


Fig. 2. Dependence of the elution volume, V_e , (in tetrahydrofuran) on the dipole moment for monobromo derivatives of *o*-carborane.

carbon atom more than it is in the derivatives with substituted boron atoms. In addition to the above effect, steric hindrances may also appear that make the formation of a solvation complex with the solvent impossible.

As expected, the effective volume of a molecule of the dibromo derivatives of *o*-carborane also depends on its dipole moment (Table II). An approximate agreement between the elution volumes of 1-phenyl-*o*-carborane and 1,2-diphenyl-*o*-carborane may be explained by the sterically hindered formation of a solvation complex observed for a disubstituted derivative, while monosubstituted 1-phenyl-*o*-carborane is able to form a complex, in a similar manner to 3-phenyl-*o*-carborane. The stability of the complex of tetrahydrofuran with a derivative substituted at the boron atom will be higher, according to the elution volume, than that of a similar carborane substituted at the carbon atom. The ethoxyl derivatives behave in a similar manner to non-substituted carboranes; the elution volume decreases with increasing dipole moment. Steric hindrance of the formation of a solvation complex in position 1 probably plays a major role for hydroxyl derivatives. It may be deduced, however, from a survey of the data measured here that the effect of the dipole moment is operative to a greater extent than effects due to steric hindrance.

Table III summarizes elution data for the gel chromatography of substituted *m*-carboranes. The same rules as for the *ortho* series are valid for the dependence of the elution volume on polarity and substitution of the molecule.

TABLE III
GEL CHROMATOGRAPHIC BEHAVIOUR OF SUBSTITUTED *m*-CARBORANES IN THF
 V_0 (THF) = 49.0 counts.

Compound	M.p. (°C)	V_a (counts)	V_0/V_a	μ (D)
1-Bromo- <i>m</i> -carborane	180 -181	79.8	0.614	2.37
9-Bromo- <i>m</i> -carborane	172	76.9	0.637	4.24
9,10-Dibromo- <i>m</i> -carborane	189	75.3	0.651	5.14 (ref. 9)
1-Phenyl- <i>m</i> -carborane	55.5	77.9	0.629	2.83
1,7-Diphenyl- <i>m</i> -carborane	116 -117	76.5	0.641	2.98

Gel chromatographic measurements on the carborane models suggest that the effect of the polarity of the molecule may play an important role in gel chromatographic separations of polar molecules. The proof of the existence of solvation complexes of carboranes and solvents by means of independent physicochemical measurements and the determination of their dissociation constants are the subject of a forthcoming study. A correlation of the data thus obtained with the results presented in this paper will allow an unambiguous characterization of the effect of sorption interactions of polar molecules with the gel packing of the column.

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