APPLICATION OF QUANTUM CHEMICAL CALCULATIONS TO THE IDENTIFICATION OF POSITIONAL ISOMERS OF POLYSUBSTITUTED ALKYLBENZENES

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Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

The problem of assignment of positional isomers of alkylbenzenes to chromatographic peaks is addressed. Probable structures are attributed based on the correlation of stabilities of the isomers, which are expressed as the total molecular energies calculated by the MINDO/3 semiempirical quantum chemical method, and the proportions of the isomers in the reaction mixture. Multicomponent alkylbenzene mixtures were prepared and separated by capillary gas chromatography, and the identity of the isomers was confirmed by the gas chromatography–mass spectrometry combination.

The analysis of multicomponent hydrocarbon mixtures, i.e. identification of the components and their quantitation in the mixture, is an important task of analytical chemistry in the petrochemical industry. High resolution capillary gas chromatography (HRCGC) and high performance liquid chromatography (HPLC) are conventionally used to solve this problem. However, data obtained by chromatographic separation are not sufficient to analyze the multicomponent mixtures in detail, and so additional experimental and theoretical methods are necessary to characterize the individual components.

Among the most powerful tools providing information on components in mixtures is the gas chromatography–mass spectrometry (GC–MS) combination. This combination makes use of the assets of both techniques – the exceedingly high separating efficiency of gas chromatography and the selectivity of mass spectrometry. The two analytical systems can be directly linked by using capillary chromatographic columns. The combination gives characteristic data of the mixture components but fails to provide sufficient information on the isomers.

Alkylbenzenes with numbers of carbon atoms exceeding ten have many isomers (for example, C_{12} has 134 isomers), and so sufficient retention characteristics from capillary

GC (usually performed on the OV-101 stationary phase) or mass spectra are lacking. Therefore, identification of higher alkylbenzenes based on a comparison of published retention characteristics is impossible.

Papers[1,2] were concerned with the problem of identification of alkylbenzenes with the numbers of carbon atoms C_{11} and C_{12}. Higher alkylbenzene standards were prepared by alkylation of benzenes or alkylbenzenes with haloalkanes. The results of synthesis were mixtures which in gas chromatographic analysis exhibited as many as over 30 components, which was due to the possibility of formation of several isomers as a result of isomerization, disproportionation and transalkylation reactions. The components were characterized by capillary GC on the OV-101 stationary phase at 100 and 120 °C and by the GC–MS combination[2].

In the analysis, the probable structures were attributed to the chromatographic peaks based on the GC–MS measurements and by using correlations between the structure and the retention characteristics (such as the Kováts retention indices or the homomorphous factors), and making use of published data. Nevertheless, the correct structure could not always be attributed because some homologous series starting with higher numbers of carbon atoms could not be set up. Mass spectrometry fails to identify the isomers in this case, and so this technique was only employed to determine the numbers of carbon atoms in the components and to identify their alkyl substituents. Therefore, theoretical methods which address the relationships between the structure of the component (its physico-chemical properties) and its retention characteristics[3 - 12] (Quantitative Structure–Retention Relationships, QSRR) have to be resorted to.

In our work[3] we centered on the modelling of alkylbenzenes in GC using the OV-101 phase. We used a thermodynamic model which made it possible to express the relation between the retention of alkylbenzenes and the theoretically calculated Gibbs energy of retention (solvation). Correlation analysis between the Kováts retention indices and the Gibbs energy of retention for seven homologous alkylbenzene series provided correlation equations with a high statistical significance of regression. The equations can be used for a fairly accurate prediction of the retention indices (RI) of higher alkylbenzene homologues in a given homologous series.

In the present work we examined the feasibility of applying quantum chemical methods to the solution of the problem of identification of positional isomers of polysubstituted alkylbenzenes.

EXPERIMENTAL

Synthetic mixed standards were prepared[1] by alkylation of benzene or alkylbenzene with alkyl halides in the presence of $AlCl_3$. Chromatographic analyses were performed on a Model 2350 gas chromatograph (Carlo Erba, Milan) equipped with a flame ionization detector and a split injection system. A glass column (50 m × 0.24 mm) containing the OV-101 stationary phase[1] (0.35 μm) was used; the carrier gas was nitrogen at a flow rate of 10 cm/s under isothermal conditions (100, 120 °C).

GC–MS measurements were carried out on an HP 5995 instrument[2] (Hewlett–Packard, Avondale, U.S.A.).

Samples were injected either after dilution with acetone and addition of $C_7 - C_{14}$ alkanes, or in the concentrated state, using 1 μl and 10 μl Hamilton syringes. The peak areas were expressed as the products of the peak heights h and the half peak widths $w_{1/2}$, which were measured with a calibrated magnifying glass with a precision of ± 0.05 mm.

The quantum chemical calculations were accomplished by using the program GEOMO[13] implemented on an IBM 360 computer. Of the feasible semiempirical quantum chemical methods, MINDO/3 (ref.[14]) appeared to suit well for the calculation of the total molecular energies of alkylbenzenes and comparison of the relative stability of the isomers. Standard geometries taken from ref.[15] were used for the MINDO/3 calculations, and the torsional angles of the alkyl substituents bonded to the benzene rings were optimized[16].

RESULTS AND DISCUSSION

The quantum chemical approach to this problem is based on the hypothesis that isomers of a given alkylbenzene are the more stable, the more negative (lower) are their total molecular energies. Furthermore, it is assumed that in the equilibrium reaction mixture, the proportion of a given isomer, hence its chromatographic peak area, is the higher the higher is its stability. The fact that the equilibrium was reached in the reaction mixture was confirmed by the time invariable areas of the chromatographic peaks. Kinetic effects, if any, were disregarded.

The alkylbenzene isomers, the calculated total molecular energies and the chromatographic peak areas are given in Tables I and II. Here A/A_{min} is the ratio of the peak

TABLE I

Calculated total molecular energies E_{tot} and chromatographic peak areas A for alkylbenzene isomers whose structures were attributed by the "homomorphous factor" method

Sample No.	Benzene derivative	E_{tot} kJ mol^{-1}	A mm^2	A/A_{min}
1	1,2,3-Me_3-5-Et	−157 486.57	450.0	75.0
	1,2,4-Me_3-5-Et	−157 482.59	449.2	74.9
	1,2,4-Me_3-6-Et	−157 474.87	99.5	16.6
	1,3,5-Me_3-2-Et	−157 470.77	96.6	16.1
	1,2,3-Me_3-4-Et	−157 460.20	6.0	1.0
	1,2,4-Me_3-3-Et	−157 448.51	–	–
2	1,3-Me_2-5-Pr	−157 532.18	338.1	9.9
	1,2-Me_2-4-Pr	−157 515.33	–	–
	1,4-Me_2-2-Pr	−157 505.36	212.2	6.2
	1,3-Me_2-4-Pr	−157 497.60	212.2	6.2
	1,2-Me_2-3-Pr	−157 482.94	92.3	3.0
	1,3-Me_2-2-Pr	−157 478.23	34.1	1.0

area of the benzene derivative under study to the smallest peak area in the series (hence, for the smallest peak this ratio is 1). In Table I, the chromatographic peaks were attributed to the isomers based on correlation between the structure and retention characteristics (homomorphous factors)[2]. Isomers for which no peak areas are given were eluted together with other alkylbenzenes, as confirmed by mass spectrometry. Table I shows that the isomer that emerged as the most stable from the calculation is identical with that attributed based on the "homomorphous factor" method. The agreement of the two approaches also holds qualitatively for the majority of the remaining isomers. For illustration, Fig. 1 shows the chromatogram of analysis of mixed sample No. 1, viz. product of alkylation of ethylbenzene with methyl iodide, chromatographed in a capillary column containing the OV-101 phase under isothermal conditions. In the analysis of the sample diluted with acetone by GC–MS, the presence of a rather small number of positional isomers of the alkylbenzenes was confirmed. A significantly higher number of isomers were identified by direct analysis of synthetic samples; a part of the chromatogram of sample No. 1 with the studied isomers of trimethylethylbenzenes is shown in Fig. 2.

Table II gives data for methylethylpropylbenzene isomers where the possible homologous series begins with the first member where the number of carbon atoms is C_{12}.

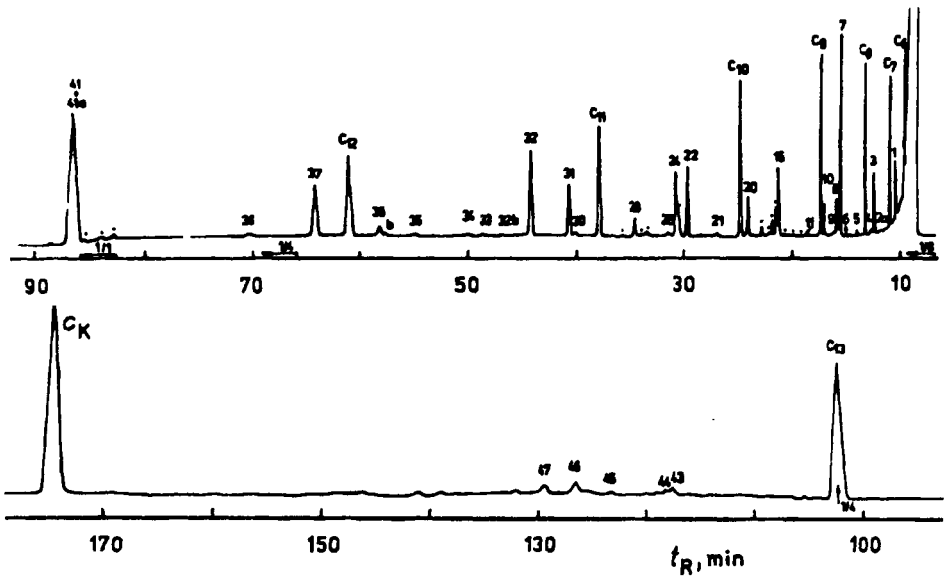

FIG. 1

Chromatogram from the separation of alkanes and products of alkylation of ethylbenzene with methyl iodide (sample No. 1 diluted with acetone) in a capillary column containing the OV-101 phase under isothermal conditions (120 °C); $C_6 - C_{13}$ alkanes, peaks 1 – 47 alkylbenzene mixture

Due to the lack of standards of higher alkylbenzenes, the problem of structure assignment can only be approached by calculation. The proposed assignment of the probable structures is based on the relation between the isomer stability (in terms of the total molecular energy) and the chromatographic peak area. Figures 3 and 4 show the chromatogram of the synthetic mixed sample and a part of the chromatogram from the direct injection of the synthetic mixture where the studied isomers were confirmed by GC–MS, respectively.

The relation between the molecular mass and structure parameters (substitution position and the alkyl chain nature) on the one side and the retention of the separated

TABLE II

Proposed structure assignment of methylethylpropylbenzene isomers based on their calculated total molecular energies of E_{tot}, and the chromatographic peak areas A

Sample No.	Benzene derivative	E_{tot} kJ mol^{-1}	A mm^2	A/A_{min}
3	1-Me-3-Et-5-Pr	-172 645.83	572.0	20.0
	1-Me-4-Et-2-Pr	-172 619.66	35.8	1.2
	1-Me-2-Et-4-Pr	-172 619.62	32.5	1.1
	1-Me-3-Et-6-Pr	-172 619.00	30.6	1.1
	1-Me-4-Et-3-Pr	-172 616.01	28.6	1.0
	1-Me-2-Et-5-Pr	-172 606.64	–	–
	1-Me-3-Et-4-Pr	-172 606.64	–	–
	1-Me-3-Et-2-Pr	-172 597.44	–	–
	1-Me-2-Et-6-Pr	-172 584.90	–	–
	1-Me-2-Et-3-Pr	-172 572.53	–	–

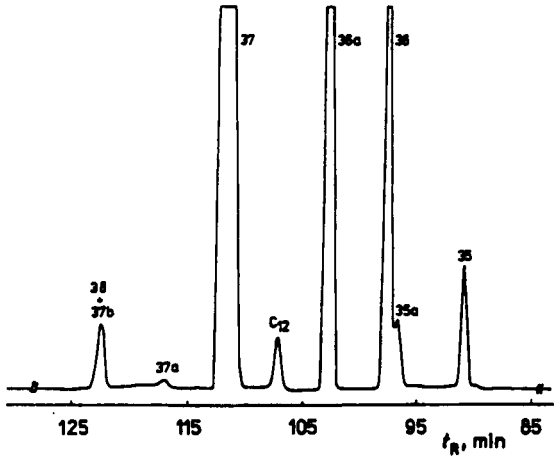

FIG. 2

A part of the chromatogram of the separation of components of sample No. 1 – positional isomers of trimethylethylbenzenes and triethylbenzenes; direct injection of products of alkylation of ethylbenzene with methyl iodide, capillary column containing the OV-101 phase, isothermal conditions (100 °C). Benzene derivative peaks: 35 1,2,4-Me_3-6-Et; 35a 1,3,5-Me_3-2-Et; 36 1,2,3-Me_3-5-Et; 36a 1,2,4-Me_3-5-Et; 37 1,3,5-Et_3; 37a 1,2,3-Me_3-4-Et; 37b 1,2,4-Me_3-Et; 38 1,2,4-Et_3; C_{12} dodecane

alkylbenzenes on the other side has also been studied chemometrically by multiparameter correlation analysis[17]. An equation has been set up[18] for the calculation and prediction of the retention indices and temperature coefficients (dI/dT) of alkylbenzenes on the OV-101 phase. A good correlation has been obtained for 94 alkylbenzenes investigated, including those included in Table I. The feasibility of employing the above equation for prediction was tested on the series of methylethylpropylbenzene isomers. The agreement with the structure assignment proposed in Table II was good for the majority of isomers.

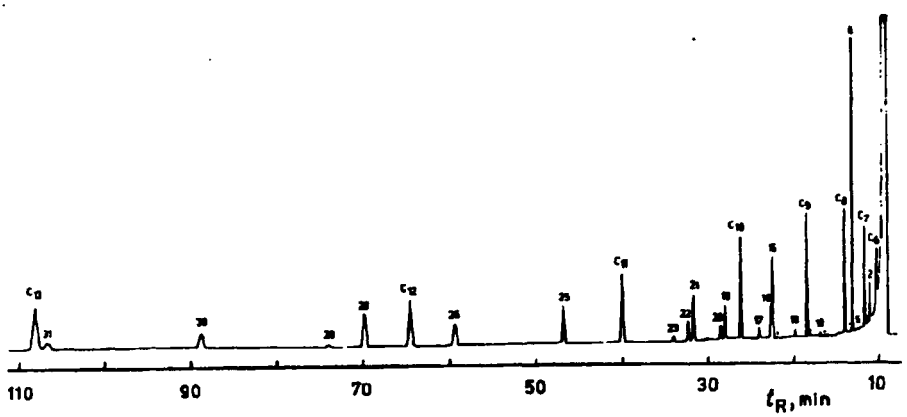

FIG. 3

Chromatogram from the separation of alkanes and products of alkylation of toluene with a mixture of ethyl and propyl bromides (sample No. 3 diluted with acetone) in a capillary column containing the OV-101 phase under isothermal conditions (120 °C); $C_6 - C_{13}$ alkanes, peaks 2 – 31 alkylbenzenes

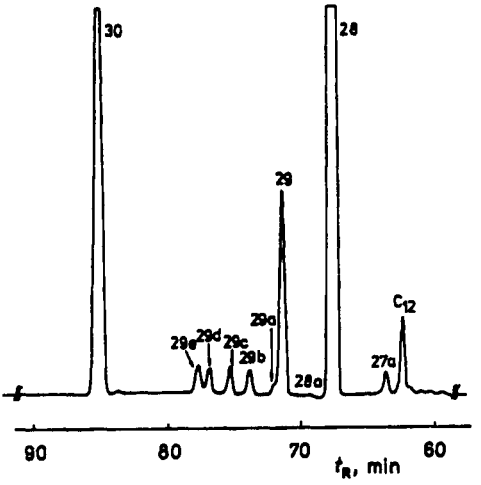

FIG. 4

A part of the chromatogram of the separation of components of sample No. 3 – positional isomers of methylethylpropylbenzenes – in a capillary column containing the OV-101 phase. Benzene derivative peaks: **27a** Me-Et-isoPr; 28 1-Me-3-Et-5-Pr; 29 Me-di-isoPr; 29b 1-Me-4-Et-3-Pr; 29c 1-Me-2-Et-4-Pr; 29d 1-Me-3-Et-6-Pr; **29e** 1-Me-4-Et-2-Pr; C_{12} dodecane; **29a** unidentified compound

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