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Figure 1 graph

Figure 1: Figure 1 graph

Abstract

Full Text

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DETERMINATION OF THE STRUCTURE OF ISOMERS FROM GAS-CHROMATOGRAPHIC RETENTION PARAMETERS

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Separation of the individual components from a mixture of isomers, determination of their boiling points, and proof of their chemical structure is, in most cases, a rather difficult task. Moreover, the boiling points and relative retained volumes of isomers are not determined by simple regularities. Thus, in the series of xylenes and diisopropylbenzenes the para isomer has the lowest boiling point, whereas in the case of most other dialkylbenzenes this property is possessed by the meta isomer. Similar anomalies in boiling points are also known for ortho isomers of the benzene series, as well as for cis and trans isomers of olefinic hydrocarbons and dialkylcyclohexanes. Therefore, it is of considerable interest to establish the affiliation of a substance with a definite isomeric series on the basis of gas-chromatographic retention parameters. Apparently, assignment of dialkylbenzenes to the ortho, meta, and para series cannot be reliable when the known gas-chromatographic relationships of the logarithm of the retained volume to the absolute temperature and to the structure of the substance are used (1-4). For example, the dependences shown in Fig. 1 of the logarithms of the retained volumes on polypropylene glycol on the logarithms of the retained volumes on squalane for isomeric dialkylbenzenes do not make it possible with complete confidence to assign a compound to the ortho, meta, or para series. On the other hand, use of the Kovats regularities (5, 6) requires knowledge of the true boiling points and, consequently, is possible only for substances that have already been described.

Fig. 1. Dependence of the logarithm of the retained volume on polypropylene glycol on the logarithm of the retained volume on squalane. *a, b, c*—ortho, meta, and para isomers of dialkylbenzenes, respectively.

While working on the analysis of mixtures of isomeric dialkylbenzenes, we found that if, as a parameter, one uses the ratio of the retained volumes, taken with respect to some standard substance, on two columns with stationary phases of different nature, then such a parameter K proves to depend on the mutual

Fig. 2. Dependence of the coefficient K on the mutual position of alkyl substituents

Figure 2: Fig. 2. Dependence of the coefficient K on the mutual position of alkyl substituents

Fig. 3. Dependence of the coefficient K on the number of carbon atoms

Figure 3: Fig. 3. Dependence of the coefficient K on the number of carbon atoms

positions of the substituents in dialkylbenzenes. Let $V_{\mathrm{I}}^{\mathrm{st}}$ and $V_{\mathrm{II}}^{\mathrm{st}}$ be the retained volume of the standard substance on phase I and on phase II, respectively. V_{I}^{o} and V_{II}^{o}, V_{I}^{m}, V_{II}^{m}, and V_{I}^{p}, V_{II}^{p} are the retained volumes of the ortho, meta, and para isomers on phase I and on phase II, respectively. Then, as we have been able to show, the following equalities hold:

$$K^{o} = K^{m} + a = K^{p} + 2a, \tag{1}$$

where

$$K^{0} = \frac{V_{\mathrm{I}}^{0}/V_{\mathrm{I}}^{\mathrm{st}}}{V_{\mathrm{II}}^{0}/V_{\mathrm{II}}^{\mathrm{st}}}; \qquad K^{m} = \frac{V_{\mathrm{I}}^{m}/V_{\mathrm{I}}^{\mathrm{st}}}{V_{\mathrm{II}}^{m}/V_{\mathrm{I}}^{\mathrm{st}}}; \qquad K^{p} = \frac{V_{\mathrm{I}}^{p}/V_{\mathrm{I}}^{\mathrm{st}}}{V_{\mathrm{II}}^{p}/V_{\mathrm{II}}^{\mathrm{st}}};$$

α is a coefficient numerically corresponding to the change in the values of K.

The experimental data are presented in Fig. 2. On the basis of the equalities established by us (1) and Fig. 2, it follows that the value of the coefficient α is constant in the transition from the ortho- to the meta- and from the meta- to the para-isomer. This constancy of α within a group of isomers characterizes the structural correspondence of the phase and of the various dialkylbenzenes dissolved in it.

Fig. 2. Dependence of the coefficient K on the mutual position of alkyl substituents

Fig. 3. Dependence of the coefficient K on the number of carbon atoms

In Fig. 3 are presented dependences of K on the structure of the substance; from them it is evident that the values of K decrease with increasing molecular weight of the components. It is significant that for all substances, irrespective of vapor pressure and the order of elution of the isomers, one may write:

$$K^{0} > K^{m} > K^{p},$$

where K^{0}, K^{m}, K^{p} are the values of the coefficients K for the ortho-, meta-, and para-isomers, respectively. In this sense our method for establishing the structure of isomers has a certain analogy with the method of Hively [7], by which a characteristic inequality was likewise derived for cis- and trans-forms of dialkylethylenes.

Experimental part. The values of the retention volumes of isomeric dialkylbenzenes C_8–C_{14} were obtained using steel capillary columns l–90 m, with internal diameter 0.25 mm, with polypropylene glycol (phase I) and squalane (phase II) as stationary phases. The chromatograms were recorded at a temperature of 125°. The carrier gas was helium. Inlet pressure, 1.5 atm. Flame-ionization detection. The standard substance was ethylbenzene.

Using isomeric dialkylbenzenes as an example, a method has been developed for establishing whether a substance belongs to the ortho-, meta-, or para-series on the basis of gas-chromatographic retention parameters.

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