

This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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 Șoimu^a

^a Institute of Chemistry Timișoara, Timișoara, Romania

To cite this Article Vceanu, Radu, Ilia, Gheorghe, Kurunczi, Ludovic and Șoimu, 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>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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 ȘOIMU
Institute of Chemistry Timișoara, Bul. Mihai Vitezu 24, 1900-Timișoara, 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

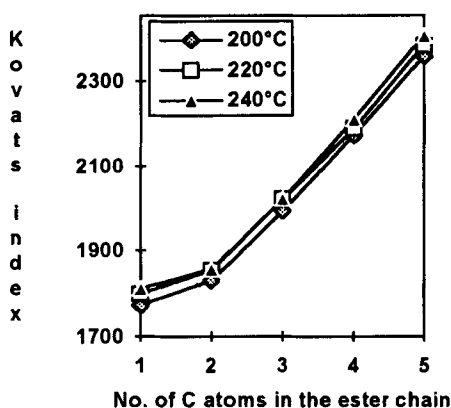


FIGURE 1 Kovats indexes versus no. of C atoms in the ester chain for OV-225 column

R	Most stable conformations				μ (D)	
	R	R	C-Ethyl	Cl	25°C	200°C
CH ₃	sc(\pm sp)	\pm sp	\pm sp(\pm ap)	ac(\pm ap)	2.01	2.20
C ₂ H ₅	\pm sp(sc)	\pm sp	\pm sp(\pm ap)	ac(\pm ap)	2.06	2.08
C ₃ H ₇	\pm sp(sc)	\pm sp	\pm sp(\pm ap)	ac(\pm ap)	2.08	2.09

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 $\text{ClC}_2\text{H}_4\text{P}(\text{O})(\text{OR})_2$ 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 \pm 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.

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