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Gas chromatographic determination of liquid vapour pressure and heat of vaporization of tetrachlorobenzyltoluenes

Anniek G. van Haelst, Frans W.M. van der Wielen, Harrie A.J. Govers*

Department of Environmental and Toxicological Chemistry, Amsterdam Research Institute for Substances in Ecosystems, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands

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Abstract

(Subcooled) liquid vapour pressures and heat of vaporization of low-volatility isomeric organic compounds (tetrachlorobenzyltoluenes, TCBTs) were determined by two gas–liquid chromatographic (GLC) methods.

By the first method vapour pressures and temperature-independent heats of vaporization of nine TCBTs were obtained at experimental temperatures (433.15–493.15 K) and linearly extrapolated to 298.15 K. By the second method vapour pressures and temperature-dependent heats of vaporization were measured for the same TCBTs and, in addition, for diphenylmethane and *p,p'*-DDT employing nonlinear extrapolations. It was concluded that the second method has several advantages over the first with respect to scope, sensitivity for selection of reference compounds and accuracy.

Keywords: Thermodynamic parameters; Vapour pressure; Retention indices; Relative retention times; Tetrachlorobenzyltoluenes; Diphenylmethane; *p,p'*-DDT

1. Introduction

Tetrachlorobenzyltoluenes (TCBTs), known under the trade name of Ugilec 141, have been used as replacements of polychlorinated biphenyls (PCBs) in hydraulic liquids resistant to inflammation, especially by underground mining, as a dielectric fluid in capacitors, and as a cooling and isolation fluid in transformers [1]. Theoretically 96 TCBT isomers are possible (Fig. 1).

Because of the large similarities in the molecular structure of PCBs and TCBTs properties of environmental relevance, such as the *n*-octanol–water partition coefficient, aqueous solubility and bioconcentration factor, were found to have similar values [2–4]. However, nothing is known about the vapour pressure of TCBTs. As equilibrium partitioning between water and a gas phase is commonly used in the prediction of the environmental fate of chemicals, it was decided to determine vapour pressures at

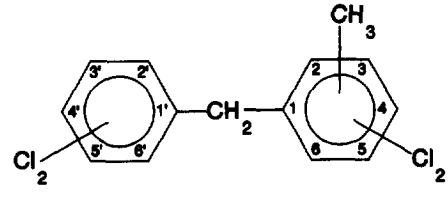

Fig. 1. Molecular structure of tetrachlorobenzyltoluenes (TCBTs, Ugilec). Diphenylmethane is the unsubstituted parent compound of Ugilec and *p,p'*-DDT is obtained after substitution of one chlorine onto each of the phenyl rings, and a $-CCl_3$ group onto the central carbon.

*Corresponding author.

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298.15 K of these environmentally interesting compounds.

The vapour pressures of low-volatility compounds are often determined by either gas saturation, effusion or gas–liquid chromatography (GLC) methods. GLC has several advantages over the other methods. It can be used for compounds at low concentrations and GLC tolerates relatively impure compounds [5]. It is based on the use of relative retention times on a nonpolar stationary phase and isothermal conditions such that the compound's retention time is directly related to its vapour pressure. The volatility or retention of a solute, however, depends on both its vapour pressure in the pure liquid phase and its activity coefficient in the stationary phase. In addition to the measurement of a single GLC retention parameter, the value of the activity coefficient is required [6]. In a first version of the GLC method [5,7–9] this problem is solved by using one reference compound with known vapour pressure and structurally similar to the compound studied. The test compound's vapour pressure is determined from changes in the relative retention time with temperature and the known vapour pressure of the reference at the pertinent temperatures. Heat of vaporization is assumed to be independent of temperature and short chromatographic columns have to be used when low-volatility compounds are run at relatively low temperatures. In a novel version of the GLC method reported by Spieksma et al. [6] liquid *n*-alkanes are used as reference compounds. The Kováts retention index used in this method expresses the retention time of a test compound relative to the liquid *n*-alkanes, eluting before and after the compound, respectively. The authors developed an expression which relates the Kováts indices at different temperatures and the McReynolds numbers of a compound to its pure liquid vapour pressure. Both methods provide vapour pressure values at different temperatures. Therefore, with both methods heats of vaporization, being important descriptors in the prediction of partition properties [10], can be calculated from these. Remaining uncertainties for both GLC methods are associated with the extrapolation of vapour pressure data from the temperature region of measurement to environmentally relevant temperatures.

In this study vapour pressures of nine TCBT isomers were determined by the two GLC methods. On account of the structural similarities with TCBTs and the availability of vapour pressures data, *p,p'*-DDT and diphenylmethane were chosen as reference compounds in the first GLC method. In addition the effect was studied of applying normal GLC temperatures and column length instead of relatively low temperatures at short columns. Vapour pressures of TCBTs and, in addition to these, of diphenylmethane and *p,p'*-DDT were determined with the second GLC method. In order to enhance the accuracy of the extrapolation to environmentally relevant temperatures special emphasis was laid on nonlinear extrapolation in this method. Results of vapour pressures were obtained at 298.15 K and at the temperature region of their measurement (433.15–493.15 K). From these the heats of vaporization at the corresponding temperatures were calculated. The performances of both methods were compared.

2. Model equations

2.1. Relative retention time (RRT) method

The relevant equations for determining vapour pressure by the first GLC method have been developed by Hamilton [9]. Vapour pressures for two substances are related through the equation:

$$\ln P_1 = (\Delta H_1/\Delta H_2)\ln P_2 + C \quad (1)$$

where 1 and 2 refer to test and reference compounds, respectively. P is the vapour pressure, ΔH is the heat of vaporization and C is a temperature-independent constant. The ratio $\Delta H_1/\Delta H_2$, also assumed to be temperature independent, and the constant C can be calculated by regression from the ratio of the net retention times, $(t_{R,1}-t_0)/(t_{R,2}-t_0)$ and the vapour pressure of the reference compound at different temperatures:

$$\ln [(t_{R,1} - t_0)/(t_{R,2} - t_0)] = (1 - \Delta H_1/\Delta H_2)\ln P_2 - C \quad (2)$$

Eq. 1 can be used to determine the vapour pressure of the test compound at any temperature given the vapour pressure of the reference compound at that temperature. In this method the heat of vaporization of the test compounds (ΔH_1) is calcu-

lated from the regression coefficient $(1-\Delta H_1/\Delta H_2)$ in Eq. 2 and the known value of the reference (ΔH_2). As the heat of vaporization is assumed to be independent of temperature only one value at the mean experimental temperature is obtained, which cannot accurately be identified as the value at 298.15 K if long distance linear extrapolations from the experimental region have to be applied.

In our case the vapour pressures of the reference compound diphenylmethane at experimental temperatures were calculated by applying the Clausius–Clapeyron equation to data collected by Ohé [11]. Vapour pressures of the reference compound *p,p'*-DDT in the experimental temperature range (and at 298.15 K) were calculated by applying the Clausius–Clapeyron equation to experimental literature data quoted and modelled by Eitzer and Hites [8].

2.2. Retention index method

The second GLC method includes assumptions on the combination of the Kováts index and an infinite dilution equilibrium fugacity model, ratios of activity coefficients of solute–*n*-alkane (γ_i/γ_z, assumed to be constant and closer to one the more both stationary phase and elutes are nonpolar) and of the subsequent *n*-alkanes (γ_{z+1}/γ_z, assumed to equal to 1) and the temperature dependence of the Kováts index [6]. The isothermal pure liquid vapour pressure ($\log P_i$) can ultimately be written as a function of the isothermal Kováts index of test compound i (I_i), the derivative of the vapour pressure of a reference alkane to its Kováts index [$(\mathrm{d}\log P_z)/\mathrm{d}I_z$], the vapour pressure of the reference "alkane" with $z=0$ ($\log P_{\mathrm{H2}}$), and the ratio of activity coefficients mentioned above [$\log(\gamma_i/\gamma_z)$]:

$$\log P_i = (\mathrm{d}\log P_z/\mathrm{d}I_z)I_i + \log P_{\mathrm{H2}} + \log(\gamma_z/\gamma_i) \qquad (3)$$

In this method the first step is the GLC measurement of net retention times of test compounds and *n*-alkanes at different temperatures and the calculation of Kováts indices from these:

$$I_i = \frac{100[\log(t_{\mathrm{R},i} - t_0) - \log(t_{\mathrm{R},z} - t_0)]}{[\log(t_{\mathrm{R},z+1} - t_0) - \log(t_{\mathrm{R},z} - t_0)]} + 100z \qquad (4)$$

Then the temperature dependence of the Kováts index of the test compound is calculated according to a linear model [$I_i(T)=B_0+B_1T$, also used previously [6]] or to the best model nonlinear in T, which in our case turned out to be (B are regression coefficients):

$$I_i(T) = B_0 + B_1T^2 \qquad (5)$$

The next step is the calculation of $\mathrm{d}\log P_z/\mathrm{d}I_z$ and $\log P_{\mathrm{H2}}$ at the appropriate temperatures (T in Kelvin) by fitting them to experimental values of $\log P_z$ (P in Torr or mmHg), leading to:

$$\begin{aligned}\log P_z = {} & (9.3327 \pm 1.0689) \\ & - (0.012683 \pm 0.003017)T \\ & - (417.269 \pm 135.115)/T \\ & + (0.000011955 \pm 0.000002991)T^2 \\ & + [(0.010425 \pm 0.002225) \\ & - (0.000012333 \pm 0.000005106)T \\ & - (3.64365 \pm 0.31875)/T \\ & + (4.84053 \pm 3.87684)10^{-9}T^2]I_z \end{aligned} \qquad (6)$$

In Eq. 6, an improved extension of data presented previously [6] is given, the first four terms give the temperature-dependent value of $\log P_{\mathrm{H2}}$, whereas the terms in between brackets before I_z provide the temperature-dependent value of $\mathrm{d}\log P_z/\mathrm{d}I_z$. By fixing the derived coefficients to their values given in Eq. 6 and subsequent regression of $\log P_z$ to $\log P_{\mathrm{H2}}$ and $\mathrm{d}\log P_z/\mathrm{d}I_z$, the inaccuracies in the latter were estimated to be about 1.7 and 1.2‰, respectively. Eq. 6 is an accurate equation, which was derived from $N=48$ experimental $\log P_z$ data [11,12] spanning z, T and P ranges of 4 to 27, 173.15 to 548.15 K and about 10^{-3} to 10^3 mmHg, respectively. Its squared correlation coefficient, adjusted for degrees of freedom, amounts to $r^2=0.9998$, whereas its standard error of regression equals 0.02 log units.

The fourth step is the selection of a model compound and stationary phase for the constant $\log(\gamma_z/\gamma_i)$ from values tabulated [6]. In our case the value of 0.092 was selected holding for 1-iodobutane and a nonpolar SE-30 phase. In case of *n*-octadecane and diphenylmethane the value of 0.000 was chosen.

Finally, $I_i(T)$ of Eq. 5, $\mathrm{d}\log P_z/\mathrm{d}I_z$ and $\log P_{\mathrm{H2}}$ of Eq. 6 and 0.092 (or 0.000) are substituted into Eq. 3 leading to $\log P_i$ at all temperatures of choice. From this equation the temperature-dependent $\Delta H_i(T)$ (in

cal mol^{-1}) was calculated by taking the derivative to T (R is the gas constant in 1.9872 cal mol^{-1} K^{-1}):

$$\Delta H_i(T) = 2.30259(RT)^2 \mathrm{d}\log P_i/\mathrm{d}T \quad (7)$$

3. Experimental

3.1. Chemicals

Nine TCBTs, numbered according to Ehmann and Ballschmiter [13], were purchased from Promochem (Wesel, Germany); (in order of gas chromatographic elution) 2,2′,4,6′Cl-5Me, no. 28; 2,2′,4,5′-5 no. 25; 2,2′,5,5′-4 no. 36; 2,2′,4,4′-5 no. 22; 2,2′,4,6′-3 no. 27; 2′,3,4,6′-6 no. 80; 2,2′,4,4′-3 no. 21; 2,3′,4,4′-5 no. 52; 2′,3,4,4′-6 no. 74. The reference compounds diphenylmethane and *p,p′*-DDT were obtained from Chem. Service (West Chester, PA, USA) and Analabs (North Haven, CT, USA), respectively. *n*-Alkanes (C_{14}, C_{16}, C_{18}, C_{20}, C_{22} and C_{24}) are a gift from TU, Eindhoven, Netherlands.

3.2. Gas chromatography

A Hewlett-Packard Model 5890 series II equipped with a flame ionisation detector and a splitless injection port was used. A 30 m×0.32 mm fused-silica column from J&W (Folsom, CA, USA) with a nonpolar DB-1 liquid phase (film thickness 0.25 μm) was applied. As carrier gas helium was used at a constant pressure of 50 kPa. The injector and detector temperature was 573.15 K. The injector was used in the splitmode with a split ratio of 1:20 (septum purge 1.5 ml/min and purge vent of 30 ml/min). Helium was used as make-up gas for the detector at 30 ml/min, the air flow amounted to 295 ml/min and the hydrogen flow was 18 ml/min. The oven temperatures of the isothermal runs were 433.15, 443.15, 453.15, 463.15, 473.15, 483.15 and 493.15 K. An aliquot of 1 μl of the sample was injected. The chromatographic data were collected on a Milton Roy integrator. Methane gas was used as unretarded component leading to t_0 values.

3.3. Calculational

Linear and nonlinear regression calculations mentioned in section 2 were carried out using the statistical program SGPLUS (Oasis, Nieuwegein, Netherlands). In order to perform the calculations of the first, third and subsequent steps of the retention index method a GWBASIC computer program (GCTHERM2) was written including calculations of both log P plus ΔH values and their inaccuracies.

4. Results

4.1. Chromatographic retention parameters

Chromatographic retention parameters measured in quadruplicate of both test compounds and references at seven temperatures are collected in Table 1.

4.2. RRT method

In Table 2 regression parameters (C, $1-\Delta H_1/\Delta H_2$), and the statistics of Eq. 2 are shown, determined in the first GLC method, using either diphenylmethane or *p,p′*-DDT as a reference compound. In both cases the statistics are satisfactory in view of results obtained by others [5,7–9].

The heat of vaporization of the references (ΔH_2) in the experimental temperature region (433.15–493.15 K, with 463.15 K as an average) were 12 534 and 22 458 cal mol^{-1} for diphenylmethane and *p,p′*-DDT, respectively (see Table 6). The reference vapour pressures (log P_2) are also included in Table 6.

In addition Table 3 reports the vapour pressures (log P_1) and the heat of vaporization (ΔH_1) of the nine TCBTs at 298.15 and 463.15 K using both reference compounds.

From these tables it can be read that large differences result from using different references. The vapour pressures (log P) of the nine TCBTs at 298.15 K with diphenylmethane as reference range from −3.46 to −3.82 log units, whereas this range amounts to −5.102 to −5.467 for *p,p′*-DDT. Similar large differences are found at the temperatures of measurement. The (mean) heat of vaporization ranges from 16 673 to 17 370 cal mol^{-1} using diphenylmethane as a reference and from 21 455 to 22 246 for *p,p′*-DDT. Most of the vapour pressure and heat of vaporization values found for the nine

Table 1
Relative retention (ln of net retention time ratios, see text) with diphenylmethane (r_{DPHM})[a] or *p,p'*-DDT (r_{DDT})[b] as reference compound and Kováts retention indices (I)[c] of Ugilec (nr.[d]), diphenylmethane (DPHM) and *p,p'*-DDT (DDT) measured by GLC in quadruplicate at seven temperatures

Cmpd[d]	Param.	T (K)						
		433.15	443.15	453.15	463.15	473.15	483.15	493.15
28	r_{DPHM}	3.023	2.900	2.766	2.643	2.552	2.467	2.480
	r_{DDT}	−0.6014	−0.5740	−0.5458	−0.5199	−0.5015	−0.4800	−0.4589
	I	2102.5	2113.3	2124.3	2135.7	2146.7	2158.7	2171.0
25	r_{DPHM}	3.132	2.999	2.857	2.725	2.628	2.535	2.543
	r_{DDT}	−0.4928	−0.4746	−0.4548	−0.4374	−0.4259	−0.4116	−0.3956
	I	2127.5	2137.4	2147.5	2157.9	2168.0	2178.9	2190.5
36	r_{DPHM}	3.166	3.031	2.887	2.754	2.655	2.562	2.574
	r_{DDT}	−0.4590	−0.4424	−0.4242	−0.4082	−0.3984	−0.3852	−0.3646
	I	2135.2	2145.2	2155.4	2165.7	2175.7	2186.7	2200.0
22	r_{DPHM}	3.226	3.091	2.948	2.814	2.715	2.621	2.626
	r_{DDT}	−0.3987	−0.3821	−0.3639	−0.3486	−0.3387	−0.3256	−0.3124
	I	2149.1	2159.8	2170.8	2181.7	2192.6	2204.4	2216.4
27	r_{DPHM}	3.245	3.115	2.975	2.846	2.741	2.659	2.668
	r_{DDT}	−0.3796	−0.3584	−0.3364	−0.3167	−0.3123	−0.2877	−0.2705
	I	2153.5	2165.6	2177.8	2190.3	2200.0	2215.7	2229.5
80	r_{DPHM}	3.307	3.172	3.040	2.894	2.795	2.700	2.706
	r_{DDT}	−0.3175	−0.3013	−0.2839	−0.2688	−0.2589	−0.2465	−0.2323
	I	2167.8	2179.4	2191.3	2203.2	2215.3	2228.1	2241.5
21	r_{DPHM}	3.373	3.236	3.089	2.952	2.851	2.754	2.757
	r_{DDT}	−0.2519	−0.2378	−0.2231	−0.2104	−0.2027	−0.1923	−0.1810
	I	2182.9	2194.8	2206.8	2219.2	2231.6	2244.4	2257.6
52	r_{DPHM}	3.447	3.305	3.150	3.006	2.898	2.796	2.794
	r_{DDT}	−0.1774	−0.1689	−0.1619	−0.1564	−0.1553	−0.1511	−0.1447
	I	2200.0	2211.8	2222.7	2233.9	2244.9	2256.7	2269.0
74	r_{DPHM}	3.463	3.320	3.168	3.026	2.922	2.821	2.821
	r_{DDR}	−0.1618	−0.1536	−0.1437	−0.1360	−0.1321	−0.1257	−0.1171
	I	2203.6	2215.5	2227.4	2239.5	2251.6	2264.4	2277.6
DPHM-I		1423.5	1429.8	1435.4	1443.2	1450.0	1459.1	1466.2
DDT-I		2241.4	2253.2	2264.6	2276.6	2289.4	2302.1	2314.3

[a] Standard deviation of the mean value varies between 0.0000 and 0.0432.
[b] Standard deviation of the mean value varies between 0.0002 and 0.0026.
[c] Standard deviation of the mean value varies between 0.00 and 3.56 (DPHM) and 0.00 and 1.16 (all other compounds).
[d] For numbering of compounds see Section 3.1.

isomers differ from each other in a statistically significant way only for *p,p'*-DDT as reference compound.

4.3. Retention index method

Using the second GLC method the results obtained for Eq. 5 (temperature dependence of I_i) are shown in Table 4 for both TCBTs and diphenylmethane plus *p,p'*-DDT. For the latter compounds also the linear temperature dependence is included as an example typical for the results found for all other compounds as well. Looking at the statistics this example clearly illustrates the necessity of using a nonlinear temperature dependence instead of a linear one.

The results reported in Table 5 show the vapour pressures and heats of vaporization at different

Table 2
Regression coefficients ($1-\Delta H_1/\Delta H_2$, C) and squared correlation coefficients (r^2) of Ugilec isomers (nr.) found with Eq. 2 for diphenylmethane or p,p'-DDT as reference compound

Compound[c]	Diphenylmethane			p,p'-DDT		
	$1-\Delta H_1/\Delta H_2$[a]	$-C$[b]	r^2	$1-\Delta H_1/\Delta H_2$[a]	$-C$[b]	r^2
28	−0.330	4.249	0.964	0.0447	−0.5520	0.998
25	−0.356	4.455	0.968	0.0302	−0.4595	0.997
36	−0.359	4.499	0.965	0.0286	−0.4284	0.994
22	−0.362	4.572	0.969	0.0269	−0.3685	0.997
27	−0.351	4.548	0.965	0.0333	−0.3425	0.988
80	−0.364	4.665	0.970	0.0264	−0.2881	0.997
21	−0.371	4.753	0.970	0.0219	−0.2270	0.996
52	−0.393	4.913	0.973	0.0095	−0.1649	0.970
74	−0.386	4.899	0.972	0.0136	−0.1465	0.992

[a] 95% confidence limits <0.0304 (DPHM as reference) and <0.0016 (p,p'-DDT as reference).
[b] 95% confidence limits <0.142 (DPHM as reference) and <0.0020 (p,p'-DDT as reference).
[c] For numbering of compounds see Section 3.1.

temperatures calculated according to Eq. 3 for the TCBTs isomers, diphenylmethane and p,p'-DDT.

Vapour pressures (log P) and heats of vaporization of the nine TCBTs at 298.15 K range from −4.677 to −5.173 log units and from 23 555 to 24 820 cal mol^{-1}, respectively. In the middle of the experimental temperature range, at 463.15 K, these ranges amount to 0.700–0.481 log units and 17 111–17 995 cal mol^{-1}. A considerable temperature dependence is found for the heat of vaporization, amounting to about −40 cal mol^{-1} K^{-1} on the average. Almost all values found for the various TCBT isomers differ significantly due to the high accuracies of the determinations.

5. Discussion and conclusions

A selection of the results obtained with the retention index method for n-octadecane, diphenylmethane and p,p'-DDT and literature data is included in Table 6. In Fig. 2 plots are given for measured log P data versus $1/T$ over the complete temperature range of 298.15–493.15 K.

Table 3
Vapour pressures (log P/Torr) at 298.15 and 463.15 K and heat of vaporization (ΔH/cal mol^{-1}) at 463.15 K of Ugilec isomers (nr.) determined by the RRT method with diphenylmethane[a] or p,p'-DDT[b] as reference compound

Compound[c]	Diphenylmethane			p,p'-DDT		
	Log P		ΔH	Log P		ΔH
	298.15 K	463.15 K	463.15 K	298.15 K	463.15 K	463.15 K
28	−3.46	0.897	16 673	−5.102	0.501	21 455
25	−3.58	0.860	16 997	−5.223	0.465	21 780
36	−3.60	0.847	17 033	−5.245	0.452	21 816
22	−3.64	0.822	17 072	−5.281	0.426	21 855
27	−3.61	0.809	16 928	−5.256	0.413	21 711
80	−3.68	0.786	17 100	−5.319	0.391	21 866
21	−3.73	0.762	17 183	−5.370	0.366	21 966
52	−3.82	0.738	17 463	−5.467	0.342	22 246
74	−3.81	0.729	17 370	−5.452	0.333	22 152

Values of reference pressures and heats of vaporization are included in Table 6 and Fig. 2. 1 Torr=1 mmHg=133.3224 Pa; 1 cal=4.184 J.
[a] Errors vary between 0.09 and 0.11 log P units and 384 and 405 cal mol^{-1}.
[b] Errors vary between 0.0024 and 0.0029 log P units and 22 and 41 cal mol^{-1}
[c] For numbering of compounds see Section 3.1.

Table 4
Temperature (T/K) dependence of the Kováts retention index (I) of Ugilec isomers (nr.), diphenylmethane (DPHM) and p,p'-DDT (DDT): regression coefficients, their 95% confidence limits, squared correlation coefficients (r^2) and standard error of regression (s.e.r.) of Eq. 5 ($I_T=B_0+B_1T^2$)

Compound	B_0	$B_1\cdot1000$	r^2	s.e.r.
28	1871.2±1.2	1.233±0.005	0.99990	0.24
25	1915.9±1.0	1.128±0.005	0.99991	0.22
36	1919.6±3.4	1.148±0.016	0.99905	0.71
22	1923.1±0.9	1.205±0.004	0.99994	0.18
27	1899.9±5.4	1.352±0.025	0.998	1.12
80	1920.0±1.0	1.321±0.005	0.99994	0.18
21	1931.4±0.6	1.341±0.003	0.99998	0.13
52	1969.8±1.7	1.230±0.008	0.9998	0.35
74	1954.9±0.7	1.326±0.003	0.99997	0.15
DPHM	1276.9±3.6	0.777±0.017	0.998	0.76
DPHM[a]	1110.7±9.6	719.4±20.7	0.995	1.00
DDT	1994.6±1.2	1.316±0.006	0.99991	0.25
DDT[a]	1712.8±5.1	1219.0±10.9	0.9995	0.53

[a] Linear equation ($I_T=B_0+B_1T$).

Correspondence with literature data of both vapour pressures and heat of vaporization turns out to be excellent for n-octadecane both at environmental and experimental temperatures (298.15 and 463.15 K), emphasizing the accuracy and scope of Eq. 6.

Correspondence for diphenylmethane is almost equally good with respect to vapour pressure except for the low-temperature region, where the literature data are slightly higher than the values found with the retention index method. The literature low-temperature data were, however, obtained through linear extrapolation from the true experimental region (493.15–553.15 K) to a temperature of about 200 K lower. This both explains their higher value and suggests a higher reliability of the retention index method values.

Results are satisfactory for p,p'-DDT as well. Vapour pressure data from other sources are lower than values obtained with the retention index method by 0.25 log units (or a factor of 1.8 for the non log-transformed pressure) at a maximum. Similar variation is found between other experimental methods [14–17] and the value at 298.15 K (−5.337) is just in between two values (−5.206 and −5.453) obtained by Bidleman [5] using the RRT method on two different columns. In addition we have to keep in mind that data obtained by other experimental methods, e.g. the gas saturation method, need to be converted from the solid phase to the (subcooled) liquid phase at low temperatures for this type of compounds. This conversion introduces errors amounting to about 0.3 log units [18], which increase with the deviation of the pertinent temperature from the melting point temperature.

Moreover, the log P values obtained for the Ugilec compounds are just in between the values found by the RRT method with diphenylmethane and p,p'-DDT as reference compounds, as is shown for Ugilec nr. 28 in Fig. 2.

Thus, the current version of the retention index method already performs quite well, confirms the results obtained previously for chlorinated benzenes and phenols [6] and allows its application to compounds of which the vapour pressure and heat of vaporization are unknown, such as Ugilec isomers. Yet the method is open to further improvement by treatment of its remaining assumptions on γ_{z+1}/γ_z and γ_z/γ_i, as is currently under investigation.

The results obtained for this application to Ugilec isomers (Table 5) turn out to be very accurate, although no literature data are available for detection of eventual systematic errors. Vapour pressure data (in the range of −4.68 to −5.17 log units at 298.15 K) are similar to vapour pressure data obtained for pentachlorobiphenyls (−4.52 to −5.19 log units) with the RRT method [5]. This is according to expectation regarding the correspondence in structure and molecular mass. Heat of vaporizations obtained

Table 5
Vapour pressures (log P/Torr)[a] and heats of vaporization (ΔH/cal mol^{-1})[b] of Ugilec isomers (nr.) at 298.15 and 463.15 K determined with the retention index method (Eq. 3)

Compound	Log P		ΔH	
	298.15 K	463.15 K	298.15 K	463.15 K
28	−4.677	0.700	23 555	17 111
25	−4.856	0.653	24 137	17 512
36	−4.883	0.636	24 183	17 545
22	−4.927	0.603	24 223	17 576
27	−4.875	0.586	23 914	17 368
80	−4.963	0.557	24 174	17 548
21	−5.029	0.524	24 319	17 651
52	−5.173	0.493	24 820	17 995
74	−5.141	0.481	24 622	17 862

1 Torr=1 mmHg=133.3224 Pa; 1 cal=4.184 J.
[a] Errors vary between 0.010 and 0.016 log units.
[b] Errors vary between 12 and 18 cal mol^{-1}

Table 6
Vapour pressures (log P/Torr) and heats of vaporization (ΔH/cal mol^{-1}) of n-octadecane (C_{18}), diphenylmethane (DPHM) and p,p'-DDT (DDT) at 298.15 and 463.15 K

	C_{18}		DPHM		DDT	
	298.15 K	463.15 K	298.15 K	463.15 K	298.15 K	463.15 K
log P[a]	−3.858	1.318	−1.568	2.072	−5.337	0.401
log P	−3.754[b]	1.317[b]	−1.212[c]	2.061[c]	−5.588[e]	0.273[e]
ΔH[a]	22 744	16 472	15 968	11 781	25 132	18 218
ΔH	21 286[b]	16 462[b]	15 564[d]	12 534[c]	22 458[e]	

1 Torr=1 mmHg=133.3224 Pa; 1 cal=4.184 J.
[a] Determined according to Eq. 5.
[b] Values according to Macknick and Prausnitz [12] (T range: 318.15–361.15 K) and Ohé [11] (T range: 447.65–590.15 K), belonging to the reference values for Eq. 6.
[c] Values according to Ohé [11] (T-range: 493.15–553.15 K), used as reference values in the RRT method.
[d] Calculated from the boiling point temperature (T_{bp}=537.45 K) according to the Hildebrand rule: ΔH (cal mol^{-1})=−2950+23.7T_{bp}+0.02T_{bp}^2 [10].
[e] Values according to Eitzer and Hites [8] (T-range: 293.15–373.15 K), used as reference values in the RRT method.

for Ugilec isomers differ significantly between isomers and will be used as descriptors for the prediction of partition constants.

With respect to our version of the RRT method we have to consider the degree of deviation from true values caused by linear extrapolations from the temperature of measurement of reference data to the temperature at which GLC relative retention times were collected. Using diphenylmethane as reference log P values are obtained higher than retention index method values, by 0.20 to more than 1.0 log units, whereas p,p'-DDT as reference produces values lower by 0.06–0.33 log units (see also Fig. 2). This observation is a direct consequence of the deviations between log P values for these reference compounds obtained with our retention index method and with other methods as discussed above. A too high value of ln P_2 (diphenylmethane) will result into under-

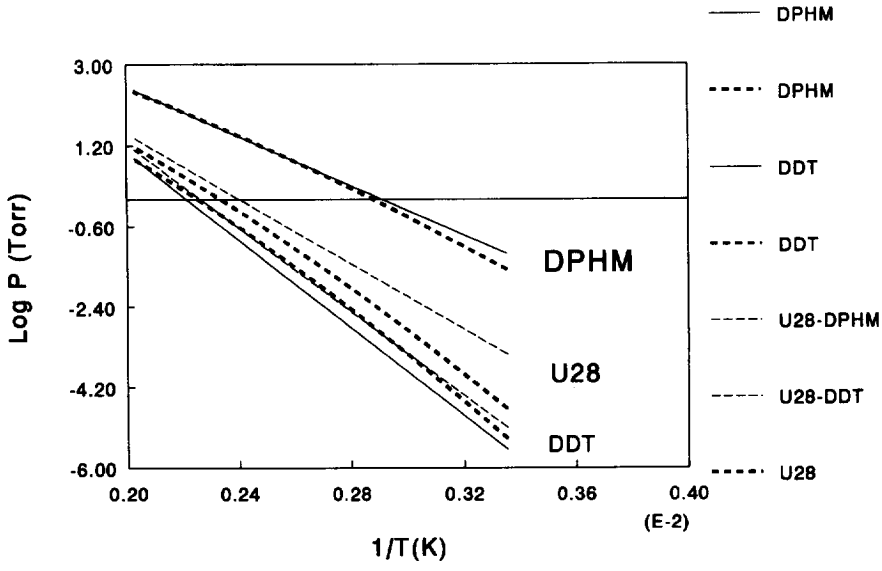

Fig. 2. Log P (Torr) versus $1/T$ (K) of diphenylmethane (DPHM), tetrachlorobenzyltoluene nr. 28 (U28) and p,p'-DDT (DDT) from literature data (solid lines), obtained by RRT method (dashed lines) with DPHM (U28-DPHM) or DDT (U28-DDT) as reference compound and by the retention index method (bold dashed lines).

estimated $(1-\Delta H_1/\Delta H_2)$ values or overestimated $\Delta H_1/\Delta H_2$ values in Eq. 3, both leading to overestimated values of $\log P_1$. The reverse holds true for *p,p'*-DDT. Also, the large differences found for the heat of vaporization applying both reference compounds can be explained (see Table 3). For diphenylmethane this heat of vaporization is based on reference data temperatures of 493.15–553.15 K and GLC data temperatures of 433.15–493.15 K. Therefore, the heat of vaporization found (about 17 000 cal mol^{-1}), has to be compared with a heat of vaporization at about 463.15 K obtained with the retention index method (Table 5). The latter indeed amounts to about 17 000 cal mol^{-1}. Similarly, the RRT method values based on *p,p'*-DDT (about 21700 cal mol^{-1}) have to be compared with a RRT value at a temperature somewhere in between the ranges of 293.15–373.15 K and 433.15–493.15 K, which again corresponds with the data found in Table 5. Due to its high sensitivity to selection of reference compounds our version of the RRT method is not suited for accurate measurements of vapour pressures (and heats of vaporization).

Finally, it must be emphasized that for Ugilec compounds in this study the lowest temperature area experimentally accessible, using column lengths and low retention times common to this type of compounds, was applied. Yet these temperatures are substantially higher than environmental temperatures. For the retention index method extrapolation problems caused by this could be solved, contrary to the RRT method. With respect to the latter the original version sticking to corresponding temperatures of reference data and GLC data has to be used accepting the limitation in available reference data and often time-consuming chromatographic runs associated with it, even if short columns are applied [8].

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