ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 8, pp. 1391–1399. © Pleiades Publishing, Ltd., 2012.
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Chromato-Mass-Spectrometric Identification Using Partition Coefficients in the System of Hexane–2,2,2-Trifluoroethanol

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Received December 1, 2011

Abstract—An additional characteristic of organic compounds, the partition coefficients in the heterophase solvent system *n*-hexane–2,2,2-trifluoroethanol, is shown to be useful for refining the results of chromatographic and gas chromatography–mass spectrometric identification. This opportunity is the most important for compounds that were not yet characterized by either mass spectra or chromatographic retention indices.

DOI: 10.1134/S1070363212080105

The most effective nowadays method for identification of trace organic compounds in complex mixtures is the gas chromatography–mass spectrometry. The objective reasons of this consist in the high informativity of mass spectra (multidimensional analytic parameters), complete "computerization" of data processing, the availability of efficient algorithms for interpreting mass spectrometric data and, more important, the availability of a sufficiently detailed database of mass spectra. For example, the latest version of the database NIST11/2011/EPA/NIH (2011) includes 243 893 standard (electron ionization) mass spectra of 212 961 compound [1]. However, the performance of mass spectrometry in no way precludes the use of known methods of chromatographic identification, primarily those based on the use of retention indices (*RI*). Although being objectively less informative (one-dimensional parameters), they allow to distinguish many types of compounds with almost identical mass spectra, including structural isomers. At the same time, the use of only the *RI* values, without any additional information, is not sufficient for unequivocal identification, so they are usually *combined* with other characteristics of the test compounds. Thus, one of the recommendations is the parallel determination of *RI* by varying the polarity of stationary phases [2,3], but in the case of multicomponent mixtures this can lead to a significant uncertainty of the results. Among all the chromatographic techniques, perhaps the only one remains important up to now: the so-called gas chromato-partition method [4, 5]. It involves the characterization of the analytes partition coefficients ($K_{\text{part.}}$) in a two-component heterophase systems formed by organic solvents partially soluble in each other. The $K_{\text{part.}}$ values are usually expressed as a ratio of equilibrium mass-volume concentrations in a nonpolar (c_1) and polar (c_2) layers. Hence, the analysis of each layer of the heterophase system is required to determine $K_{\text{part.}}$, which roughly doubles the total time of the measurement:

$$K_{\text{part.}} = c_1/c_2 \approx S_1/S_2, \tag{1}$$

where S_1 and S_2 are the peak areas of the respective component measured at equal volumes of the respective layers.

An important advantage of this technique is that it, unlike the determination of *RI* on the phases of different polarity, completely eliminates the ambiguity at comparing the signals of a compound in various chromatograms.

In determining the $K_{\text{part.}}$ using Eq. (1) the results accuracy depends on the constancy of the ratio c_1/c_2 and reproducibility of measurements of the peak absolute area. To provide the condition $c_1/c_2 \approx$ const, the total concentration of analytes in heterophase systems should not exceed about 3% [5]. To assess the influence of the second factor, the known relation (2) is used, in which the relative standard deviation (coefficients of variation, $\delta X = s_X/X$) is marked by δ:

$$\delta K_{\text{part.}} = [\delta S_1^2 + \delta S_2^2]^{1/2}. \qquad (2)$$

In order to reduce the influence of the dosing accuracy on the accuracy of $K_{\text{part.}}$, an internal reference is added sometimes to the heterophase system with known $K_{\text{part.}}$ value, so the absolute peak area can be replaced by the more reproducible relative area:

$$K'_{\text{part.}} \approx K_{\text{part.ref.}}\,(S_1/S_{\text{ref.1}})/(S_2/S_{\text{ref.2}}), \qquad (3)$$

where $S_{\text{ref.1}}$ and $S_{\text{ref.2}}$ are the reference peaks area in layer 1 and 2, respectively.

$$\delta K'_{\text{part.}} = [\delta K_{\text{part.ref2}} + \delta(S_1/S_{\text{ref.1}})^2 + \delta(S_2/S_{\text{ref.2}})^2]^{1/2}. \qquad (4)$$

However, actually: $\delta(S_i/S_{\text{ref.i}})^2 < \delta S_i^2 < \delta S_i^2 + \delta S_{\text{ref.i}}^2$, but $\delta K_{\text{part.ref}} \approx \delta K_{\text{part.}}$, so, in general, $\delta K'_{\text{part.}} > \delta K$ and, consequently, the use of internal standards do not reduce the random errors in the determination of partition coefficients.

General requirements for sample preparation in gas chromato-partition method are similar to the well-known guidelines for the preparation of derivatives (derivatization) of the test compounds for the chromatographic analysis [6]. To obtain the derivatives, the sample is treated with an excess of reagent (the exact amount is not determined commonly) and, sometimes left to stand for some time to complete the reaction (heat is permissible). In the second case (at the measuring $K_{\text{part.}}$) a part of the sample is dosed into a heterophase system, stirred vigorously and, after splitting the system, each layer is analyzed separately. It is desirable to avoid keeping the samples at a controlled temperature since the contributions to the $K_{\text{part.}}$ variations due to variations of ambient temperature should not exceed the random errors at the dosage, estimated by the expressions (2) and (4).

One of the most interesting algorithms of using $K_{\text{part.}}$ in conjunction with retention indices is the ability to classify analytes according to homologous series (group identification) and the use of differential analysis parameter j [5]:

$$j = k\,RI - \log K_{\text{part.}}, \qquad (5)$$

where the coefficient $k = 10^{-2} \log K_{\text{part.}}(\text{CH}_2)$ is proportional to the difference in free solvation energies of homologous difference CH_2 in the two phases of the system [5]; it characterizes selectivity of the system with respect to different homologous series.

The values of k and j are calculated by the method of least-squares from the data for the known analytes, and then they can be used for group identification of the homologs of the same series not characterized previously. The applicability of this relation was shown by the example of heterophase systems hexane–acetonitrile [5], hexane–nitromethane [7] and hexane–2,2,2-trifluoroethanol [8]. A feature of the latter system is that its polar component contains active hydrogen atoms. Among such systems, only the heptane–2,2,2-trifluoroethanol combination has previously been described [9], for which the values of $K_{\text{part.}}$ of various compounds were measured and a possibility of calculating them using multilinear regression equations were demonstrated. However, the features of heterophase systems containing polar components with active hydrogen atoms for identification of analytes so far have not been characterized in detail.

The present work considers the capabilities and features of refining interpretation of the results of chromatographic and gas chromatography–mass spectrometry data for identification of organic compounds using the partition coefficients in the hexane–2,2,2-trifluoroethanol system.

There are no chemical constraints of the use of polar solvents containing active hydrogen atoms in the hydroxy groups in the chromato-partition method. The value of $\text{p}K_a$ of 2,2,2-trifluoroethanol is 12.4 [10], which is higher than, for example, the value of $\text{p}K_a$ used in gas chromato-partition method for nitromethane [7] (a CH acid, $\text{p}K_a = 10.4$). However, a common problem in application of any polar solvent is the presence of uncontrolled water impurities [11], which may significantly affect the value of $K_{\text{part.}}$.

The effect of water impurities in a polar solvent on the values of partition coefficients. Comparing the published results of studies, it may be noted that unfortunately in measuring the partition coefficients the testing of water content in polar solvent, as well as removal of water when its content is too high, are often neglected. This can introduce significant additional errors in the measurement of $K_{\text{part.}}$ because the impurity of such polar compound as water ($\varepsilon \sim 78$–80, $\mu \sim 1.8$ D) in the polar solvent affects the mutual solubility of the components of heterophase systems and, consequently, the value of $K_{\text{part.}}$. The NIST database illustrated a considerable scatter in the data on the mutual solubility of nonpolar and polar organic solvents caused probably by the presence of water in the polar component [12]. For example, the solubility of acetonitrile in hexane according to various estimates falls to the range from 2.87 to 6.02 wt % at the same temperature 298.2 K.

Table 1. Effect of trace amounts of water in the polar solvent (before and after drying with the molecular sieves) on the partition coefficients of organic compounds in the hexane–2,2,2–trifluoroethanol heterophase system

Compound	$K_{\text{part.}} \pm s_K$ (water content 1.1 wt %)	$K_{\text{part.}} \pm s_K$ (water content < 0.01 wt %)
Low polar compounds ($K_{\text{part.}} > 1$)		
1-Bromodecane	37.1±1.6	37.1±0.6
p-Pentylbenzene	13.6±1.5	13.2±0.2
1-Bromo-4-methylbenzene	5.5±0.1	5.5±0.1
Compounds of moderate polarity ($K_{\text{part.}} < 1$)		
n-Butyl acetate	0.23±0.05	0.13±0.01
n-Hexyl acetate	0.35±0.04	0.22±0.02
2-Hexanone	0.16±0.04	0.08±0.01
2-Heptanone	0.20±0.03	0.10±0.02

Another example of the adverse effects of water contained in polar solvents is given in [13]. To obtain trimethylsilyl derivatives of the analyzed compounds in the 0.5 ml of *n*-hexane and 0.5 ml of nitromethane (Aldrich) containing 1 mg of the studied compound Kotowska et al. [13] had to add to the mixture 20 μl of pyridine and 50 (!) μl of *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA). The necessity to use large amounts of silylating reagent is due to the fact that it mainly reacted with the water admixture in the nitromethane (hydrolyzed) and not with the analyte. As a result, the concentration of additional components in the polar layer reaches ~(20 + 50)/(500 + 20 + 50) ≈ 12%, well above the recommended permissible value of ~3% [5] and, hence, leads to the inevitable distortions of all $K_{\text{part.}}$ values identified in [13].

The need of drying polar organic solvents used for the determination of $K_{\text{part.}}$ has been mentioned specifically in several articles. In the case of aprotic compounds (acetonitrile [5], nitromethane [7]) it is possible to use anhydrous magnesium sulfate for this purpose. In the case of hydroxy-containing solvents (including 2,2,2-trifluoroethanol) it is preferable to use molecular sieves [8]. Table 1 illustrates the effect of impurity of water in the polar component of the hexane–2,2,2-trifluoroethanol system on the values of $K_{\text{part.}}$ of some compounds (a more complete version of Table 1 is given in [8]). While the values of $K_{\text{part.}} > 1$ for weakly polar compounds (alkyl bromides, alkylarenes) with variations in the water content from 1.1 to < 0.01wt% (below the limit of detection using katharometer) remain practically the constant, the value of $K_{\text{part.}} < 1$ of the compounds of medium polarity is reduced 1.6–2.0-fold.[1]

Consequently, it is necessary to check the water content in polar organic solvents forming heterophase systems and, if necessary, to carry out their dehydration. The example (3) below shows that some compensation of the water effect on the value of $K_{\text{part.}}$ can be obtained at the stage of data processing, but, in general, this leads to additional errors in the results.

The partition coefficients in the hexane–2,2,2-trifluoroethanol system of 67 compounds belonging to 12 homologous series were measured in [8]. Combining these data with the *RI* reference values for standard nonpolar polydimethylsiloxane stationary phases allows us the estimation of the value of the differential parameter *j* [Eq. (5)] for 13 homologous series. The values obtained are listed in Table 2 in comparison with the *j* values for the same series in the system of hexane–acetonitrile.

Features of the hexane–2,2,2-trifluoroethanol heterophase system. The most significant distinction of the heterophase system hexane–2,2,2-trifluoroethanol from the previously characterized systems of hexane–acetonitrile [5] and hexane–nitromethane [7] consists in the closeness of the parameters *j* in the series of compounds containing the same heteroatoms but differing in the values of the

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[1] In keeping with the used terms the compounds with $K_{\text{part.}} \approx 0$ should be classed as strongly polar where the influence of trace quantities of water is negligible.

Table 2. The values of the *j* parameter [Eq. (5)] in the system hexane–2,2,2-trifluoroethanol (**I**) for some homologous series [8] (in ascending order) in comparison with the values of the *j* parameter of the same series in the hexane–acetonitrile system (**II**) [5]

Homologous series	General formula[a]	$j \pm 2s_j$ (**I**)	$j \pm s_j$ (**II**)
Alkanes	C_nH_{2n+2} (0)	–0.17±0.06	–0.40±0.07
Alkenes	C_nH_{2n} (1)	0.20±0.18	–0.19±0.09
Alkyl iodides	$C_nH_{2n+1}I$ (0)	0.64±0.04	0.62±0.18
Alkyl bromides	$C_nH_{2n+1}Br$ (0)	0.69±0.08	0.60±0.04
Alkylarenes	C_nH_{2n-6} (4)	0.84±0.04	0.70±0.05
Aryl bromides	$C_nH_{2n-7}Br$ (4)	0.96±0.04	1.00±0.09[b]
Alkyl trihloracetates	$C_nH_{2n-3}O_2Cl_3$ (1)	1.52±0.08	1.18±0.07
Alkyl benzoates	$C_nH_{2n-8}O_2$ (5)	1.58±0.04	1.68±0.25
Alkyl acetates	$C_nH_{2n}O_2$ (1)	2.26±0.08	1.02±0.12
Alkanols	$C_nH_{2n+2}O$ (0)	2.37±0.06	1.61±0.12
Alkanones	$C_nH_{2n}O$ (1)	2.41±0.04	1.23±0.11
Arylalkanols	$C_nH_{2n-6}O$ (4)	2.65±0.16	–
Alkyl aryl ketones	$C_nH_{2n-8}O$ (5)	2.79±0.10	1.69±0.08

[a] The values of formal incertainty are given in parentheses. [b] Rating by additive scheme using the values of *j* for alkylarenes, alkyl bromides, and alkanes.

formal unsaturation (*FU*) by unity. They include such pairs of series as alkanols (2.37±0.03) and alkanones (2.41±0.02), arylalkanols (2.65±0.08) and alkyl aryl ketones (2.79±0.05). In all these cases, the difference in the parameter *j* does not exceed the sum of the corresponding standard deviations, $|j_1–j_2| < (s_1 + s_2)$, which was not observed for the previously investigated heterophase systems. Thus, when the hexane–2,2,2-trifluoroethanol system is used for the homologous series of compounds differing by structural fragments C–X and C=X (at least for X = C, O), the *j* values are close. Apparently, the reason for this is the fundamentally different nature of intermolecular interactions of analytes with polar solvents lacking or containing functional groups with active hydrogen atoms (in the latter case the main interaction is apparently the hydrogen bonding). No less interesting properties of this system is the similarity of *j* values of alkanols (2.37±0.03) and alkyl acetates (2.26±0.04), as well as the fact that the *j* value of alkyl benzoates (1.58±0.02) is much smaller than that of alkyl acetates (2.26±0.04). These features of the combined hexane–2,2,2-trifluoroethanol solvent, on the one hand, reduce the informativity of the $K_{part.}$ values, but, on the other hand, can be effectively used for the identification of unknown substances [see example (3)]. The difference between the maximum and minimum *j* values listed in Table 2 is 2.79–0.17 = 2.62 for the system hexane–2,2,2-trifluoroethanol {value of the coefficient *k* in Eq. (5) is $(1.67\pm0.12)\times10^{-3}$] and 1.69 – (–0.40) = 2.09 for the system hexane–acetonitrile [$k = (1.0\pm0.2)\times10^{-3}$ [5]}, which illustrates the great selectivity of the first of them in relation to different homologous series.

The use of a heterophase system hexane–2,2,2-trifluoroethanol in the chromatographic and chromatography–mass spectrometric identification. The simplest version of the identification of individual components of analyzed samples includes an independent comparison of the retention indices (*RI*) and the partition coefficients ($K_{part.}$) with reference data. The same is used for the group identification (assignment to the respective homologous series): it is based on the combinations of *RI* and $K_{part.}$ in the form of differential parameter *j*. After the assignment to a series, further refinement of the structure of the homolog is performed, based on the detailed interpretation of the *RI* values.

Example (1). An illustration of the "standard" use of hexane–2,2,2-trifluoroethanol system is the identification of major components of essential oils of cow parsnip (*Heracleum*) [14], which include a limited

Table 3. Retention indices, partition coefficients, and *j* parameters used for the identification of the products of reaction of cyclohexanone with PCl_5 [see example (2)]

RI	$K_{part.}$	*j*	Δ*j*	Result of the identification
981±2	5.3	0.91		1,1-Dichlorocyclohexane
1188±2	2.3	1.62	0.71	1,1,2-Trichlorocyclohexane
1414±2	1.1	2.32	0.70	1*r*-*cis*-2-*trans*-3-*cis*-4-Tetrachlorocyclohexane

number of series of the compounds, mainly monoterpenes $C_{10}H_{16}$ and alkyl alkanoates RCO_2R'. But more interesting is the possibility to use the chromato-partition method for the identification of compounds that have never been characterized previously by mass spectra, gas chromatographic retention indices or the partition coefficients.

Example (2). Application of chromato-partition method is effective in the identification of the products of regio nonselective organic reactions even in the absence of pre-defined $K_{part.}$ values of the components of the reaction mixtures and/or *j* parameters of the corresponding series. As an example consider the identification of the minor product of the reaction between cyclohexanone and phosphorus pentachloride, the main ones being 1,1-dichlorocyclohexane and 1,1,2-trichlorocyclohexane [15]. Among the minor components, a compound with *RI* = 1414±2 predominated. The determination of *RI* and $K_{part.}$ of these products in a heterophase system hexane–2,2,2-trifluoroethanol (they regularly decrease from 5.3 to 1.1, which is consistent with the increasing number of chlorine atoms in the molecule) allows the evaluation of the corresponding *j* values (listed in Table 3). The difference between the *j* values of 1,1,2-trichlorocyclohexane and 1,1-dichlorocyclohexane (0.71) corresponds to the increment of the chlorine atom. Note that the *j* value of the compound with *IR* = 1414 differs from the *j* value of 1,1,2-trichlorocyclohexane by almost the same magnitude (Δ*j* = 0.70). Such additivity evidences that this product should be attributed unambiguously to tetrachlorcyclohexanes. Further refinement of its structure requires a comparison of the *RI* value of this component with the estimates of *RI* values for all the isomeric tetrachlorocyclohexanes (including diastereomers) by the additive scheme considered in [16], which indicates the highest probability of the 1*r*-*cis*-2-*trans*-3-*cis*-4-tetrachlorocyclohexane. Note that in this example the identification is carried out without the involvement of the mass spectrometric information, but only on the basis of gas chromatographic data.

Hence the regularities in the changes of the parameters like $K_{part.}$, $\Delta K_{part.}$, *j*, and Δ*j* in the taxonomic groups of isomers, homologs (the variable structural fragment is the homologous difference), and of congeners (the variable structural fragment is the number of heteroatoms or functional groups) in dependence on the type of the structural variations in the organic molecules can be represented as follows:

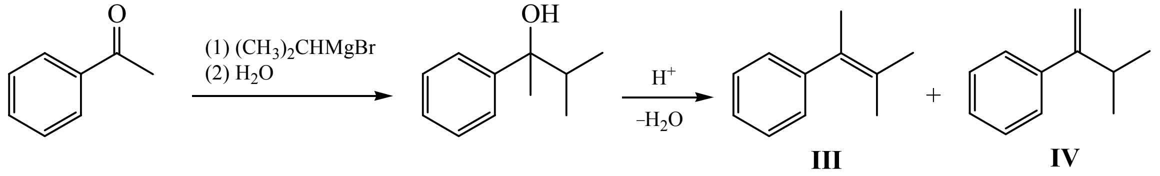
Taxonomic group of organic compounds	$K_{part.}$	$\Delta K_{part.}$	*j*	Δ*j*
Isomers	≈ const	–	≈ const	–
Homologs	≠ const	≈ const	≈ const	–
Congeners	≠ const	≠ const, sign($\Delta K_{part.}$) = const	≠ const	≈ const

These capabilities of the chromato-partition method confirm its effectiveness in solving such problems as the identification of products of alkylation of arenes [17], which include not only a large number of isomers, but, in some cases, homologs (a consequence of the fragmentation of the intermediately formed carbenium ions). It is appropriate to note that such a comparison of trends in the values of $K_{part.}$, $\Delta K_{part.}$, *j*, and Δ*j*, rather than their absolute values, for the identification of the sample components belonging to different taxonomic groups is valid for any heterophase system. Such systems may not necessarily be the two-component, that is, the removal of the water traces (third component) from the polar solvents is not necessary, and the total concentration of analytes in such systems can significantly exceed the allowable ~3% for the determination of $K_{part.}$ [5]. Similar principles form the basis of the rapid chromatographic monitoring of the “heterogeneity” of multicomponent samples [18].

The last example concerns one of the complicated cases of identification of previously unknown compounds using the partition coefficients in the heterophase system hexane–2,2,2-trifluoroethanol taking into account specific features of the system.

Example (3). In a sample of (1,2-dimethyl-1-propenyl)benzene stored for a long time eight components were revealed in an amount exceeding 1%. Table 4 shows their absolute retention times, estimated relative content in the mixture obtained by internal normalization, retention indices obtained by two modes of analysis, partition coefficients in the system of hexane–2,2,2-trifluoroethanol, the corresponding values of the j parameter, and the standard mass spectra. A feature of this example is the use of 2,2,2-trifluoroethanol that has not been preliminary dried, which requires an additional correction of the $K_{\text{part.}}$ values.

The mass spectrometric data allow us to identify some of the detected components, but some of these results require further clarification using the RI values. The detected compounds are α-phenylethyl alcohol (**I**) ($RI_{\text{exp.}}$= 1060±1, $RI_{\text{ref.}}$ = 1048±11), acetophenone (**II**) ($RI_{\text{exp.}}$= 1065±1, $RI_{\text{ref.}}$ = 1041±9), pentenylbenzene [the main component of **III,** the responses include (1-isopropylethenyl)benzene], pentenylbenzene with undetermined structure **IV**, and butyrophenone **VI**. The $RI_{\text{exp.}}$ = 1188±2 of the last component does not match $RI_{\text{ref.}}$ = 1225±12 of butyrophenone, so it must be identified as isobutyrophenone ($RI_{\text{ref.}}$ = 1174±12). It is reasonable to assume that the main component of the mixture is the expected (1,2-dimethyl-1-propenyl) benzene, but it is not directly supported by the uncertain results of mass spectrometric identification. The set of revealed minor components clearly points to the scheme of synthesis of this compound on the basis of acetophenone, since from the practice of monitoring the purity of chemicals it is known that they usually contain traces of substances used in the final stages of their synthesis:



The retention index of the main component (1094±2) corresponds to the reference value $RI_{\text{ref.}}$ of (1,2-dimethyl-1-propenyl)benzene (1094±3) that allows its unambiguous identification, despite the uncertainty of the interpretation of mass spectra. As for the second isomer $C_{11}H_{14}$ ($RI_{\text{exp.}}$ = 1112±2, $RI_{\text{ref.}}$ is unknown), it naturally must be identified as (1-isopropylethenyl)benzene, consistently with the estimates of boiling points of isomers obtained by using the ACD software: 191.7±7.0°C (isomer **III**) and 199.9±7.0°C (isomer **IV**) [19].

Two components of the sample, **V** and **VII,** are characterized by the same molecular weight (M = 162) and similar mass spectra [main signals belong to fragmentation ions with even mass numbers, $(m/z)^{100}$ = 104] and hence they are isomers. Due to unique nature of their mass spectra the results of their identification using the NIST database[1] are negative. In such cases, to solve the problem, all of the available analytical parameters should be used, including partition coefficients in heterophase solvent systems.

The influence of traces of water in polar solvents on the values of $K_{\text{part.}}$ of the compounds with moderate polarity ($K_{\text{part.}}$ <1, in this example the compounds **II**, **V**, **VI**, and **VIII**) can be partially compensated by introducing corrections accounting for the j values. To do this, one must either add to the analyzed sample the compounds with known j value, or use the data for the components already present in the mixture. In this case, two of them (acetophenone **II**, j = 2.44, and isobutyrophenone **VI**, j = 2.35) belong to the series of alkyl aryl ketones that have been characterized (j = 2.79±0.05, Table 2), hence, Δj = 0.35 and 0.44, respectively (mean value is 0.40). Table 4 lists the $j_{\text{corr.}}$ values adjusted for this correction. Their comparison shows that all values are in the range 2.57–2.84, that is, correspond to the j values of arylalkanols (2.65±0.08) and aryl alkyl ketones (2.79±0.05), as well as the respective isomeric compounds with the same molecular formulas $C_{11}H_{14}O$ and $C_{11}H_{12}O$.

Taking into account the above chemical information (method of synthesis and prolonged

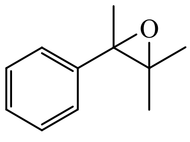
Table 4. The chromatographic and mass spectrometric characterization of the components in the sample of (1,2-dimethyl-1-propenyl)benzene [see example (3)]

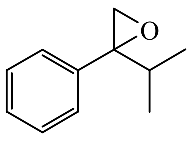
Comp. no.[a]	Relative content in the mixture, %	Retention index[b]	$K_{part.}$[c]	j[d] ($j_{corr.}$)	Mass spectrum [$m/z \geq 40$, $I_{rel.} \geq 2\%$]
I (9.46)	~1	1068±3, 1060±1	–	–	123(4), 122(39) [*M*], 121(4), 108(8), 107(100), 104(3), 91(2), 80(7), 79(97), 78(20), 77(36), 74(2), 65(2), 63(3), 53(9), 52(5), 51(18), 50 (6), 45(4), 43(28)
II (9.59)	~1	1077±3, 1065±1	0.23	2.44 (2.84)	121(4), 120(41) [*M*], 106(8), 105(100), 78(8), 77(82), 76(3), 75(2), 74 (3), 65(2), 63(2), 52(3), 51(30), 50(11), 43(13)
III (10.65)	55	1094±2, 1102±1	9.6	0.84	147(6), 146(43) [*M*], 145(5), 132(12), 131(100), 130(3), 129(11), 128 (6), 127(2), 117(5), 116(10), 115(10), 105(3), 104(5), 103(27), 102(5), 92(4), 91(41), 89(2), 79(2), 78(4), 77(19), 76(3), 75(2), 68(4), 67(4), 65(6), 64(4), 63(3), 53(5), 52(2), 51(11), 50(3), 41(4)
IV (11.09)	18	1112±2, 1117±1	9.2	0.89	147(8), 146(75) [*M*], 145(12), 132(11), 131(100), 130(5), 129(17), 128(10), 127(4), 118(2), 117(10), 116(14), 115(16), 105(10), 104(2), 103(9), 102(3), 92(4), 91(49), 89(3), 78(5), 77(13), 76(2), 71(2), 68 (2), 67(5), 65(7), 64(5), 63(4), 58(2), 53(7), 52(2), 51(10), 50(3), 41(6)
V (12.14)	5	1147±2, 1154±1	0.56	2.17 (2.57)	163(2), 162(17) [*M*], 161(62), 147(5), 143(2), 129(2), 121(2), 120(3), 119(9), 105(18), 104(100), 103(41), 102(4), 91(8), 79(5), 78(58), 77 (27), 76(3), 65(2), 63(3), 59(6), 52(4), 51(13), 50(4), 43(18), 41(6)
VI (13.46)	11	1188±2, 1201±1	0.43	2.35 (2.75)	148(12) [*M*], 106(8), 105(100), 78(3), 77(40), 76(2), 51(12), 50(3), 43 (2), 41(3)
VII (13.94)	2	1211±3, 1218±1	–	–	162(5) [*M*], 147(8), 129(3), 128(3), 119(7), 115(2), 105(10), 104(100), 103(13), 102(4), 91(11), 79(2), 78(12), 77(13), 76(2), 74(3), 65(2), 63 (2), 60(2), 59(52), 52(2), 51(7), 50(2), 43(13), 41(6)
VIII (14.21)	7	1225±3, 1228±1	–	2.23 (2.63)	163(3), 162(34) [*M*], 161(100), 147(11), 143(5), 134(2), 133(14), 132 (2), 131(15), 130(2), 129(9), 128(5), 121(2), 120(5), 119(13), 118(5), 117(50), 116(8), 115(33), 105(13), 104(2), 103(4), 102(2), 92(7), 91 (83), 90(2), 89(4), 79(2), 78(7), 77(17), 76(2), 71(3), 65(12), 64(3), 63 (5), 57(2), 55(6), 53(3), 52(2), 51(14), 50(4), 43(17), 41(8)

[a] The retention time for the option 3 is given in parentheses. [b] The values of *RI* for options 1 and 3, respectively. [c] The partition coefficients are determined with the option 2 and calculated using the *RI* for option 1. For the minor components (< 1–2%), the determination of $K_{part.}$ with an acceptable accuracy is impossible. [d] The values of *j* are calculated using *RI* determined with option 1, $K_{part.}$ with option 2. $j_{corr.}$ is the *j* value for compounds of moderate polarity ($K_{part.}$ < 1) corrected according to the data for acetone and isobutyrophenone.

keeping of the test sample), the compounds with the molecular formula $C_{11}H_{12}O$ ($M = 162$) can be assigned to the series of arylalkanols, arylalkenols and aryl-substituted cyclic ethers (in all cases different types of coupling of different structural fragments of molecules are possible). However, the unique characteristics of the mass spectra of isomers **V** and **VII** [$(m/z)^{100} = 104$], allows the exclusion of all options save aryl-substituted oxiranes. Actually only the known mass spectra of the compounds of this class beginning with the simplest representatives contain the peaks of fragment ions with even mass numbers. For example, the mass spectra of (*E*)- and (*Z*)-2-methyl-3-phenyloxiranes ($M = 134$) which contain a structural fragment >CH–CH_3 show characteristic peaks of the ions $[M - CH_3CHO]^+$ with $(m/z)^{100} = 90$ [1]. Consequently, the presence in the molecular structure of compounds **V** and **VII** ($M = 162$) of the fragment >$C(CH_3)_2$ should give rise to the peaks of the homolog ions $[M - (CH_3)_2CO]^+$, with $m/z = 104$.

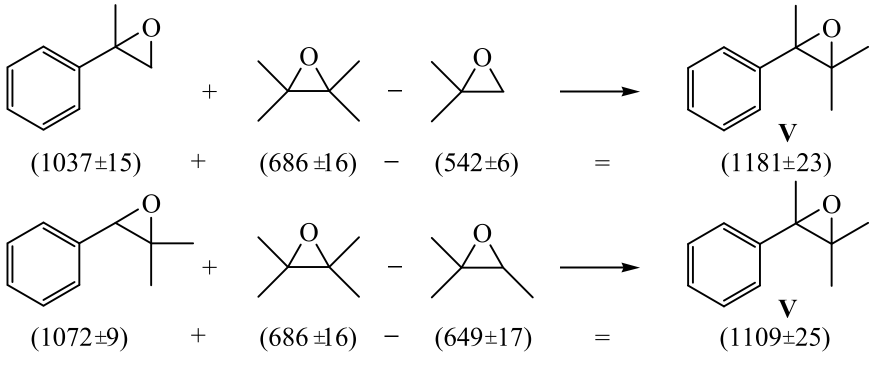
Thus, the compounds **V** and **VII** are isomeric oxiranes corresponding to the isomeric alkenylbenzenes **III** and **IV**:


V



VII

This assumption is confirmed by the ratio of such isomers (~5:2, similar to 55:18) and a similarity in the sequence of their gas chromatographic elution. The latter follows from the estimates of boiling points using the ACD software: 212.9±9.0°C (trimethylphenyloxirane) and 227.9±9.0°C [2-(1-methylethyl)-2-phenyloxirane]. Getting the absolute estimates of *RI* for such strained structures is difficult, but, as a first approximation, we can apply the algorithm involving the calculation of *RI* by analogy with the schemes of "assembling" the target structures from less complex precursors [20, 21]:



The two obtained *RI* estimates differ considerably, but their average value (1145±34) agrees with the experimental value of the *RI* of compound **V** (1147±2).

The mass spectrum of the last component detected in the sample with M = 162 and *RI* = 1225±3 (**VIII**) also cannot be identified using the database [1]. Given the value of $j_{\mathrm{corr.}}$ of this compound (2.63), we can assume that it belongs to the series of arylalkenols, but unequivocal establishment of its structure is not possible. Additive estimates similar to the above do not coincide with the experimental *RI* values for any of the proposed structures.

Thus, using the mass spectra, chromatographic retention parameters, and partition coefficients in heterophase systems we showed in this example that in the alkenylbenzene sample during its storage the respective oxiranes accumulated. It is possible that they are not the primary products of oxidation, but originate from the intermediately formed hydroperoxides. As for the partition coefficients proper, we can conclude that they do not belong to the most informative analytical parameters, but in combination with other characteristics of the analytes are certainly useful in solving the problems of identification.

EXPERIMENTAL

Determination of water in 2,2,2-trifluoroethanol. Gas chromatographic determination of water content in 2,2,2-trifluoroethanol was performed by the method of adding a reference substance [11]. Conditions of analysis: chromatograph GCHF 18.3 with a thermal conductivity detector, the circuit current 170 mA, column 2 m×4 mm, sorbent SEPARON BD, column temperature 190°C, evaporator temperature 200°C. Dosing was performed with a MSH-10 syringe, sample volume 2 μl. Under identical conditions initial samples and those with the addition of a known amount of water (100 μl water per 5 μl of 2,2,2-trifluoroethanol, dilution of samples is not taken into account) were analyzed.

To eliminate the influence of the water traces on the partition coefficients of polar compounds, trifluoroethanol was dried over zeolites NaX pre-calcined at a temperature of 300°C for 4 h. The initial water content in trifluoroethanol varied within 1.0–1.5 wt %, after drying, it was below the detection limit (0.01 wt %).

Determination of partition coefficients in heterophase system hexane–2,2,2-trifluoroethanol. In order to determine $K_{\mathrm{part.}}$, in a stoppered 10 ml vial containing 0.5–2 ml of hexane and 0.5–2 ml of 2,2,2-trifluoroethanol was dosed 10–50 μl of analyzed sample so that the total concentration of all components based on the total volume of the solvent should not exceed 2%. The resulting two-phase system was intensively shaken for 5–10 s and then, after separation of layers, each layer was analyzed.

Determination of $K_{\mathrm{part.}}$ was performed by analysis of equal volumes of each phase of the solvent system in accordance with the guidelines given in [5]. Dosing of samples was carried out with a MSH-10 syringe, the sample volume 3.2 μl. The $K_{\mathrm{part.}}$ value was taken equal to the ratio of the peak areas of each component in two layers, $K_{\mathrm{part.}} \approx S_1/S_2$.

Gas chromatographic analysis was performed on a Biokhrom-1 chromatograph with a flame ionization detector and a WCOT quartz column 25 m × 0.20 mm filled with OV-101 (film thickness 0.20 mm), ramp from 60 to 220°C at the rate 6°C min^{-1}, carrier gas nitrogen, linear rate 20 cm s^{-1}, split ratio 1:30, the evaporator temperature 200°C, detector temperature 250°C (mode 1), and on a Tsvet-100 chromatograph with a flame ionization detector and glass column 3 m × 3 mm packed with 5% SE-30 on Chromaton N (0.20–0.25 mm), ramp from 60 to 200°C at the rate 6.4°C min^{-1} (mode 2). Carrier gas nitrogen, the flow volume rate 30 ml min^{-1}, evaporator temperature 200°C. To measure the peak areas a TR-2213 integrator and UniChrom software (version 4.x-5) was used. In order to determine the semi-logarithmic retention indices, to the analyzed samples was added a mixture of reference *n*-alkanes C_8–C_{14}; for the *RI* calculation the program QBasic contained in the manual [22] was used and the Microsoft Excel software. The source of *RI* reference values is the NIST database [1].

Chromatography–mass spectrometry analysis of the sample of (1,2-dimethyl-1-propenyl)benzene (no. 3) was performed on a gas chromatograph–mass spectrometer QP-2010 Plus (Shimadzu, Japan) using a WCOT quartz column 25 m×0.20 mm with a stationary phase DB-5 MS (0.33 mm film thickness) at ramp from 50°C (1 min) to 200°C (10 min) at the rate 10°C min^{-1} (option 3). The temperature of evaporator 250°C, interface 280°C, ion source 200°C. Sample volume 0.1 ml, split ratio 1:150. The ionization energy 70 eV, mass range 35–450 Da.

The reaction conditions of cyclohexanone with phosphorus pentachloride in CCl_4 are in line with the recommendations of [15]. The sample of (2,3-dimethyl-1-propenyl)benzene [bp 67.5°C (9 mm Hg), n_D^{20} 1.5985, d_4^{20} 0.9004] is selected from the collection of prof. B.V. Ioffe (St. Petersburg State University).

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