

CHROM. 7235

GAS CHROMATOGRAPHIC SEPARATION OF ISOMERIC HYDROCARBONS OF THE NORBORNANE SERIES ON GRAPHITIZED CARBON BLACK

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SUMMARY

The possibility of using graphitized thermal carbon black for the separation of hydrocarbons, such as methyl-substituted cyclohexanes and alkyl-substituted bicyclo[2.2.1]heptane, has been investigated. The retention sequence found for different isomers makes it possible to draw a conclusion about their structure.

INTRODUCTION

Graphitized thermal carbon black (GTC) is one of the most homogeneous non-specific adsorbents. From this point of view, GTC is useful in the separation of complicated hydrocarbons particularly when the molecules to be separated have similar physical properties but different geometries¹⁻³. The retention sequence depends upon the geometry of the molecules and their orientation on the plane surface and adsorption on an adsorbent is dependent on the distance of the atoms or molecular links from the plane surface of the adsorbent, *i.e.*, on the geometry of the molecules. Substances that have more atoms or molecular links in contact with the adsorbent are retained more strongly⁴.

EXPERIMENTAL

Sterling MT 3100° D4 GTC with a specific surface area of 7.6 m²/g was used as the adsorbent. The pellets of the carbon black were prepared by shaking and the 0.3-0.4-mm fraction was used. The work was carried out on a Pye chromatograph with a β -ionization argon detector. The glass column, 1.20 m long and 2.5 mm I.D., contained 4.4 g of GTC. The flow-rate of argon was 30-40 ml/min and was measured by a soap-film flow meter. The samples of hydrocarbons were introduced in the vapour state with a syringe (without dilution).

The substances investigated were 22 derivatives of bicyclo[2.2.1]heptane (norbornane), containing 8-10 carbon atoms, as well as C₉-C₁₂ polymethylcyclohexanes.

RESULTS AND DISCUSSION

The separation of geometrical isomers of C_9-C_{12} polymethylcyclohexanes, differing by equatorial or axial arrangements of the substituents in the chair configuration of cyclohexane, is very difficult and is possible only by using capillary columns with liquid stationary phases⁵. In our work, these isomers were separated successfully on a short column containing GTC (Fig. 1).

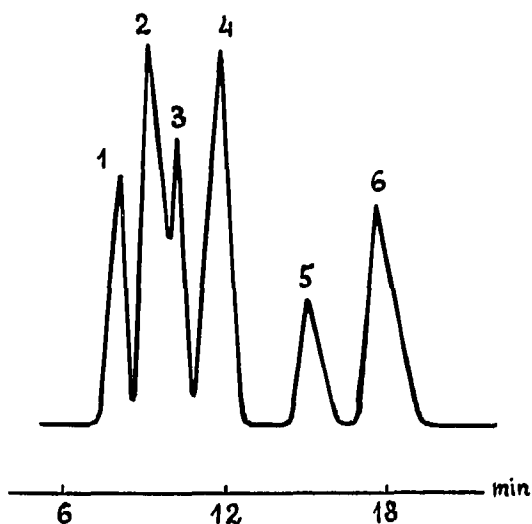
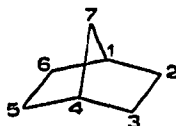


Fig. 1. Chromatogram of the separation of geometrical isomers of 1,2,3,4-tetramethylcyclohexane on a 120 cm \times 2.5 mm I.D. column containing GTC at 160°. Isomers: 1 = *eeaa*; 2 = *eaae*; 3 = *eaea*; 4 = *aeae*; 5 = *eaee*; 6 = *eeee*.

The approximate theoretically calculated potential energies of adsorption on the basal face of graphite were compared with the heats of adsorption at zero coverage obtained from the chromatograms. This comparison made it possible to draw a conclusion about the preferential orientation of the investigated molecule on the surface of GTC. It has been ascertained, for example, that of all the geometrical isomers of polymethylcyclohexane, the last to be eluted from the column containing GTC is the isomer that has all substituents in equatorial positions.

Recently, in oil hydrocarbons with bridge structures have been discovered. The investigation of these hydrocarbons, having one or more substituents, is difficult because of the great number of possible isomers.

Interesting results have been obtained using GTC for the separation of bicyclic hydrocarbons of the bicyclo[2.2.1]heptane (norbornane) series, with a skeleton



The only separation of hydrocarbons of the norbornane series has been achieved by gas-liquid chromatography on efficient capillary columns⁶.

TABLE I

RELATIVE RETENTION VOLUMES OF UNSATURATED HYDROCARBONS OF THE BICYCLO[2.2.1]HEPTANE SERIES

Hydrocarbon	GTC at 100°	Squalane at 90°
<i>endo</i> -5-Methylbicyclo[2.2.1]heptene-2	1.00	1.00
<i>exo</i> -5-Methylbicyclo[2.2.1]heptene-2	1.36	1.02
<i>endo</i> -5-Vinylbicyclo[2.2.1]heptene-2	2.72	1.95
<i>exo</i> -5-Vinylbicyclo[2.2.1]heptene-2	3.65	1.98
<i>cis</i> -5-Ethylidenebicyclo[2.2.1]heptene-2	4.42	2.40
<i>trans</i> -5-Ethylidenebicyclo[2.2.1]heptene-2	3.43	2.50

The molecules of bicycloheptane hydrocarbons differ in their geometrical structure when they have different substituents in different positions. Therefore, one may expect that they can be separated advantageously by gas-solid chromatography on GTC. Of all the bicycloheptanes investigated, the compounds with one substituent (methyl group) are retained less strongly, the 1-position being energetically less advantageous than the 2-position. For dimethylbicycloheptane, substances with two methyl groups on one carbon atom are retained less strongly than the derivatives that have the two substituents on different carbon atoms. It is especially characteristic that all mono- and di-substituted *endo*-isomers of bicycloheptane, both saturated and unsaturated, have absolute retention volumes and heats of adsorption less than those

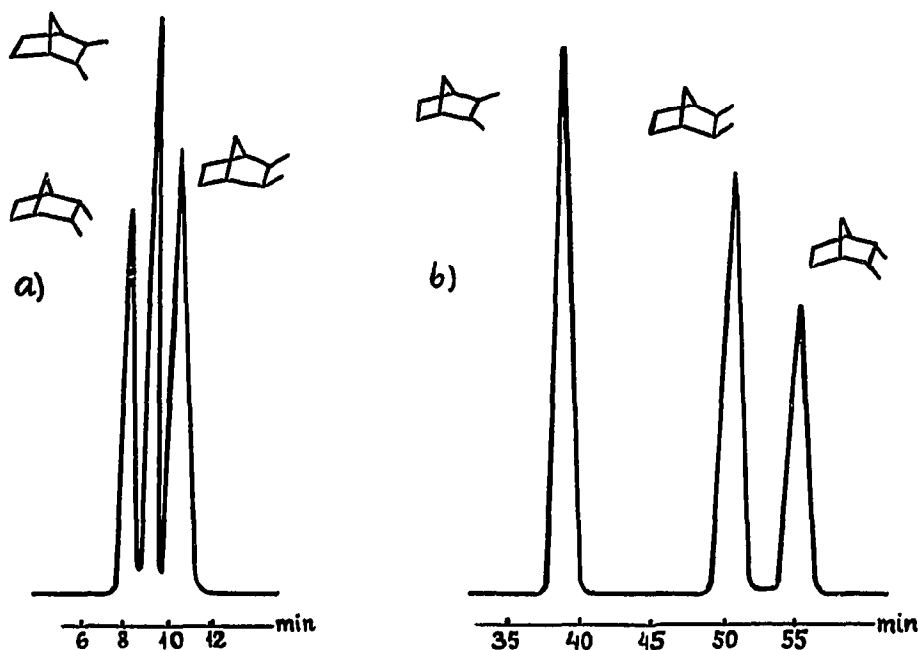


Fig. 2. Chromatogram of the separation of the *endo*- and *exo*-isomers of 2,3-dimethylbicyclo[2.2.1]heptanes (a) on a 120 cm \times 0.25 cm I.D. column containing GTC at 100° and (b) on a 90m \times 0.25 mm I.D. capillary column coated with squalane at 90°.

of the *exo*-isomers⁷. It is evident that in all instances when the molecules have the energetically most advantageous position on the surface, the links of an *endo*-isomer are farther from the basal face of graphite than in the case of the corresponding *exo*-isomer. Also, for every pair of *exo*- and *endo*-isomers, the differences in relative retention volumes on GTC were found to be higher than with liquid phases (Table I).

The differences in retention volumes permitted the separation of all *exo*- and *endo*-isomers in the mixtures investigated. In all instances the separation on GTC was more satisfactory than on capillary columns, although the efficiency of the column with GTC is lower. Also, the separation time on a GTC column is shorter than on a capillary column (Fig. 2).

From the results presented in this paper, it can therefore be concluded that GTC is a good adsorbent for the separation of substances with different geometrical structures.

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