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Note

Gas chromatographic behaviour of some carboranes

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Carboranes are a new class of boron hydrides in which carbon atoms are part of the borane skeleton with localized electrons. The position of the carbon atoms in a carborane is the main factor determining the polarity of the molecule. The insertion of two further carbon atoms results in a higher thermal stability and a lower reactivity toward various reagents.

For the qualitative and quantitative characterization of borane derivatives, thin-layer[1], liquid column[2–5] and gas chromatography (GC)[6–15] have been used. Carborane derivatives have been analysed by high-performance liquid chromatography (HPLC) on a non-polar stationary phase[2] or on a styrene–divinylbenzene gel[3]. Silica gel has also been used for the separation of various heteroboranes by HPLC[4,5]. GC has found use in air pollution and industrial hygiene studies and as a control method in the preparation of borane derivatives[6–15].

In this work the GC behaviour of six carboranes (Apiezon L, SF-96, QF-1, XE-60 and Carbowax 20M) on five stationary phases was studied over a temperature range of 140–200°. The calculated retention indices and differential heats of solution are discussed in connection with the structure and properties of the carborane studied.

EXPERIMENTAL

Materials

Hydrocarbons (nonane to docosane) were obtained from Fluka (Buchs, Switzerland). Carboranes were prepared in the Institute of Inorganic Chemistry, ČSAV (Řež near Prague, Czechoslovakia). The properties of the carboranes studied are given in Table I.

The chromatographic column packings were 3% (w/w) Apiezon L, 3% SF-96, 3% Carbowax 20M and 8.4% XE-60 on Chromosorb W DMCS (60–80 mesh) and 10% QF-1 on Chromaton N (60–80 mesh).

Apparatus

The measurements were carried out on a Chrom 3 gas chromatograph (Laboratorní přístroje, Prague, Czechoslovakia) using flame-ionization and thermal conductivity detectors. The carrier gas (nitrogen) flow-rate was 60 ml/min.

TABLE I

PROPERTIES OF CARBORANES STUDIED

Carborane	*Mol. wt.*	*M.p. (°C)*	*Dipole moment (D)*
1,2-$C_2B_{10}H_{12}$	144.23	295	4.31
1,7-$C_2B_{10}H_{12}$	144.23	272	2.82
1,12-$C_2B_{10}H_{12}$	144.23	259	0
2,3-$C_2B_9H_{11}$	132.41	212	—
1,2-$C_2B_8H_{10}$	120.59	181	—
5,6-$C_2B_8H_{12}$	122.61	98	—

Stainless-steel columns 2.4 m long and 6 mm I.D. were used. Carborane samples were injected with a 1-μl Hamilton syringe as 10% solutions in benzene or hexane.

RESULTS AND DISCUSSION

The retention data were measured for six carboranes on five stationary phases of various polarities over the temperature range 140–200°. The calculated values of the retention indices at two temperatures and the $\Delta I/\Delta T$ coefficients (where ΔT is 10°) are given in Table II.

The carboranes studied have similar retention indices on non-polar stationary phases, Apiezon L and the SF-96 silicone oil. The pair of carboranes 1,7-$C_2B_{10}H_{12}$ and 5,6-$C_2B_8H_{12}$ are poorly separated on Apiezon L; the carborane 1,2-$C_2B_8H_{10}$ also has a similar I value on SF-96. As follows from a comparison of the retention indices with the molecular weights given in Table I, the size of the carborane molecules has no pronounced effect on the carborane retention.

On the QF-1 medium-polarity stationary phase, the dipole moments affect the results in a series of isomeric *o*-, *m*- and *p*-carboranes. The greatest retention is exhibited by the *o*-carborane 1,2-$C_2B_{10}H_{12}$, which has the strongest electron-acceptor properties and the highest polarity; *m*-carborane (1,7-$C_2B_{10}H_{12}$) and *p*-carborane (1,12-$C_2B_{10}H_{12}$) are less polar and therefore more volatile. The dependence of log V_N on the square of the dipole moment is given in Fig. 1 and is lenear on QF-1.

The retention order of the carboranes changes on polar stationary phases, XE-60 nitrile silicone oil and Carbowax 20M polyethylene glycol. Whereas 2,3-$C_2B_9H_{11}$ is most strongly retained on Apiezon L, SF-96 and QF-1, 1,2-$C_2B_{10}H_{12}$ has the highest retention on XE-60; 5,6-$C_2B_8H_{12}$ is also strongly retained on Carbowax 20M.

XE-60 contains strongly dipolar –C≡N groups. It interacts selectively with chromatographed substances as a function of their dipole moments and polarizabilities. The best separation of all of the carboranes studied was attained on this phase (see Fig. 2).

The strong retention of 5,6-$C_2B_8H_{12}$ on Carbowax 20M can be explained by its ability to form a three-dimensional network of hydrogen bonds. 5,6-$C_2B_8H_{12}$ is a substance with an open skeleton and hydrogen bonds between atoms 8–9 and 9–10, which behave as acidic bonds ($pK_a = 6.18$). The dipole moment was not measured but is similar to that of 1,7-$C_2B_{10}H_{12}$. 1,2-$C_2B_8H_{10}$ has a dipole moment similar to that of 1,2-$C_2B_{10}H_{12}$, but it much more volatile and therefore also exhibits a lower

TABLE II

RETENTION INDICES OF CARBORANES ON FIVE STATIONARY PHASES AT TWO TEMPERATURES AND $\Delta I/\Delta T$ VALUES ($\Delta T = 10°$)

Carborane	*Apiezon L*			*SF-96*			*QF-1*			*XE-60*			*Carbowax 20M*		
	160°	*200°*	$\Delta I/\Delta T$	*160°*	*200°*	$\Delta I/\Delta T$	*160°*	*180°*	$\Delta I/\Delta T$	*160°*	*200°*	$\Delta I/\Delta T$	*160°*	*200°*	$\Delta I/\Delta T$
1,2-$C_2B_{10}H_{12}$	1312	1336	6.0	1283	1310	6.75	1684	1714	14.7	2010	2086	19.0	2175	2216	10.2
1,7-$C_2B_{10}H_{12}$	1150	1172	5.5	1124	1147	5.6	1370	1401	14.6	1512	1584	18.0	1616	1640	6.0
1,12-$C_2B_{10}H_{12}$	1098	1112	3.5	1070	1083	3.2	1229	1245	7.9	1324	1393	17.2	1418	1438	6.0
2,3-$C_2B_9H_{11}$	1569	1595	6.5	1516	1542	6.6	1742	1779	18.7	1891	1930	9.7	2078	2140	15.5
1,2-$C_2B_8H_{10}$	1132	1148	4.0	1120	1138	4.5	1482	1509	13.2	1754	1824	17.5	1925	1935	2.5
5,6-$C_2B_8H_{12}$	1161	1188	6.75	1114	1135	5.3	1386	1409	11.8	1727	1798	17.75	2174	2213	9.8

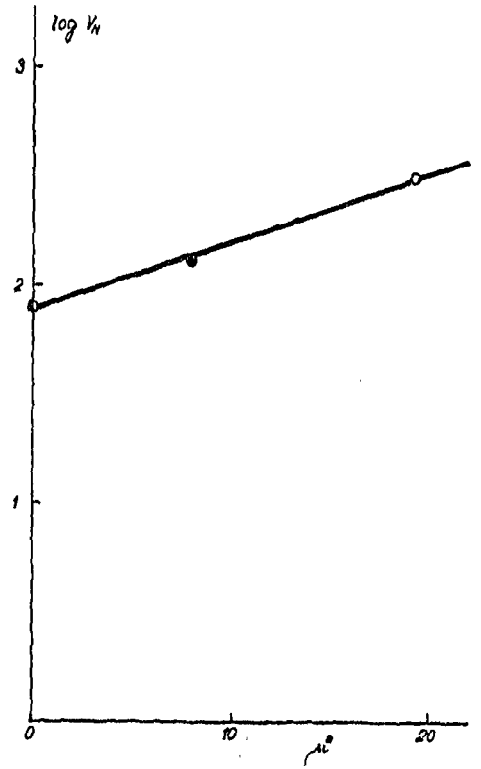

Fig. 1. Dependence of log V_N on μ^2 on QF-1.

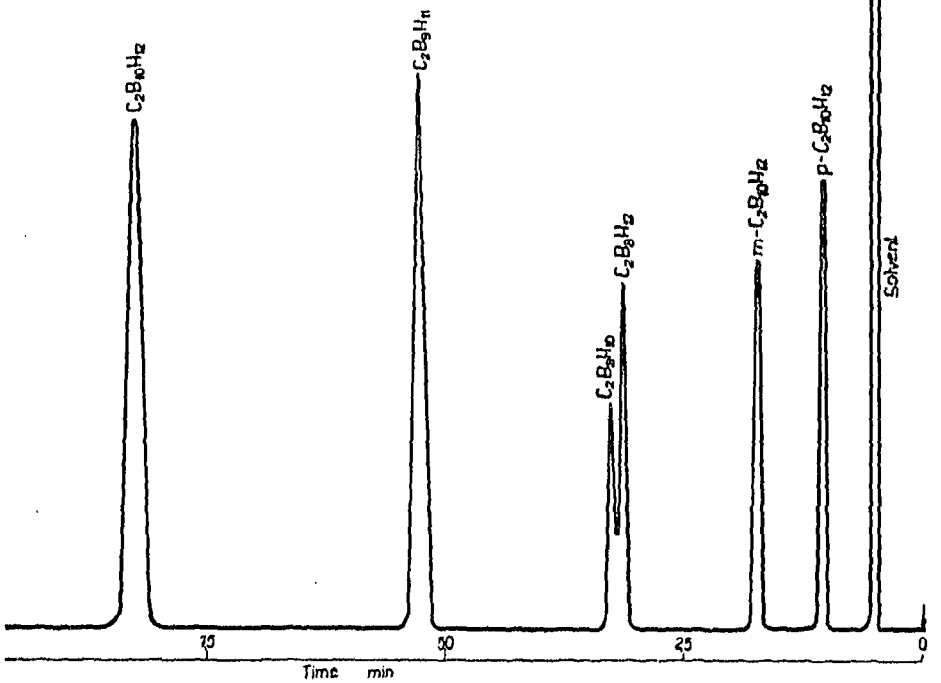

Fig. 2. Separation of carboranes on XE-60 at 180°.

retention. In the *o*-, *m*- and *p*-carborane series log V_N *versus* μ^2 dependence is the same as on QF-1.

The differential molar heats of solution, calculated from the slope of the log V_N *versus* $1/T$ dependence, are given in Table III. These heats, which are a measure of the interaction between the substances chromatographed and the stationary phases used, confirm the conclusions drawn on the basis of the measured retention indices. The lowest heats of solution were obtained on non-polar SF-96, on which the separation of the carboranes studied is poorest. The strongest interactions occur between the carboranes and Carbowax 20M. A strong hydrogen bond interaction is reflected in the high value of $\Delta H_s = 17.05$ kcal/mole for 5,6-$C_2B_8H_{10}$.

TABLE III

MOLAR HEATS OF SOLUTION (kcal/mole) OF CARBORANES ON FIVE STATIONARY PHASES

Carborane	*Apiezon L*	*SF-96*	*QF-1*	*XE-60*	*Carbowax 20M*
1,2-$C_2B_{10}H_{12}$	12.88	11.30	12.59	13.92	17.16
1,7-$C_2B_{10}H_{12}$	11.74	9.54	10.61	10.66	14.27
1,12-$C_2B_{10}H_{12}$	10.93	8.90	9.90	9.56	13.65
2,3-$C_2B_9H_{11}$	15.29	14.84	13.02	14.38	16.75
1,2-$C_2B_8H_{10}$	11.13	9.80	11.62	12.92	16.43
5,6-$C_2B_8H_{12}$	11.89	9.54	10.81	12.19	17.05

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