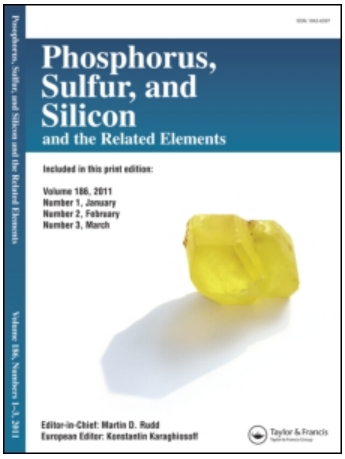

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Explanation of Anomalous Gas-Chromatographic (Gc) Behaviour in a Homologous Series of 2-Chloroethyl Phosphonic Acid Dialkyl Esters

Radu Vceanu[a]; Gheorghe Ilia[a]; Ludovic Kurunczi[a]; Petria Şoimu[a]
[a] Institute of Chemistry Timişoara, Timişoara, Romania

To cite this Article Vceanu, Radu , Ilia, Gheorghe , Kurunczi, Ludovic and Şoimu, Petria(1996) 'Explanation of Anomalous Gas-Chromatographic (Gc) Behaviour in a Homologous Series of 2-Chloroethyl Phosphonic Acid Dialkyl Esters', Phosphorus, Sulfur, and Silicon and the Related Elements, 111: 1, 10
To link to this Article: DOI: 10.1080/10426509608054639
URL: http://dx.doi.org/10.1080/10426509608054639

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 10
Reprints available directly from the publisher
Photocopying permitted by license only

EXPLANATION OF ANOMALOUS GAS-CHROMATOGRAPHIC (GC) BEHAVIOUR IN A HOMOLOGOUS SERIES OF 2-CHLOROETHYL PHOSPHONIC ACID DIALKYL ESTERS

RADU VÂLCEANU, GHEORGHE ILIA, LUDOVIC KURUNCZI, PETRIA ŞOIMU
Institute of Chemistry Timişoara, Bul. Mihai Vitezu 24, 1900-Timişoara, Romania

The study of GC separation of 2-chloroethylphosphonic acid di-*n*-alkyl (1-5 C atoms) esters (synthesised by us) on silicone stationary phases (OV-1, OV-17, OV-225) revealed a deviation from the expected linear dependence of retention indexes (RI) versus the number of C atoms of the alkyl chain: the first member of the series presents stronger retention than one can expect. This anomalous behaviour was observed especially on polar stationary phase (OV-225, see Figure 1), and was emphasised with the increase of the column temperature. In an attempt to rationalise the above mentioned facts, we tried to relate the RI values to a global polarity parameter: the dipole moment, μ. The μ values for $ClC_2H_4P(O)(OR)_2$ were calculated by a method described in [1] (tested by comparing the calculated μ values with experimental ones for alkyl phosphonic acid dialkylesters), using molecular mechanics (COSMIC package) in the search of the conformational space, AM1 method (MOPAC 6.0) for the μ values of the conformers, and Boltzmann distribution for the global value (see Table I). At low temperature, the μ values are not related to the Kovats indexes. Those calculated at 200°C (column temperature range) demonstrate that, indeed, only in the case of the methyl derivative, the temperature rising led to a higher μ (enhanced population of the more polar conformers: *ac* position for the C-Ethyl group - *ac* for the Cl, $\mu \approx 2.7$ D, or ±*ap* for one R, $\mu \approx 3.8 \div 4.3$ D). It can be concluded that dipole-dipole forces contribute to the separation process of the first members of the series.

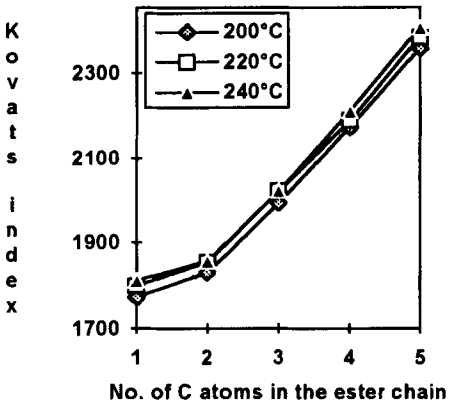

FIGURE 1 Kovats indexes versus no. of C atoms in the ester chain for OV-225 column

TABLE I Conformations and μ values

R	Most stable conformations				μ(D)	
	R	R	C-Ethyl	Cl	25°C	200°C
CH_3	*sc*(±*sp*)	±*sp*	±*sp*(±*ap*)	*ac*(±*ap*)	**2.01**	**2.20**
C_2H_5	±*sp*(*sc*)	±*sp*	±*sp*(±*ap*)	*ac*(±*ap*)	2.06	2.08
C_3H_7	±*sp*(*sc*)	±*sp*	±*sp*(±*ap*)	*ac*(±*ap*)	2.08	2.09

[1] L. Kurunczi, T. Sulea and T.I. Oprea, *J. Mol. Struct. (Theochem)*, **306**, 93 (1994)