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Thin-layer chromatography of dicarba-closo-dodecaboranes and their bromoderivatives on silica gel

Thin-layer chromatography (TLC) is the simplest and almost universal method for the separation and identification of less volatile carboranes and their derivatives[1]. The best separation has been achieved on silica gel plates with gypsum as binder[2], although mention has been made of the control of reaction mixtures by chromatography on a layer of Al_2O_3 without a binder[3,4]. This adsorbent has also been used for the preparative separation of mixtures of some mono- and polyhalogen-*o*-carboranes[5].

Limitations in the use of TLC were due mainly to the low sensitivity of carborane compounds towards detection[6]. The 1,2- (I), 1,7- (II) and especially the 1,12-dicarba-closo-dodecaborane (III) nuclei are very stable towards oxidants and the detection was therefore based on the response of the remaining organic part of the molecule. Detection with iodine vapour was useful but the detection threshold was in the range of 10–100 μg or more. An outstanding increase in the sensitivity was achieved by the alkaline degradation of the carborane nucleus to the $C_2B_9H_{12}^-$ (or substituted) anion on the plate followed by spraying with $AgNO_3$ solution[2]. This process is general for all *o*-carboranes (Type I), but is less sensitive for *m*- (II) and insensitive for *p*-carboranes (III).

In this paper we report the identification and separation of *o*-, *m*- and *p*-carboranes and bromo-*o*-carboranes on Silufol silica gel sheets (Kavalier n.p., Votice, Czechoslovakia) with starch as binder. We found that the presence of starch enables carboranes to be made visible by iodine vapours at a concentration of 0.1–1.0 μg in the spot. This detection is universal for all types of carboranes and their derivatives without having any influence on the very high sensitivity.

Experimental

The chromatography was performed on the Silufol sheets with starch as binder. Chromatograms were developed by the ascending technique to a distance of 135 mm in a 20 × 20 × 8 cm tank. The time of development with hexane and chloroform is *ca.* 10 min, and with carbon tetrachloride *ca.* 25 min.

Detection with iodine vapour. The dry, developed chromatogram is immersed for 10–20 sec in the tank saturated with iodine vapour. The carboranes appear as white spots on a pink-violet background. The colour intensity increases during the exposure to air up to a period of 10–20 min, then slowly decreases and after 2 h the colour disappears. The detection is reliable when relative humidity of the air is $>75\%$ or after a short exposure to steam. The highest sensitivity was found for compound I (0.1 μg in the spot), the lowest for compound III (1 μg in the spot). This detection is also useful for the determination of the volatility of appropriate carboranes. On exposure to air, the compounds disappear from the chromatogram according to their volatility, and a second detection with iodine vapour will develop only the remaining less volatile carboranes. In this way, the compounds disappear in the following order: III $>$ II, IVa $>$ I, IVb $\gg$ IVc–e, V, VI.

Detection with silver nitrate. Without previous degradation[2], it is possible to detect directly compounds IVa, Va–c and VI with 5 % $AgNO_3$ in dilute aqueous ammonia or ethylenediamine: they are identified as black spots. This detection can be applied after the detection with iodine vapour, when the colour of the iodine disappears and the white spots change to black. The chromatogram, developed with $AgNO_3$, cannot be detected by using iodine again. The highest sensitivity was found for compound IVa (0.05 µg in the spot).

Results and discussion

The comparison of *o*-carborane (I), *m*-carborane (II), *p*-carborane (III), monobromo-*o*-carboranes (IV; a = 1-Br; b = 3-Br; c = 4-Br; d = 8-Br; e = 9-Br), dibromo-*o*-carboranes (V; a = 9,12-Br_2; b = 1,9-Br_2; c = 1,12-Br_2) and 8,9,12-tribromo-*o*-carborane (VI) showed that the relative R_F values (RR_F) are to a great extent inversely proportional to the dipole moments of the chromatographed compounds (see Table I). On the other hand, very similar R_F values were found for unsubstituted compounds as well as their monobromo, and dibromo derivatives, if they had similar dipole moments (Table I).

TABLE I

RELATIVE R_F VALUES AND DIPOLE MOMENTS OF $C_2B_{10}H_{12}$ ISOMERS AND MONOBROMO-, DIBROMO- AND TRIBROMO-*o*-CARBORANES

S_1 = CCl_4, S_2 = hexane and S_3 = $CHCl_3$.

RR_F^a = R_F value of compound relative to *o*-carborane = 100 (R_F of *o*-carborane in S_1 = 0.29, in S_2 = 0.10).

RR_F^b = R_F value of compound relative to azobenzene = 100 (R_F of azobenzene in S_3 = 0.75).

Compound	*Dipole moment (Debye)*	RR_F^a		RR_F^b
		S_1	S_2	S_3
p-Carborane (III)	0.0 (ref. 7)	260	620	front
m-Carborane (II)	2.8 (ref. 7)	225	450	front
1-Bromo-*o*-carborane (IVa)	3.3 (ref. 8)	203	330	front
1,9-Dibromo-*o*-carborane (Vb)	—	115	90	front
o-Carborane (I)	4.5 (refs. 7–8)	100	100	front
1,12-Dibromo-*o*-carborane (Vc)	—	103	70	front
3-Bromo-*o*-carborane (IVb)	3.7 (ref. 8)	97	80	front
4-Bromo-*o*-carborane (IVc)	4.5 (ref. 8)	52	30	85
8-Bromo-*o*-carborane (IVd)	5.5 (ref. 8)	27	start	75
9-Bromo-*o*-carborane (IVe)	6.0 (ref. 8)	27	start	76
9,12-Dibromo-*o*-carborane (Va)	7.2 (ref. 9)	7	start	56
8,9,12-Tribromo-*o*-carborane (VI)	—	start	start	37
Azobenzene	—	—	80	100

The best separations of compounds I–VI were obtained with carbon tetrachloride, while hexane is advantageous only for compounds with dipole moments < 4 D, and chloroform for compounds with dipole moments > 5 D.

Compounds with similar R_F values can, in some cases, be distinguished by repeated elution. The separation of compounds I, IVb and Vc was successful after a four-fold elution in hexane or carbon tetrachloride.

To distinguish some compounds with similar R_F values, it is possible to use the fact that some isomeric halocarboranes are directly detectable with $AgNO_3$. This is valid for those substituted *o*-carboranes (Type I) where the halogen activates the B-3 skeletal atom, which is easily removed by hydrolysis with the formation of a substituted $C_2B_9H_{12}^-$ anion, which is reactive towards $AgNO_3$. This detection is successful with compounds IVa, Va–c and VI. The stepwise detection with iodine vapour and then silver nitrate makes it possible to distinguish the apparently homogeneous spot of a mixture of I and Vc.

The method described made it possible to identify the products of the thermal rearrangement of compound IVa as a mixture of I, IVa, c and e and Va and c.

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1 S. HEŘMÁNEK, in L. LÁBLER AND V. SCHWARZ (Editors), *Chromatografie na tenké vrstvě*, Nakladatelstvi ČSAV, Prague, 1965, p. 401.
2 S. HEŘMÁNEK, V. GREGOR AND J. PLEŠEK, *Collect. Czech. Chem. Commun.*, 33 (1968) 1609.
3 L. I. ZAKHARKIN AND A. V. GREBENIKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1967) 1376.
4 L. I. ZAKHARKIN, V. N. KALININ, A. P. SNYAKIN AND B. A. KVASOV, *J. Organometal. Chem.*, 18 (1969) 19.
5 V. N. KALININ AND L. I. ZAKHARKIN, *Zh. Obshch. Khim.*, 37 (1967) 1713.
6 S. HEŘMÁNEK, *Thesis*, Pardubice, 1965.
7 A. W. LAUBENGAYER AND W. R. RYSZ, *Inorg. Chem.*, 4 (1965) 1513.
8 V. GREGOR, V. JEHLIČKA AND J. STUCHLÍK, *Collect. Czech. Chem. Commun.*, 37 (1972).
9 R. MARUCA, H. SCHROEDER AND A. W. LAUBENGAYER, *Inorg. Chem.*, 6 (1967) 572.

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