

GRAPHITIZED CARBON BLACK IN GC/MS: PERSPECTIVES IN THE STRUCTURE ELUCIDATION OF NOVEL ISOMERS

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Introduction

The phenomena of isomerism play an important part in organic and physical chemistry. The search and structure elucidation of novel isomers in most cases are related with methods of determination of molecular structure, in particular, NMR and GC/MS. NMR spectroscopy easily performs the structure elucidation of novel isomers that are either individual or rather abundant in a mixture. The structure elucidation of isomers available in a family (or in a sample) only in a minor amounts by this method is hardly possible. GC/MS is more sensitive, as compared to NMR, and, as a rule, solves the problem of a search of novel isomers in composite mixtures. Usually a mass spectra is sufficient to establish the belonging of a novel isomer to its family, but not enough for structure elucidation without an additional data. In this respect seems to be great of interest to consider GC-data as a potential source of an additional structural information.

Experimental

The optimization of hypothetical molecular structures and the molecular-statistical calculations of thermodynamic characteristics of adsorption of PHTX isomers on GTCB were carried out as described before [1]. Atom-atom potential function $\varphi_{s...c(GTCB)}$ were used with the coefficients founded by Buryak et al. [2]. The measurements of mass spectra and thermodynamic characteristics of adsorption were carried out by MAT 112S gas chromatograph - mass spectrometer according the procedure described in detail earlier [3].

Results and Discussion

To contribute to the solution of the problem being discussed the gas chromatography of isomers have to accomplish of two important conditions:

1. It should provide the complete separation of all stable isomers being expected in a sample.
2. It should be possible to predict the separation order of isomers proceeding from their hypothetical structure.

The accomplishment of the first condition now is not difficult. The modern capillary gas-liquid chromatography provides the highest efficiency of separation and a good sensitivity in coupling with MS due to a sharp GC-peaks profile. The latter is very important for minor components of mixtures.

The second condition is the main and much more difficult and implies the possibility of the establishment of quantitative relationships between retention parameters and hypothetical molecular structure of isomers. Now only gas-solid chromatography with graphitized thermal carbon black (GTCB) as an adsorbent corresponds to this requirement. GTCB was investigated in detail in series of fundamental work of A.V.Kiselev, generalized in monograph [4]. As have been found this adsorbent exhibits a unique feature. The intermolecular interaction of an isolated, adsorbed molecule with a homogeneous monatomic flat surface of GTCB and, thence, the thermodynamic characteristics of adsorption and adsorption chromatography at low (zero) surface coverage depend in a large degree on the molecular geometry of the adsorbate. The retention parameters and, consequently, separation order on columns packed with GTCB of adsorbates of known structure can be calculated with a good accuracy using Kiselev's molecular-statistical method (chromatocopy) [5].

This method corresponds to our purpose in hand with the only but important difference that is the way to get atomic coordinates of an adsorbate molecule. According to the traditional approach for this purpose were used an experimentally obtained by independent methods (electron diffraction, X-ray) molecular parameters. In some cases (mainly for aromatic compounds), the molecular geometry have been represented as a simple combination of already known structural parameters [4]. Obviously, in case of novel compounds this approach hardly could be valid. Therefore, recently we encountered a new approach, based on computerized modeling of hypothetical molecular structures [1]. As a test mixture were selected eleven stereoisomers of perhydroanthracene (PHA) and perhydrophenanthrene (PHP), cis-isomers of those are characterized by strong 1,3- and 1,4-diaxial nonvalence intramolecular interactions. The

order of their separation on the column packed with GTCB was calculated using both approaches and compared with the experimental one, which was established earlier [6]. The order of separation calculated on the traditional approach appeared erroneous, whereas the results based on molecular modeling with regard to intermolecular interactions were coincident with the experiment [1].

More complicated objects - stereoisomers of perhydroxanthene (PHX) and perhydrothioxanthene (PHTX) were studied in this work as a further step in the examining of potentialities of GTCB. In contrast to PHA and PHP, in this case along with mixtures, the individual trans-anti-cis and cis-syn-cis isomers of both families were available. This enabled to carry out accurate experimental measurements of thermodynamic characteristics of their adsorption on GTCB by traditional method [3,4] and to compare the obtained values with the calculated ones. For molecular-statistical calculations were used hypothetical molecular structures of these isomers optimized by molecular mechanics.

One of the results of the present study shows Figure 1, where is exhibited the dependence of $\ln K_1$ (K_1 is Henry's constant, subscript "1" refers to zero surface coverage) on reciprocal absolute temperature of GC-column for trans-anti-trans and cis-syn-cis PHTX. The latter forms two conformers (a and b),



a

b

which are under equilibrium due to the inversion of the middle ring. The filled dots, corresponding to the experimental values of $\ln K_1$ for trans-anti-trans PHTX are rather close to the calculated values (straight line). In case of cis-syn-cis PHTX the experimental dots are located more close to the straight line corresponding to conformer b of cis-syn-cis PHTX (0.7 kJ/mol more stable as compared with conformer a).

The calculated thermodynamic characteristics of adsorption for stereoisomers of PHX appeared even more close to the experiment. Due to calculated retention parameters and, therefore, order of separation all theoretically expected stereoisomers of PHX were elucidated in mixtures, in spite of the similarity of their mass spectra.

Conclusions

The lack of the structural specificity of mass spectrometry to novel isomers to a considerable extent compensate for the combination with gas-solid chromatog-

raphy with graphitized thermal carbon black. The obtained results demonstrate that potentialities of this adsorbent in GC/MS could be largely extended providing if modern methods of molecular modeling along with the Kiselev's molecular-statistical method (chromatocopy) are used for a calculation of an separation order of compounds being studied.

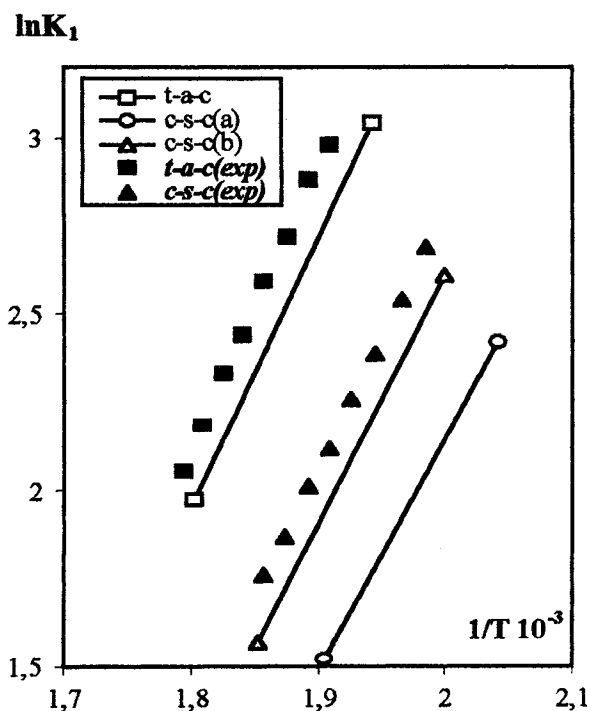


Figure 1. Theoretically calculated and experimentally measured (*exp*) dependencies of $\ln K_1$ vs. $1/T$ for perhydrothioxanthene isomers.

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