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Note

Studies on the gas chromatographic behaviour of organophosphorus esters

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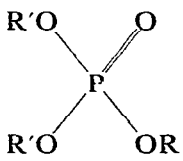
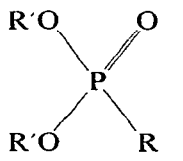
Although extensive gas–liquid chromatographic (GLC) data have been collected on commercially important organophosphorus (OP) esters, their retention behaviour has not been subjected to any systematic study and analysis. We report here the retention indices of diethyl alkyl phosphates (I), diethyl alkylphosphonates and di-*n*-propyl alkylphosphonates (II) on OV-17 stationary phase with *n*-alkanes as references. The calculated δI value for methylene addition at different side chains showed the possibility of predicting the retention index of a higher member with the help of the index of the parent compound.



Phosphates (I)



Phosphonates (II)

R′ = $-C_2H_5$ or $-C_3H_7$
R = $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$

EXPERIMENTAL

All the solvents and reagents used were of AnalaR grade (BDH, Poole, Great Britain) except *n*-alkanes which were obtained from Fluka (Buchs, Switzerland).

Synthesis of phosphates and phosphonates

Diethyl alkyl phosphates were synthesized[1] by reaction of diethyl chlorophosphate with sodium alkoxide in an inert solvent and purified by distillation under reduced pressure.

Diethyl and dipropyl alkylphosphonates were prepared from alkyl iodides and sodium diethyl phosphites under Michaelis–Becker reaction[2] conditions and purified by distillation.

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Gas chromatography

Three stainless-steel columns (6 ft. × 2 mm I.D.) packed with Gas-Chrom Q (80–100 mesh) loaded with 1.5%, 10% and 20% OV-17, respectively, were prepared and conditioned at 250°C for more than 8 h before use and checked for reproducibility.

The gas chromatograph used was a Perkin-Elmer Model 3920 B, with flame ionization detector. The temperatures of the injection port, column oven and detector were 200, 160 and 200°C respectively. The dead volume of the column was measured by injecting methane. Mixtures of the phosphates or phosphonates together with *n*-alkane reference were prepared in benzene. A 2-μl volume of the mixture was injected on the column and the retention times for each component were measured with the help of stop-watch. Each mixture was injected three times to check the reproducibility of retention times. The chromatograms were recorded on a Perkin-Elmer Model 23 recorder with sensitivity 1 mV for full scale deflection.

The raw retention data were corrected for dead volume and then used to calculate Kováts' retention indices[3].

RESULTS AND DISCUSSION

Kováts' indices are sensitive to column temperature[4], stationary phase loading and sample size[5,6]. The sensitivity to column loading in case of OP compounds had not previously been studied. Our results given in Table I showed that with 20% loading the indices are very consistent compared to those with low loadings.

TABLE I

EFFECT OF PERCENTAGE LIQUID LOADING ON KOVÁTS' RETENTION INDICES (*I*) OF TRIALKYL PHOSPHATES AND PHOSPHONATES AT 160°C

Compound	*I*		
	1.5% OV-17	*10% OV-17*	*20% OV-17*
Diethyl ethyl phosphate	1302	1298	1296
Diethyl butyl phosphate	1488	1483	1484
Diethyl hexyl phosphate	1682	1676	1674
Diethyl ethylphosphonate	1257	1250	1246
Dipropyl propylphosphonate	1520	1514	1510
Dipropyl pentylphosphonate	1702	1700	1700

The retention indices in Table II calculated by Kováts' method clearly show the dependence on chain length in phosphates and phosphonates. The average δI_a value for the addition of a methylene group was 93 ± 4 instead of 100. Such a deviation has been reported previously for esters of dibasic acids[7].

The difference in retention indices, δI_b, between phosphates and phosphonates having similar alkyl groups is 50 ± 2 for the various pairs studied (see Table III). This

TABLE II

KOVÁTS' RETENTION INDICES FOR AN HOMOLOGOUS SERIES OF PHOSPHATES AND PHOSPHONATES ON 20% OV-17 AT 160°C

Compound No.	*R'*	*R*	*I*	δI_a
Diethyl alkyl phosphates (A)				
1	$-C_2H_5$	$-CH_3$	1205	–
2	$-C_2H_5$	$-C_2H_5$	1296	91
3	$-C_2H_5$	$-C_3H_7$	1390	94
4	$-C_2H_5$	$-C_4H_9$	1482	92
5	$-C_2H_5$	$-C_5H_{11}$	1579	97
6	$-C_2H_5$	$-C_6H_{13}$	1674	95
Diethyl alkylphosphonates (B)				
7	$-C_2H_5$	$-C_2H_5$	1246	–
8	$-C_2H_5$	$-C_3H_7$	1340	94
9	$-C_2H_5$	$-C_4H_9$	1430	90
10	$-C_2H_5$	$-C_5H_{11}$	1525	95
Di-n-propyl alkylphosphonates (C)				
11	$-C_3H_7$	$-C_2H_5$	1420	–
12	$-C_3H_7$	$-C_3H_7$	1510	90
13	$-C_3H_7$	$-C_4H_9$	1604	94
14	$-C_3H_7$	$-C_5H_{11}$	1700	96

Average = 93 ± 4

difference appears to be due to the difference in polarities of phosphate and phosphonate esters.

Table IV shows the difference between the retention indices, δI_c, of phosphonates having the same R but different R' groups. This averages to 87 ± 3 and is significantly less than δI_a.

TABLE III

DIFFERENCE IN RETENTION INDICES BETWEEN PHOSPHATES AND PHOSPHONATES, δI_b, HAVING THE SAME ALKYL GROUPS ON 20% OV-17 AT 160°C

δI_b = *I* (phosphate) − *I* (phosphonate); *I* values from Table II.

R'	*R*	δI_b
$-C_2H_5$	$-C_2H_5$	50
$-C_2H_5$	$-C_3H_7$	50
$-C_2H_5$	$-C_4H_9$	52
$-C_2H_5$	$-C_5H_{11}$	49

Average = 50 ± 2

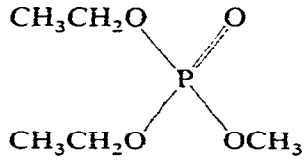
TABLE IV

EFFECT OF ADDITION OF A METHYLENE GROUP IN R′ FOR PHOSPHONATES ON 20% OV-17 AT 160°C

Values of indices taken from Table II.

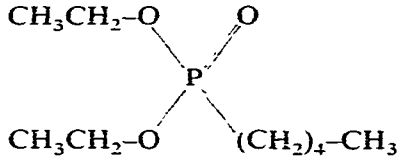
Phosphonate series B		*Phosphonate series C*		*Difference in methylene group at R′*	*Difference in index, δI_c, per methylene group*
R′	*R*	*R′*	*R*		
$-C_2H_5$	$-C_2H_5$	$-C_3H_7$	$-C_2H_5$	1 × 2	174/2 = 87
$-C_2H_5$	$-C_3H_7$	$-C_3H_7$	$-C_3H_7$	1 × 2	170/2 = 85
$-C_2H_5$	$-C_4H_9$	$-C_3H_7$	$-C_4H_9$	1 × 2	174/2 = 87
$-C_2H_5$	$-C_5H_{11}$	$-C_3H_7$	$-C_5H_{11}$	1 × 2	175/2 = 88
					Average = 87 ± 2

Amongst the compounds reported, it was possible to predict the retention indices of higher members by making use of the δI_a, δI_b and δI_c values. Thus taking diethyl methyl phosphate (a)



(a)

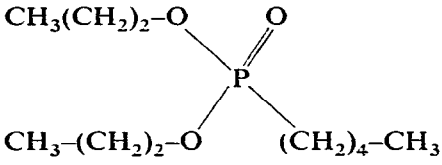
as the parent compound for the series, the retention index of diethyl pentylphosphonate (b) can easily be calculated.



(b)

The parent compound has a retention index of 1205, the contribution due to δI_a for the above compound is 4 × 93 = 372 and δI_b is −50, giving the retention index as

1527 which agrees well with the observed value of 1525 (Table II). Again, for dipropyl pentylphosphonate (c)



(c)

δI_a is $4 \times 93 = 372$, $\delta I_b = -50$ and $\delta I_c = 2 \times 87 = 174$. Adding this to 1205, the value obtained is 1691 compared with the observed value of 1700 (Table II).

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