PHYSICAL CHEMISTRY OF SEPARATION PROCESSES. CHROMATOGRAPHY

Relationship between Gas Chromatographic Retention Indices and Chemical Shifts in the 13C NMR Spectra of Structural Isomers of Compounds of Tetracoordinated Phosphorus

A. K. Zhokhov, P. V. Fomenko, A. M. Aparkin, and E. B. Belousov

Central Experimental Scientific and Research Institute 33, RF Ministry of Defense, Vol'sk-18, Saratov oblast, 412918 Russia
e-mail: may.50@mail.ru

Abstract—A method for determining the gas chromatographic retention indices of structural isomers of compounds of tetracoordinated phosphorus, based on the correlation between chemical shifts in 13C nuclear magnetic resonance (NMR) spectra and the retention indices of the structural isomers, and on the theory of intermolecular interactions, is proposed. The capabilities of the method are demonstrated for structural isomers of O-alkylmethylfluorophosphonates, which are typical representatives of compounds from the class of tetracoordinated phosphonates. The results from using the correlation approach are compared to experimental data.

Keywords: gas chromatographic retention indices, structural isomers, chemical shifts in 13C nuclear magnetic resonance spectra, intermolecular interactions, gas chromatographic system, static polarizability, charges, compounds of the class of tetracoordinated phosphorus, O-alkylmethylfluorophosphonates.

INTRODUCTION

Measurements of physical and chemical characteristics (boiling temperature, volatility, dipole moment, and Henry constants) are normally used to determine gas chromatographic retention indices (RIs) [1–4]. At present, very few RIs are known for compounds of the class of O-alkylmethylfluorophosphonates, which are typical representatives of tetracoordinated phosphorus compounds. On the other hand, the data in [1–3] testify to the need for and practical significance of developing new methods for determining gas chromatographic retention indices for compounds of this class and products of their destruction for, e.g., environmental monitoring [5]. To develop new methods of RI determination, it is necessary in turn to improve the current methodological approaches while considering the level of modern analytical methods [6, 7].

The aim of this work was to develop a method for determining the gas chromatographic retention indices of structural isomers of O-alkylmethylfluorophosphonates, based on the correlation between chemical shifts in 13C nuclear magnetic resonance spectra and the retention indices of structural isomers using the theory of intermolecular interactions.

The relationship between intermolecular interaction and gas chromatographic characteristics was described in [8–10]. In [8] in particular, the relationship between gas chromatographic RIs and the parameters of intermolecular interactions, calculated using the following equation, was demonstrated:

$$R_i = 100[n + \ln(K_1/K_n)/\ln(K_{n+1}/K_n)],$$

where $K_1 < K_n < K_{n+1}$ are Henry constants, and n is the index for an n-alkane containing n number of carbons.

The procedure for calculating the Henry constants is in turn described by the equations

$$K_i = (A\rho_i \exp X_i)/X_i^{0.5},$$

$$X_i = -Q_i(U_0/RT + 0.5),$$

$$\rho_i = 0.5 + [(\pi/\alpha)^{0.5}Q^{0.5}]/2F_i,$$

where A is a constant proportional to the Van der Waals size of adsorbent atoms and is equal to 10×10^{-4} μm; R is a gas constant, 8.314 J/(K mol); T is absolute temperature, K; U_0 is the potential energy of a standard system, J; α is the degree of adsorbent uniformity; ρ_i is the average equilibrium distance of a molecule from the adsorbent surface, rel. units; F_i is the steric factor; Q is the generalized charge of a molecule, i.e., the parameter of intermolecular interaction

$$Q = ((3n_m + 1 - s)/2)^{0.75},$$

n_m is the number of carbon atoms; and s is the number of hydrogen atoms shielded from the adsorbent.

Let us now turn to determining the main type of intermolecular interactions that occur in a gas chromatographic system: O-alkylmethylfluorophosphonates (OAMFP) with 5% phenyl-methylpolysiloxane.

It was noted in [9] that different types of adsorbate—adsorbent intermolecular interactions are observed in gas chromatographic systems, from nonspecific universal interactions to various specific interactions, e.g., orientational electrostatic interactions, hydrogen bonds, and the formation of the charge-transfer complexes. It is assumed in this work that the intermolecular interactions between the isomers of O-alkylmethylfluorophosphonates and the phase in a capillary column are of the dispersion type, since there are no protonated atoms or other electron acceptor fragments in the adsorbate structure, while the structure of adsorbent consists of weakly polar 5% phenyl-methylpolysiloxane.

In [11], the dispersion type of intermolecular interactions was due to the correlation between the movement of electrons in interacting molecules, as a result of which the average distance between the electrons of these molecules grew slightly. This lowered the energy of their interaction, resulting in molecular attraction. The energy of dispersion interaction, V_{disp}, for two atoms or spherically symmetrical molecules at $2R < l$ (where R is the molecular radius and l is the distance between the centers of the molecules) is approximately described by the London formula according to the equation

$$V_{disp} = -3\alpha_A \alpha_B I_A I_B / 2(I_A + I_B)R^6,$$

where I_A and I_B are the ionization potentials of molecules A and B, respectively, J; α_A and α_B are the static polarizabilities of molecules A and B, respectively, in atomic units; R is the radius of a molecule, m; and l is the distance between the centers of the molecules, m.

It can be seen from the above equation that static polarizability [11], which is determined by the spatial intramolecular distribution of charges [12—14], plays a considerable role in disperse interaction. Since the intermolecular interactions between the isomers of O-alkylmethylfluorophosphonates and the phase in a capillary column are of a dispersion character, we may assume that static polarizability contributes to these interactions.

The effect the strength of the molecules' electrical field has on such spectral characteristics as spin—spin interaction constants or NMR chemical shifts were studied in [15, 16]. The functional relationship between the NMR chemical shift and static polarizability is described by the equation

$$\delta = (1/\alpha_2)(q\nu_1 \langle m_2^2 \rangle)/[2(\nu_1 + \nu_2)],$$

where $\langle m_2^2 \rangle$ is the mean square of the oscillating dipole moment of a free molecule of a substance, D; α_2 is the static polarizability of the substance's molecules; ν_1 and ν_2 are the frequencies of adsorption for the solvent and dissolved substance, respectively, Hz; q is the ratio

of the dipole moment and electric field strength, determined using the equation

$$q = [(2n_c^2 - 1)/(2n_c^2 + 2)](1/R^3),$$

where n_c is the refractive index of the medium; and R is the radius of the molecule.

The relationship between polarizability and NMR chemical shift also follows from both these values being results of the charge distribution in interacting systems. We should clarify that with carbon, fluorine, and phosphorus atoms, their own electronic shells (i.e., the charges on the atoms) have a considerable effect on chemical shifts [17—19]. The dependence of the chemical shift of ^{19}F nuclei on the electrical field strength, which is functionally associated with polarizability, was demonstrated in [14], yet another reliable proof of the relationship between polarizability and chemical shift.

Our calculations for the polarizability of OAMFP structural isomers O-1-butylmethylfluorophosphonate (I), O-1-methylpropylmethylfluorophosphonate (II), and O-1,1-dimethylethylmethylfluorophosphonate (III) testify to the effect the isomerism of O-alkyl radicals have on their values.
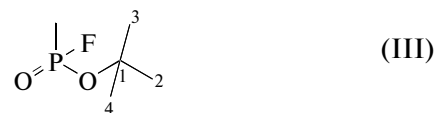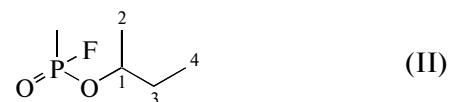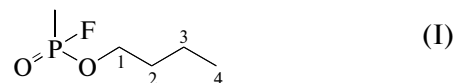
The above analysis of the interactions in an O-alkylmethylfluorophosphonate—5% phenyl-methylpolysiloxane gas chromatographic system, performed on the basis of the theory of intermolecular interaction, allows us to assume there is a relationship between gas chromatographic retention indices and NMR chemical shifts. This assumption was tested for the ^{13}C NMR chemical shifts of structural isomers of O-alkylmethylfluorophosphonates and their gas chromatographic retention indices.

The existence of a correlation between the RIs of structural isomers of O-alkylmethylfluorophosphonates and the ^{13}C NMR chemical shifts of O-alkyl fragments that determine the RIs of the investigated compounds was verified as follows: The total value of the chemical shifts of the ^{13}C nuclei, which reflects the effect the degree of branching of an O-alkyl radical has on the electron structure of structural fragments and their mutual position, was used to describe the isomeric state of the carbon backbone of an O-alkyl radical. The sum of the values of the chemical shifts of carbon atoms located in a side branch, relative to the

longest carbon chain, was designated as the total value of the ^{13}C NMR chemical shifts.

Examples of calculating the total value of chemical shifts for three OAMFP isomers with four carbon atoms in an O-alkyl radical are presented in Table 1.

There is thus no branching in the isomer with the *n*-butyl O-alkyl radical, so the total value of the chemical shift for the carbons of the radical is taken as 0.0. For the 1-methylpropyl isomer, the total value of chemical shifts of O-alkyl radical is 22.9 ppm. If there are several side branches in a radical relative to the longest hydrocarbon chain, the chemical shifts of each atom located in the branch are summed. In a O-1,1-dimethylethyl radical, there are thus two carbon atoms in the branch. The ^{13}C chemical shifts in NMR for each carbon atom are 30.5 ppm, so the total value is 61.0 ppm.

Let us consider the relationship between RIs and the NMR chemical shift of ^{13}C for OAMFP isomers with five carbon atoms in an O-alkyl radical.

An experimental study of the retention parameters was performed on an Agilent 6890/5973N chromatograph−mass spectrometer (Agilent Technologies). A DB-5HT fused-silica capillary column 30 m × 0.25 mm with a film thickness of 0.1 μm and a low polarity stationary liquid phase (5% phenyl dimethylpolysiloxane) was used to separate the components of the mixture. The thermostat temperature programming mode calls for an initial temperature of 70°C; hold for 3 min, heat to 300°C at a rate of 15 K/min, and hold for 5 min at the final temperature. A solution of linear saturated hydrocarbons containing from 8 to 24 carbon atoms in benzene was used as our external standard.

The ^{13}C NMR spectra were registered using a FT-80A NMR spectrometer (Varian) at the ^{13}C nuclei resonance frequency of 20 MHz in CDCl$_3$ solutions. Tetramethylsilane was used as the standard compound in relation to which the chemical shifts of the investigated compounds' ^{13}C NMR spectra were calculated.

For compounds of phosphonates with five carbon atoms in the O-alkyl radical (four compounds), the correlation described by the following equation was found from the known chromatographic and spectral data:

$$R_i = -1.9\Sigma\delta_C + 1063.5, \qquad (1)$$

where R_i is the retention index, in index units; $\Sigma\delta_C$ is the total value of chemical shifts, ppm. The approximation coefficient for this equation is 0.992.

The RI values were calculated using correlation dependence (1) for compounds of phosphonates with five carbon atoms in the O-alkyl radical (four compounds) for which only spectral data are known. The mean value of the error of R_i determination for these OAMFP isomers is 2.6 index units and does not exceed the limit of interlaboratory reproducibility. The results from RI calculations are presented in Table 2 and compared to the experimental data.

Table 1. Values of chemical shifts of the ^{13}C nuclei (δ, ppm) for each carbon atom in the O-alkyl radical of OAMFP isomers

Number of atom	I	II	III
1	66.9	77.5	77.6
2	32.3	22.9	30.5
3	18.6	30.3	30.5
4	13.5	9.4	30.5

The total value of chemical shifts of atoms located in the side branch are $\Sigma\delta_C$ = 0.0, 22.9, and 61.0 ppm for I, II, and III isomers, respectively.

Table 2. (I) Experimental and (II) calculated RI values (RI, index units) of OAMFP isomers with five carbon atoms in the O-alkyl radical

Radical	I	II
1,1-Dimethylpropyl	948.0	947.6
2,2-Dimethylpropyl	967.0	962.8
1,2-Dimethylpropyl	987.0	990.5
1-Ethylpropyl	1013.0	1013.0
1-Methylbutyl	1016.0	1021.7
2-Methylbutyl	1032.0	1033.3
3-Methylbutyl	1026.0	1025.0
Pentyl	1068.0	1063.5

The dependence of the experimental values of retention indices R_{ie} on the total value of the ^{13}C NMR chemical shifts of OAMFP isomers with 5 carbon atoms in the O-alkyl radical is presented in the figure. The graph shows that the relationship between the RI values and the total value of the ^{13}C NMR chemical shifts is expressed by a linear dependence; slight deviations are observed, however, and the lower RI values correspond to the higher total value of the ^{13}C NMR chemical shifts.

RIs for the class of OAMFP isomers are generally calculated as follows:

• First, the chemical shifts of carbon atoms located in the branches of O-alkyl radical carbon skeletons are determined for isomers with known RI values, and their values are summed.

• Second, the correlation between the RI values and the total values of the ^{13}C NMR chemical shifts is found.

R_{i_e}, index units
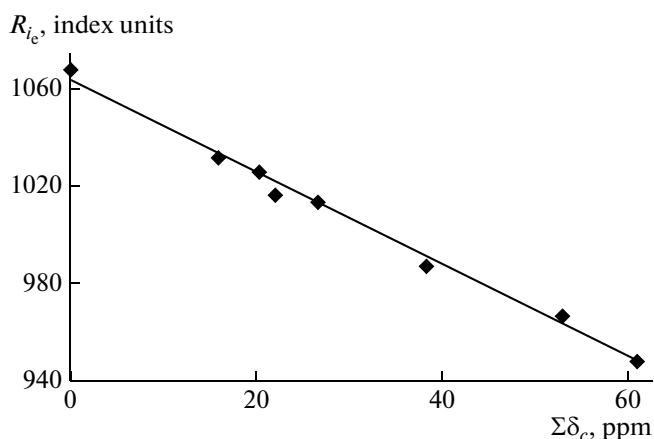
Shifts in the ^{13}C NMR spectra of OAMFP isomers with five carbon atoms in the O-alkyl radical.

• Third, the total value of the chemical shifts of carbon atoms located in the branches of O-alkyl radical carbon skeletons is determined for isomers with unknown RI values, and the RIs of these isomers are calculated using the established correlation.

CONCLUSIONS

The correlation between chemical shifts in ^{13}C nuclear magnetic resonance spectra and the retention indices of the structural isomers of O-alkylmethylfluorophosphonates (typical compounds with tetracoordinated phosphorus) was found using the theory of intermolecular interactions, allowing us to develop a method for determining the gas chromatographic retention indices for the structural isomers of compounds of the above class.

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Translated by I. Duchovny