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# GAS CHROMATOGRAPHIC SEPARATION OF ISOMERIC MONOBROMO-1,2-DICARBA-CLOSO-DODECABORANES (12)

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## SUMMARY

A method for qualitative and quantitative separations of isomeric monobromo-1,2-dicarba-closo-dodecaboranes (*o*-carboranes) by gas–liquid chromatography (GLC) on silicone oil QF-1 is described. The method shows a linear relationship of the specific relation volume, $V_g$, to dipole moments in the temperature range 140–180°.

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## INTRODUCTION

The position of the C atom in icosahedral carborane is a basic factor of the polarity of the molecule[1]. Values of the dipole moments decrease in the order *o*- > *m*- > *p*-, the *p*-isomer having zero value[1,2]. These differences are produced by a different distribution of charge in the molecule[3]. From electrophilic substitution of *o*-carborane it would appear that the highest electron density in the molecule is at the boron atom lying opposite the carbon atom. With replacement of a proton by bromine five possible isomers occur. Substitution at the C-atom markedly decreases the dipole moment of the molecule[4], whereas substitution at position 9 strongly increases the dipole moment in relation to non-substituted *o*-carboranes. Substitution at the other boron atoms is given by the position of the skeletal boron. In the equatorial region the change is least. At position 3 there is a small decrease and at position 8 there is an increase in the dipole moment. On the basis of published data[5,6] it can be expected that dipole moments will have a marked effect on chromatographic separation. Since thin-layer chromatography (TLC) and column chromatography has not been able to separate derivatives of 8-Br- from 9-Br-*o*-carborane[7], we applied gas–liquid chromatography (GLC) to the separation of all the isomers[8]. An analytical method for qualitative and quantitative evaluation of these substances has been worked out in order to study the course of thermal isomerisation of 1-bromo-*o*-carborane, to estimate purity and to measure thermal stability of isomeric monobromo derivatives of *o*-carboranes. Grafstein and Dvorak[9], Kaesz *et al.*[6] and Zakharkin *et al.*[10] have all used gas chromatography to separate some derivatives of *o*-carboranes; for the stationary phase they used polyesters or polyglycols. In the present work a method of separation of all isomeric bromo-*o*-carboranes on fluorinated silicone oil QF-1 is presented.

## EXPERIMENTAL

### *Preparation of standard substances for GLC*

Substances were prepared according to the literature, as indicated in Table I.

Melting points shown in Table I were measured on a Kofler block in sealed capillaries and were not corrected. The purity of standard substances was analysed using GLC, TLC and IR spectroscopy.

TABLE I

PREPARATION OF STANDARD SUBSTANCES

| *Substance* | *M.p. (°C)* | *Reference* | *Remarks* |
|---|---|---|---|
| 1-Br-*o*-carborane | 180 | 11 | |
| 3-Br-*o*-carborane | 122–123 | 12 | Cryst. from hexane 3 ×, resublimated |
| 4-Br-*o*-carborane | 142 | 13 | |
| 8-Br-*o*-carborane | 185.5–186 | 8, 14 | |
| 9-Br-*o*-carborane | 191.5 | 15 | Cryst. from heptane 5 ×, resublimated |
| *o*-Carborane | 295–296 | 16 | Cryst. from hexane 3 ×, resublimated |

### *Instruments*

A Chrom-3 instrument (Laboratorní přístroje, Prague, Czechoslovakia) with a flame ionisation detector and with an amplifier for capillary columns was used. Column temperature was regulated to ± 0.2°. The injection block was heated 50 ± 5° higher than column temperature. The carrier gas was nitrogen, dried by a Calsit 5 molecular filter. Samples were applied as 10% solutions with a 1-μl Hamilton syringe (Hamilton, Reno, Nev., U.S.A.).

TABLE II

COLUMNS

| *Length (m)* | *I.D. (mm)* | *Support** | *Stationary** phase* | *Column type* |
|---|---|---|---|---|
| 2.4 | 6 | Chromosorb W silane | QF-1 (20) | Packed |
| 2.4 | 6 | Chromosorb W silane | QF-1 (10) | Packed |
| 2.4 | 6 | Chromosorb W silane | SF-96 (3) | Packed |
| 2.4 | 6 | Chromosorb W silane | Si-200 (3) | Packed |
| 2.4 | 6 | Chromosorb W silane | Apiezon L (3) | Packed |
| 2.4 | 6 | Chromosorb G AW | QF-1 (3) | Packed |
| 0.7 | 6 | Chromosorb W silane | Carbowax (3) | Packed |
| 50 | 0.2 | — | QF-1 | Capillary |
| 2 | 25 | Chromosorb | QF-1 (20) | Preparative |

* All supports were of 60–80 mesh.

** The %-w/w is given in brackets.

Preparative separation was carried out on a Fractovap P (Carlo Erba, Milan, Italy) instrument with flame-ionisation detection. Column temperature was 180°. The carrier gas was nitrogen dried by a Calsit 5 molecular filter.

## RESULTS AND DISCUSSION

On a column with QF-1, GLC gave symmetrical peaks without tailing which indicate the presence of even a minimal amount of substance. These were reproducible both qualitatively and quantitatively. Table III shows the specific retention volumes of all the isomeric monobromo *o*-carboranes, *o*-carborane and comparative hydrocarbons at temperatures of 140–180°. It would appear that retention volume increases in direct relation to the position of the bromine atom in the carborane skeleton, from carbon to the most distant boron. This is in agreement with the distribution of electronic charge in the substituted molecule[5]. This relation is valid at all of the above temperatures. A typical course of the chromatographic separation is shown in Fig. 1.

TABLE III

SPECIFIC RETENTION VOLUMES OF MONOBROMO CARBORANES AND RELATED HYDROCARBONS

A 2.4-m column packed with Chromosorb G, coated with 3% QF-1, at the given temperatures and flows, was used.

| *Substance* | *Flow of $N_2$ in ml/sec and temp.* | | | | |
|---|---|---|---|---|---|
| | *2.50, 180°* | *2.89, 170°* | *3.25, 160°* | *3.08, 150°* | *2.98, 140°* |
| 1-Br-*o*-carborane | 5.49 | 7.41 | 9.00 | 13.26 | 19.96 |
| 3-Br-*o*-carborane | 10.30 | 14.13 | 18.77 | 26.53 | 34.72 |
| 4-Br-*o*-carborane | 18.11 | 25.41 | 35.28 | 48.59 | 69.44 |
| 8-Br-*o*-carborane | 33.10 | 47.90 | 69.04 | 98.27 | 143.18 |
| 9-Br-*o*-carborane | 38.72 | 56.50 | 80.30 | 116.88 | 172.33 |
| *o*-Carborane | 7.49 | 9.77 | 13.13 | 17.91 | 24.00 |
| *n*-$C_{16}H_{34}$ | 5.65 | 7.65 | 10.40 | 14.32 | 19.63 |
| *n*-$C_{22}H_{46}$ | 34.28 | 53.71 | 85.90 | 133.10 | 209.90 |

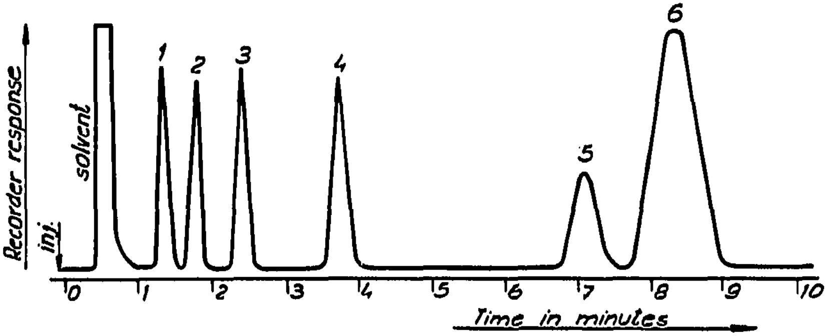

Fig. 1. Gas chromatogram of bromo isomers on 2.4-m stainless-steel column (I.D., 6 mm) packed with Chromosorb G coated with 3% (w/w) of QF-1. Column temperature, 150°. 1 = 1-Br-*o*-Carborane, 2 = *o*-carborane, 3 = 3-Br-*o*-carborane, 4 = 4-Br-*o*-carborane, 5 = 8-Br-*o*-carborane, 6 = 9-Br-*o*-carborane.

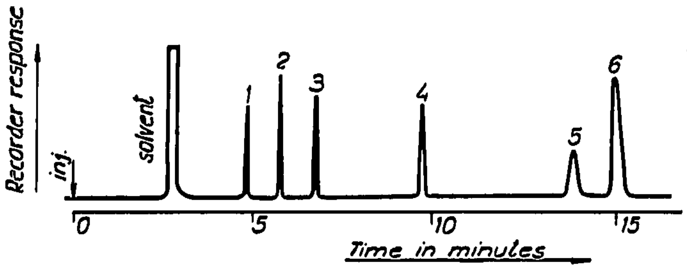

Fig. 2. Gas chromatogram of bromo isomers on 50-m long stainless-steel open tubular column (I.D., 0.25 mm). Stationary phase, QF-1. Column temperature, 208°. For identification of peaks, see Fig. .1

The best separation occurred on the capillary column containing QF-1, as can be seen in Fig. 2.

This information was used for a preparative separation[8]. In this way it proved possible to prepare separate monobromo derivatives in analytical purity.

On the contrary, it would appear from Table IV and Fig. 3 that separation on packed columns with a liquid phase of Apiezon L, Silicone oil 200, SF-96 or Carbowax 20M is complete in the given temperature range only with 1-Br-, 3-Br- and 4-Br-*o*-carboranes. The 8-Br- and 9-Br-derivatives were incompletely separated.

TABLE IV

SPECIFIC RETENTION VOLUMES OF MONOBROMO CARBORANES WITH DIFFERENT STATIONARY PHASES AT DIFFERENT TEMPERATURES*

| *Substance* | *3% Apiezon L* | | | | *3% Silicone oil 200* | | *3% Silicone oil SF-96* | *Carbowax 20M* |
|---|---|---|---|---|---|---|---|---|
| | *200°* | *190°* | *180°* | *170°* | *150°* | *140°* | *150°* | *208°* |
| 1-Br-*o*-carborane | 11.47 | 14.74 | 19.20 | 24.60 | 18.90 | 24.79 | 22.48 | 5.27 |
| 3-Br-*o*-carborane | 16.46 | 21.52 | 28.51 | 36.86 | 27.89 | 37.66 | 32.48 | 18.10 |
| 4-Br-*o*-carborane | 23.86 | 31.81 | 42.77 | 57.12 | 54.38 | 61.49 | 51.42 | 45.12 |
| 9-Br-*o*-carborane | 34.77 | 47.02 | 63.42 | 85.65 | 77.52 | 106.76 | 85.61 | 108.11 |
| *o*-Carborane | 8.57 | 10.76 | 13.97 | 17.47 | 16.08 | 20.98 | 18.53 | 12.60 |

* Incomplete separation was obtained for the 8-Br-derivative.

According to the equation, as given in ref. 17,

$$n_{\text{req}} = 36 \left(\frac{\alpha}{\alpha - 1}\right)^2 \cdot \left(\frac{1 + k'}{k'}\right)^2$$

—where $n_{\text{req}}$ = number of plates required, $\alpha$ = relative retention and $k'$ = partition ratio— the number of theoretical plates of the column necessary for complete separation of 8-Br- and 9-Br-*o*-carboranes can be calculated. At a temperature of 180° the number of theoretical plates (TP) is 3000 but at 140° only 1400. The filled column used here had 3000 TP. It was shown that for the required separation this value was sufficient. The Kováts indices (see ref. 17) are given in Table V.

TABLE V

KOVÁTS INDICES FOR MONOBROMO CARBORANES IN A COLUMN PACKED WITH QF-1

| *Substance* | *180°* | *170°* | *160°* | *150°* | *140°* | $\partial I_{QF\text{-}1}/10°$ |
|---|---|---|---|---|---|---|
| 1-Br-*o*-carborane | 1600 | 1591 | 1582 | 1573 | 1564 | 9.00 |
| 3-Br-*o*-carborane | 1800 | 1788 | 1776 | 1765 | 1753 | 11.75 |
| 4-Br-*o*-carborane | 1996 | 1976 | 1957 | 1937 | 1918 | 19.50 |
| 8-Br-*o*-carborane | 2190 | 2167 | 2145 | 2122 | 2100 | 22.50 |
| 9-Br-*o*-carborane | 2240 | 2216 | 2192 | 2169 | 2145 | 23.75 |
| *o*-Carborane | 1686 | 1677 | 1668 | 1659 | 1650 | 9.00 |

The dependance of retention volume on dipole moments is linear, as can be seen in Fig. 4. With the exception of the 4-Br-derivative this dependence is satisfactorily described by the equation

$$(V_g)_t = K_t \cdot (\mu - \mu_0)$$

where $(V_g)_t$ = retention volume at $t°$, $K_t$ = change in retention volume with a change in dipole moment at $t°$, $\mu$ = dipole moment of the derivative, $\mu_0$ = constant for the given group of substances (extrapolated value of functional dependance for $V_g = 0$).

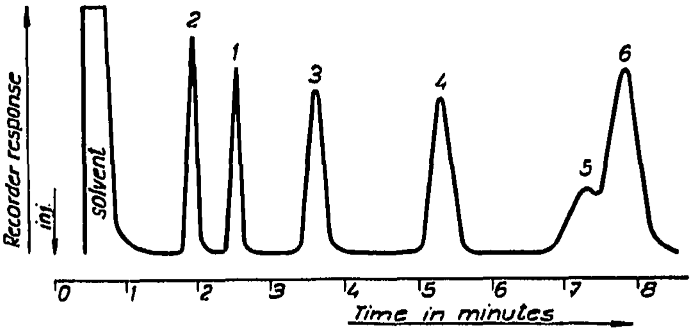

Fig. 3. Gas chromatogram of bromo isomers on 2.4-m stainless-steel column (I.D., 6 mm) packed with Chromosorb W coated with 3% (w/w) Apiezon L. Column temperature, 170°. For identification of peaks, see Fig. 1.

Values of the slopes, $K_t = \left(\frac{dV_g}{d\mu}\right)_t$ for the temperature range 140–180° are given in Table VI.

From Fig. 4 it would appear that while the 1-Br-, 3-Br-, 8-Br- and 9-Br-derivatives agree precisely with the given relation at all the temperatures used, the 4-Br derivative gives satisfactory agreement only at higher temperatures. With decreasing temperature there is an increasing deviation from expected values. This phenomenon cannot be satisfactorily explained on present knowledge.

The above suggests that from the retention volume one can fairly accurately predict values of the dipole moment in this group of substances. It seems to be a purely polar effect, as all the investigated molecules have the same shape and differ only in

TABLE VI

SLOPE VALUES, $K_t$, FOR MONOBROMO DERIVATIVES OF *o*-CARBORANE

| *t (°C)* | *$K_t$ (ml)* |
|---|---|
| 140.0 | 57.7 |
| 150.0 | 39.3 |
| 160.0 | 27.3 |
| 170.0 | 18.9 |
| 180.0 | 13.4 |

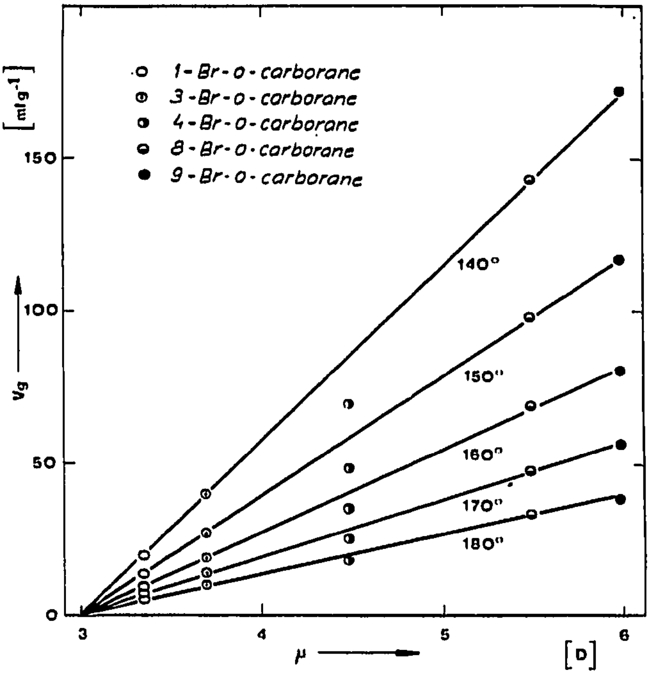

Fig. 4. Dependence of specific retention volume on the dipole moments of monobromo carboranes.

the size of the dipole moment. One would expect that the same relations will hold for the similar isomeric derivatives of *m*-carborane.

## ACKNOWLEDGEMENT

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