THE INVESTIGATION OF THE STRUCTURE OF MOLECULES BY GAS ADSORPTION CHROMATOGRAPHY

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SUMMARY

The sequence of emergence of substances from the surface of graphitized carbon black principally depends on the energy of the nonspecific interaction, which is connected with the orientation of the molecules on the plane surface. This allows us to use graphitized carbon black successfully, not only for the chromatographic analysis of different isomers but also for the identification of structural isomers. Some examples of identification of the *cis*- and *trans*-configuration of 3-methylpentene-2 and 3,4-dimethylpentene-2 and of the configurations of cyclic hydrocarbons C_6–C_{12} are given.

The energy of adsorption on a flat surface depends upon the geometrical structure of the adsorbate molecules and their orientation on the surface. The influence of the geometrical structure of a molecule on the gas chromatographic separation is especially noticeable when it is adsorbed on graphitized carbon blacks, which are typical of adsorbents with flat surfaces. The adsorption properties of such carbon blacks are principally determined by the properties of the system adsorbate–basal faces of graphite. The adsorption of molecules of different electronic structure on the surface of carbon black is "nonspecific"[1,2] and can be defined by the geometry of the molecule and by the polarizability of its bonds and a special role is played by the number of points of contact with the plane surface of the adsorbent. Therefore, the adsorption energy and the retention volumes determined by gas chromatography depend on the geometrical structure of the molecules. Thus graphitized carbon black can be used successfully not only for the chromatographic analysis of structural isomers and deuterium-substituted molecules, but also for the identification of structural isomers and isotopic molecules.

The interaction of any molecule with the basal face of the graphite depends on dispersion forces. Even in the case of dipole molecules the interaction due to induction is very low. The energy of repulsion is only 35% of the energy of attraction. The additivity of the dispersion interaction and the fact that the molecules of organic compounds are made up of a few atoms or groups allows one to express the potential

energy of interaction with the basal face of graphite by means of a few potential functions of atom–atom interaction or group–atom interaction. For example, for all hydrocarbons the interaction is determined only by two atom–atom potential functions $\varphi_{C...C}$ and $\varphi_{C...H}$ (refs. 3 and 4). These potential functions can be calculated satisfactorily by means of the theory of dispersion interaction[3-5].

The additivity of the energy of adsorption on the basal face of graphite of different molecules is shown in Fig. 1 where we see the calculated values of potential energy of adsorption (for the most advantageous position of molecules) and the measured heats of adsorption at low surface coverages of graphitized carbon black. The theoretically calculated potential functions on graphite Φ are close to the heats of adsorption Q measured by means of gas chromatography, therefore the slope of the curve nears 45°.

In this way, graphitized carbon black is a unique nonspecific adsorbent, and the energy of interaction of all the force centers of the molecule with this adsorbent can be considered additive. The adsorption on such an adsorbent is especially sensitive to the distance of the atoms or molecular links from the plane surface of the adsorbent, *i.e.* to the geometry of the molecule. This property can be used successfully for the analytical separation of structural and stereoisomers on graphitized carbon black[1,3,5-9]. It can, however, also be used for a reverse purpose: that is the determination of the geometrical structure of the molecules by their sequence of emergence and by the values of the retention volumes. This property is of interest in structural chemistry
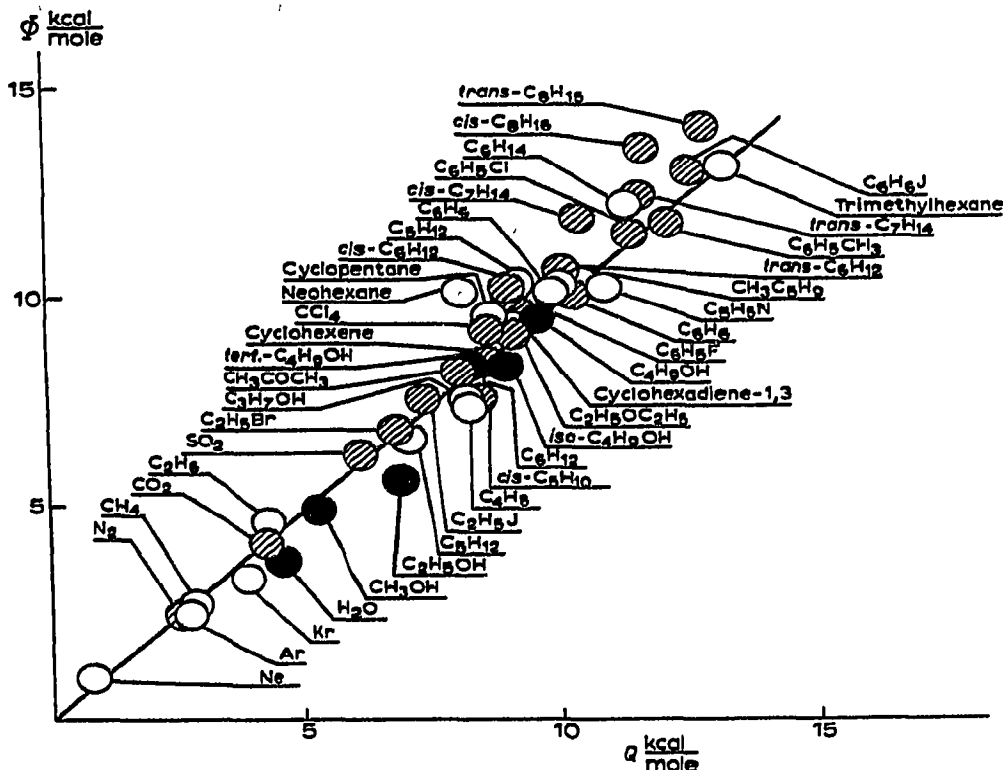

Fig. 1. The potential energies of adsorption (theoretically calculated) Φ for different molecules and heats of adsorption Q of the same compounds on graphitized carbon black obtained experimentally. The slope is 45°.

problems such as the identification and investigation of the structure of *cis*- and *trans*-isomers.

For example, the connection between the structure of the molecules and their adsorption properties on graphitized carbon black can be demonstrated by gas chromatography.

It has already been mentioned that in a series of unsaturated hydrocarbons the *cis*-configurations, having higher boiling points, are retained less strongly than the *trans*-isomers with the same carbon number. Even slight differences in boiling points yield rather different retention times. This is connected with the diverse orientation of the molecules of these isomers. The *trans*-configurations of the olefins have a more advantageous position, energetically, on the surface of graphitized carbon black as compared with the *cis*-isomers. This allowed us to use gas chromatography for the investigation of the structure of *cis*- and *trans*-configurations of 3-methylpentene-2 and 3,4-dimethylpentene-2. In the literature we find contradictory information about the configuration of these compounds and it is difficult to determine which has a *cis*-configuration and which a *trans*. The investigation of the retention volumes and heats of adsorption of these compounds showed that 3-methylpentene-2, with a boiling point of 70.4°, is the first to elute from the column at 65° in 9 min 40 sec and 3-methylpentene-2 with a boiling point of 67.6° in 11 min 34 sec and is the second. This allows us to conclude that the first compound has a *cis*-configuration and the second a *trans*-configuration (Fig. 2). The heat of adsorption of the *cis*-isomer is 9.6 kcal/mole and that of the *trans*-isomer 9.9 kcal/mole.
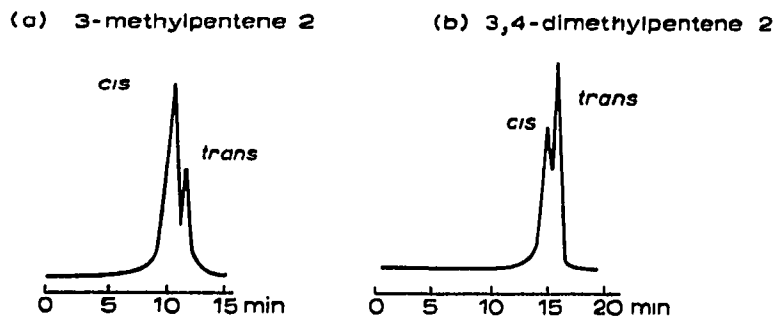
(a) 3-methylpentene 2   (b) 3,4-dimethylpentene 2

Fig. 2. Chromatogram on graphitized thermal carbon black at 65° of (a) 3-methylpentene-2, (b) 3,4-dimethylpentene-2. Column 120 cm × 4 mm; detector β-ionization.

In the case of 3,4-dimethylpentene-2, the mixture of these compounds with boiling point 87° gives two peaks—the first emerging after 15 min 25 sec is the *cis*-configuration. The *trans*-configuration elutes in 16 min 36 sec at 65°. The heat of adsorption of *cis*-3,4-dimethylpentene-2 calculated from the chromatographic values is 10.0 kcal/mole, and for *trans*-3,4-dimethylpentene-2 10.6 kcal/mole.

The energy of a nonspecific interaction decreases rapidly as the distance between the surface and the force centers increases. Therefore the adsorption on the plane faces of particles of graphitized carbon black is very sensitive to the geometrical structure of the molecules.

We have investigated a number of hydrocarbons with six-membered rings (cyclohexane, cyclohexene, cyclohexadiene-1,3 and benzene), but whose molecules differ geometrically and in the number of their hydrogen atoms, while the number of
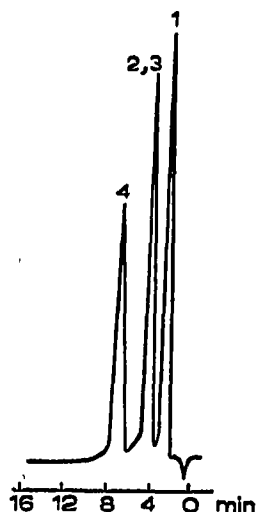
Fig. 3. Chromatogram of separation on graphitized thermal carbon black at 67° of 1 = cyclohexane; 2 = cyclohexene; 3 = 1,3-cyclohexadiene; and 4 = benzene. Column 120 cm × 4 mm; detector β-ionization.
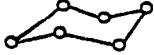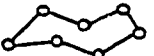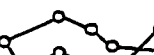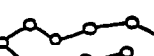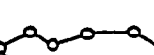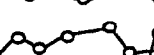
carbon atoms remains the same. Retention volumes, obtained experimentally, and heats of adsorption of these substances show that in this group of cyclic substances an increase of retention volumes and heats of adsorption is observed when we proceed from cyclohexane to benzene (see the chromatogram on Fig. 3). Nevertheless, in this group of substances benzene, although it has both the lowest boiling temperature and the lowest molecular weight, is retained more strongly on the surface of carbon black than the other substances. This confirms once more that the chromatographic behavior of the molecules on the surface of the carbon black depends mainly on their geometrical structure and on their orientation at the surface of the basal graphite face. The molecule of cyclohexane, having a preferential chair configuration, only makes contact with the carbon black surface with three of its carbon atoms, the other three carbon atoms being some distance from the surface. Since cyclohexene and cyclohexadiene-1,3 have flatter molecules, the distance between the carbon atoms and the surface of carbon black becomes shorter, therefore, the energy of interaction with the surface of the adsorbent, which is characterized by the heat of adsorption, increases as the retention volume increases. The differences in retention volumes of cyclohexene and cyclohexadiene-1,3 are not enough for their separation. This allows us to conclude, that cyclohexene and cyclohexadiene-1,3 have similar structural configurations. This sequence of the retention volumes agrees with the values of the potential energy of nonspecific interaction by the adsorption of these substances on the basal face of graphite.

Cyclic hydrocarbons having different configurations are of special interest, even cyclooctane has five configurations. With an increase in the number of carbon atoms the number of configurations increases still further. The information concerning all cyclanes obtained synthetically is far from being available.

Retention volumes of seven cyclic hydrocarbons have been investigated at different temperatures. They were: cyclohexane, cycloheptane, cyclooctane, cyclononane, cyclodecane, cycloundecane and cyclododecane. Their heats of adsorption

TABLE I

HEATS OF ADSORPTION Q AND THE POTENTIAL ENERGY OF ADSORPTION Φ OF C_6-C_{12} CYCLANES ON GRAPHITIZED CARBON BLACK

Compounds	Structure	Mol wt M	Boiling point (°C)	Q kcal/ mole	Φ kcal/ mole
Cyclohexane		84	81.4	8 0	8.0
Cycloheptane		98	117–118	9.2	9.4
Cyclooctane		112	150.7	10.7	9.3 10 5 12.1 13.5
Cyclononane		126	178.4	12.4	12.1
Cyclodecane		140	70.5/11 mm	14.9	14.0
Cycloundecane		154	105–105 2/21	16.1	15.6
Cyclododecane		168		17.7	16.9

and the theoretical potential energy of adsorption were calculated (see Table I). The heat of adsorption of the cyclanes is linear with respect to the number of carbon atoms. The comparison of the heats of adsorption with the calculated potential energies for all possible configurations is only given in Table I for cyclooctane. The most stable configuration in the case of cyclooctane is the crown configuration. The value of the potential energy of adsorption theoretically calculated for this configuration is 10.5 kcal/mole which is in good agreement with the value of the heat of adsorption obtained experimentally, 10.7 kcal/mole. The calculation of the potential energy of adsorption for other configurations of cyclooctane gives the following values: 9.2; 9.3; 12.1 and 13.5 kcal/mole. These values are rather different from the experimental value for the heat of adsorption. Values of potential energies for the most stable configurations of other cyclic hydrocarbons are given in Table I. As is seen from Table I these values are in good agreement with experimental values of heats of adsorption. In the case of undecane it is still not known which configuration is the most stable. The configuration of undecane chosen which is shown in Table I gives a value for the potential energy of adsorption of 15.6 kcal/mole, which approximates to the value of 16.1 kcal/mole for the heat of adsorption obtained experimentally. Thus one may assume that the configuration chosen is correct. The calculation of potential energies for other configurations shows that the values differ considerably from the heat of adsorption obtained experimentally.

From the above examples we can see that gas chromatography on graphitized carbon black can be used not only for analytical purposes, but can also be used in

conjunction with other methods for the investigation of the geometrical structure of molecules.

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