Determination of Ambient Temperature Vapor Pressures and Vaporization Enthalpies of Branched Ethers

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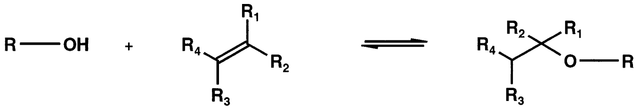
The standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ of 11 branched *tert*-butyl alkyl ethers, *tert*-amyl alkyl ethers, and tert-octyl alkyl ethers have been determined from the temperature dependence of the vapor pressure measured by the transpiration method. The temperature dependences of retention indices for a set of 31 ethers with branched molecular structures were measured using a nonpolar gas chromatographic column. Values of $\Delta_l^g H_m^\circ$ for 13 ethers obtained from the transpiration method in this work (as well as some values selected from the literature) together with data for these ethers obtained from the correlation gas-chromatography method were used to derive a correlation for the prediction of the standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ for branched ethers at the temperature $T = 298.15$ K. Experimental values of $\Delta_l^g H_m^\circ$ for 19 branched ethers were obtained with the help of this correlation. The procedure of the correlation gas-chromatography method was modified and substantially simplified by introduction of the Kovat's index for the correlation of the retention indices with the experimental $\Delta_l^g H_m^\circ$.

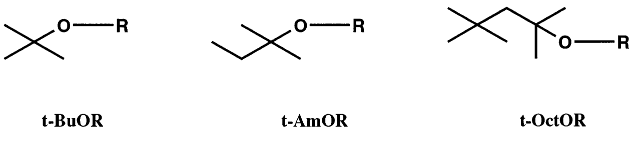
1. Introduction

To face serious environmental concerns, it is generally accepted that the worldwide trend for gasoline formulation will be toward the reduction of the emissions of exhaust gases with the help of new oxygenated additives (e.g. methyl *tert*-butyl ether or methyl *tert*-amyl ether), produced from iso-olefins and alcohols. Various ethers have been suggested[1] as fuel additives that either alone or with other ethers or alcohols can enhance the octane rating and reduce pollution effects arising from the combustion process. Thus, there is considerable interest in utilizing all available olefin and alcohol resources for the production of the oxygenated additives. On one hand, processing of light gasoline by thermal or catalytic cracking as well as by industrial polymerization of olefins is accompanied by the formation of a large amount of mixtures containing C_4 to C_{12} olefins as byproducts (oligomers). The most important are dimers and trimers of ethene, propene, and isobutene. Utilization of such mixtures without further separation is of great interest. On the other hand, diverse mixtures of alcohols are also available in the chemical industry as side products (e.g. by hydration of olefins). Thus, the production of the mixture of tertiary ethers could be suggested for utilization of both types of feedstocks. An accurate knowledge of the vaporization enthalpies and vapor pressures of pure olefins, alcohols, and ethers is vital for the optimal design of such processes and products. Information on their vapor pressures and vaporization enthalpies will form a basis for their characterization. In our previous work, the vaporization enthalpies of numerous olefins[2] and alcohols[3,4] and their vapor pressures were measured by the transpiration method. Continuing this line of research, the vaporization enthalpies of tertiary ethers have been measured using two techniques in order to provide the reliability of the experimental results: the transpiration method and the correlation gas-chromatography method. While several different group-additivity methods[5] give excellent correlations between observed and calculated $\Delta_l^g H_m^\circ$ values for linear homologues, deviations may arise for the branched members of the series. Very few systematic investigations of vaporization enthalpies of branched ethers are available in the literature.[6] We report here a systematic determination of the vaporization enthalpies of a series of branched ethers.

Some years ago we started an investigation of the chemical equilibrium of the reaction



where R and R_1 to R_4 are alkyl substituents of different chain length.[7−9] Results reported in this work refer to the reactions involving individual primary and secondary C_1 to C_6 alcohols with 2-methylpropene (isobutene), 2-methyl-2-butene (isoamylene), and 2,4,4-trimethyl-2-pentene (diisobutene). The products of these reactions are the appropriately branched ethers,



tert-butyl alkyl ethers (*t*-BuOR), *tert*-amyl alkyl ethers (*t*-AmOR), and *tert*-octyl alkyl ethers (*t*-OctOR). Our studies[7−9] of chemical equilibria in the liquid state have demonstrated that activities rather than mole fractions are necessary to obtain thermodynamic equilibrium constants for these reactions. The activity coefficients in the liquid mixtures could be estimated by the UNIFAC[10] or ERAS[11] models. However, the validity of activity coefficients of associated species calculated by these methods remains questionable.

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Therefore, it is desirable to possess a criterion to check the consistency of experimental results with estimates for the liquid state. An independent way to obtain such a criterion is to calculate enthalpies of the same reactions, alcohol + olefin ↔ ether, from standard enthalpies of formation, $\Delta_f{}^{l}H^\circ_m$, of the reaction participants in the liquid state. Concurrence between measured and estimated enthalpies can be a valuable test of the ability of the UNIFAC and ERAS models to predict the deviation from ideal behavior in the reactive associated mixtures. Liquid-state standard enthalpies of formation, $\Delta_f{}^{l}H^\circ_m$, of alcohols and olefins are available from the literature.[12] Experimental data for the branched ethers are scarce, but the developers of the MM3 force field calculation method[13] claim to predict the gaseous standard enthalpies of ethers with acceptable accuracy. Thus, a knowledge of vaporization enthalpies of the appropriate branched ether could provide the possibility of estimating enthalpies of formation of the products of the aforementioned reaction in the liquid state. The part of our work concerning equilibrium studies will be reported separately. In this study, the enthalpies of vaporization of a number of branched ethers are measured using the transpiration method and correlation gas-chromatography. We used our new experimental results together with literature data to obtain practical correlation equations that could be used to predict values for as yet unmeasured $\Delta_l^g H^\circ_m$ values of ethers. These predictions should help chemists and engineers to design and develop new processes more accurately.

2. Experimental Section

2.1. Materials. Samples of branched ethers were synthesized by alkylation of an appropriate alcohol with an olefin in the presence of a catalytic amount of cation-exchange resin in H^+ form (Amberlist 15, Aldrich) at 343 K. Prior to the experiments, the cation-exchange resin Amberlist 15 in the H^+ form was dried for 8 h at 383 K in a vacuum oven at reduced pressure. Liquid branched ethers were purified by distillation in a vacuum. The structures of the ethers used were established by NMR spectroscopy. The purities of all samples determined by GC were better than 0.99 mole fraction.

2.2. Transpiration Method. The enthalpies of vaporization of the branched ethers (see Table 1) were determined using the method of transference in a saturated N_2-stream.[3,4] About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. The amount of condensed product was determined by GC analysis using an external standard (hydrocarbon). Assuming that Dalton's law of partial pressures of ideal gaseous mixtures applied to the saturated nitrogen stream is valid, values of the vapor pressure p were calculated according to

$$p = mRT_a/V_{N_2}M \tag{1}$$

where $R = 8.314\,51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$; m is the mass of transported compound; V_{N_2} is the volume of transporting gas; M is the molar mass of the compound; and T_a is the temperature (±0.1 K) of the soap bubble meter. The volume of the gas V_{N_2} transferred through the tube was determined from the flow rate and time measurements. The flow rate was maintained constant using a high precision needle valve (Hoke). The accuracy of the volume V_{N_2} measurements from the flow rate was assessed to be (±0.02 to 0.03)%. The vapor pressure p at each saturation temperature was calculated from the mass of sample collected within a definite time period, according to eq 1. The uncertainties in the vapor pressures obtained by the transpiration method were assessed to be (1 to 2)%, depending on the pressure range.

The relation expressing the equilibrium existing between the vapor and the liquid phase of a pure substance is given by

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_l^g H^\circ_m}{T\Delta_l^g V_m} \tag{2}$$

where $\Delta_l^g V^\circ_m$ is the molar volume difference between the vapor phase and the liquid phase. $\Delta_l^g H^\circ_m$ depends on the temperature along the coexisting phase line. The correct expression has already been derived long ago:[14,15]

$$\frac{\mathrm{d}\Delta_l^g H_m}{\mathrm{d}T} = \Delta_l^g C_p + \left(\Delta_l^g V_m - T\,\frac{\partial \Delta_l^g V_m}{\partial T}\right)\frac{\Delta_l^g H_m}{T\Delta_l^g V_m} \tag{3}$$

where $\Delta_l^g C_p = C_p^g - C_p^l$ is the difference of the molar heat capacities at constant pressure for the gaseous and liquid phases. At low pressure, the molar volume of the liquid phase may be neglected in comparison to that of the vapor, and for nonassociating or weakly associating vapors, the ideal gas law may be adopted and contributions arising from the second virial coefficient can be neglected. With $\Delta_l^g H^\circ_m \approx RT/p$, one obtains the Clausius−Clapeyron equation,

$$-\frac{R\ \mathrm{d}(\ln p)}{\mathrm{d}\left(\frac{1}{T}\right)} = \Delta_l^g H^\circ_m \tag{4}$$

and eq 3 reduces to

$$\frac{\mathrm{d}\Delta_l^g H_m}{\mathrm{d}T} = \Delta_l^g C_p \tag{5}$$

Provided $\Delta_l^g V^\circ_m$ is independent of temperature in the temperature range considered, it follows that

$$\Delta_l^g H^\circ_m \cong \Delta_l^g H^\circ_{m,T_0} + \Delta_l^g C_p(T - T_0) \tag{6}$$

After substituting eq 6 into eq 4, an integration gives

$$R \ln p = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \tag{7}$$

where the vaporization enthalpy at the temperature T is given by

$$\Delta_l^g H^\circ_m(T) = -b + \Delta_l^g C_p T \tag{8}$$

where T_0 in eqs 6 and 7 is an arbitrarily chosen reference temperature.

Equation 7 was adjusted to the experimental vapor pressure data using the adjustable parameters a and b, and the molar enthalpies of vaporization $\Delta_l^g H^\circ_m(T)$ have been calculated using eq 8. The results together with the parameters a and b according to eq 7 are listed in Table 1. The reference temperature of $T_0 = 298.15$ K was chosen. Values of $\Delta_l^g C_p$ have been derived from experimental results for the isobaric molar heat capacities C_p^l of liquid

Table 1. Results for the Vapor Pressure p and $\Delta_l^g H_m^\circ$ Obtained by the Transpiration Method

T^a	m^b	$V(N_2)^c$	p^d	$p_{exp} - p_{calc}$	$\Delta_l^g H_m^\circ$	T^a	m^b	$V(N_2)^c$	p^d	$p_{exp} - p_{calc}$	$\Delta_l^g H_m^\circ$
K	mg	dm^3	Pa	Pa	kJ·mol^{-1}	K	mg	dm^3	Pa	Pa	kJ·mol^{-1}
tert-Butyl Isobutyl Ether; $\Delta_l^g H_m^\circ(298.15\ \mathrm{K}) = (41.19 \pm 0.38)\ \mathrm{kJ{\cdot}mol^{-1}}$ $\ln(p/\mathrm{Pa}) = 290.004/R - 66552.428/[R(T/\mathrm{K})] - 85.05/R\ \ln[(T/\mathrm{K})/298.15]$											
273.3^e	33.54	0.941	678.8	25.8	43.31	280.4	12.58	0.244	980.3	−74.3	42.70
278.6^e	34.53	0.701	938.0	1.3	42.86	282.5	12.39	0.195	1207.2	−0.8	42.53
283.5^e	23.43	0.328	1362.0	74.4	42.44	284.6	12.55	0.171	1397.6	17.3	42.35
288.4^e	19.23	0.207	1768.7	22.9	42.02	287.6	11.74	0.134	1663.8	1.2	42.09
293.4^e	16.20	0.131	2354.3	4.4	41.60	290.6	12.03	0.115	1995.7	2.8	41.84
298.4^e	18.20	0.109	3186.6	64.1	41.17	293.6	15.98	0.125	2439.2	61.8	41.58
303.4^e	13.85	0.066	4025.5	−73.4	40.75	295.6	14.89	0.106	2685.8	18.7	41.41
308.4^e	20.85	0.076	5224.2	−94.6	40.32	298.7	15.85	0.096	3146.1	−28.9	41.15
275.4	11.87	0.303	746.3	−8.6	43.13	301.8	26.26	0.134	3722.6	−39.3	40.88
276.4	10.69	0.255	798.1	−10.1	43.04	304.8	29.16	0.125	4451.4	37.3	40.63
278.5	11.55	0.244	900.0	−30.4	42.87						
tert-Amyl Methyl Ether; $\Delta_l^g H_m^\circ(298.15\ \mathrm{K}) = (35.27 \pm 0.39)\ \mathrm{kJ{\cdot}mol^{-1}}$ $\ln(p/\mathrm{Pa}) = 261.729/R - 55308.639/[R(T/\mathrm{K})] - 67.22/R\ \ln[(T/\mathrm{K})/298.15]$											
274.2	4.33	0.039	2692.7	7.1	36.88	287.8	12.20	0.052	5690.2	−24.1	35.96
276.2	4.82	0.039	2997.5	−21.3	36.74	292.9	16.30	0.052	7602.5	188.1	35.62
278.2	5.33	0.039	3314.6	−71.4	36.61	297.8	14.70	0.039	9141.6	−279.7	35.29
280.2	6.11	0.039	3799.7	9.5	36.47	302.8	19.80	0.039	12313.2	405.2	34.95
282.8	7.11	0.039	4421.6	46.1	36.30	307.8	23.40	0.039	14552.0	−352.5	34.62
283.8	10.03	0.052	4678.1	58.3	36.23						
tert-Amyl Ethyl Ether; $\Delta_l^g H_m^\circ(298.15\ \mathrm{K}) = (39.22 \pm 0.39)\ \mathrm{kJ{\cdot}mol^{-1}}$ $\ln(p/\mathrm{Pa}) = 284.162/R - 63230.221/[R(T/\mathrm{K})] - 80.53/R\ \ln[(T/\mathrm{K})/298.15]$											
274.2	28.44	0.443	1412.5	−0.1	41.15	287.2	33.42	0.222	3213.8	48.7	40.10
276.2	29.37	0.388	1613.9	4.5	40.99	290.2	29.20	0.166	3744.0	−19.1	39.86
278.2	29.53	0.360	1821.0	−8.3	40.83	293.2	28.85	0.139	4439.3	−14.6	39.62
280.2	32.06	0.333	2055.4	−18.9	40.67	296.2	34.27	0.139	5272.5	24.4	39.38
282.2	33.47	0.305	2340.8	−6.2	40.50	299.2	39.27	0.139	6128.0	−29.7	39.14
284.2	34.71	0.277	2670.0	20.5	40.34	302.2	48.46	0.139	7186.5	−8.6	38.89
tert-Amyl Propyl Ether; $\Delta_l^g H_m^\circ(298.15\ \mathrm{K}) = (43.76 \pm 0.65)\ \mathrm{kJ{\cdot}mol^{-1}}$ $\ln(p/\mathrm{Pa}) = 297.728/R - 70019.432/[R(T/\mathrm{K})] - 88.06/R\ \ln[(T/\mathrm{K})/298.15]$											
274.2	7.91	0.376	400.2	3.7	45.87	287.3	9.31	0.178	997.4	16.2	44.72
276.2	6.84	0.293	444.8	−13.7	45.70	290.3	7.90	0.125	1198.6	8.6	44.46
278.1	7.61	0.272	532.9	7.7	45.53	293.3	7.87	0.105	1433.6	−2.2	44.19
280.2	8.40	0.261	612.1	3.6	45.35	296.2	9.88	0.105	1799.4	85.6	43.94
282.2	8.65	0.230	716.1	17.7	45.17	299.2	11.38	0.105	2071.8	23.5	43.67
284.2	8.72	0.209	793.8	−5.6	44.99	302.2	12.81	0.105	2332.2	−104.8	43.41
285.1	13.24	0.314	803.4	−45.5	44.91						
tert-Amyl Butyl Ether; $\Delta_l^g H_m^\circ(298.15\ \mathrm{K}) = (48.30 \pm 0.56)\ \mathrm{kJ{\cdot}mol^{-1}}$ $\ln(p/\mathrm{Pa}) = 311.153/R - 76794.271/[R(T/\mathrm{K})] - 95.56/R\ \ln[(T/\mathrm{K})/298.15]$											
278.2^e	14.57	1.563	160.2	9.0	50.21	274.2	2.630	0.407	111.12	1.04	50.59
283.2^e	7.18	0.526	234.4	12.8	49.73	276.2	2.874	0.386	127.82	−1.41	50.40
288.2^e	9.00	0.479	323.2	4.2	49.25	278.2	2.856	0.325	150.84	−0.43	50.21
293.2^e	9.78	0.351	478.4	26.2	48.78	281.3	2.616	0.244	184.22	−7.80	49.91
298.2^e	10.20	0.263	665.8	34.5	48.30	283.2	3.352	0.264	217.89	−3.63	49.73
303.2^e	10.04	0.191	901.0	31.8	47.82	285.2	3.266	0.224	250.90	−5.91	49.54
308.2^e	12.22	0.175	1199.1	18.6	47.34	286.2	2.647	0.173	263.16	−13.08	49.45
278.2^e	14.57	1.563	160.2	9.0	50.21	290.2	3.152	0.153	355.14	−12.31	49.06
283.2^e	7.18	0.526	234.4	12.8	49.73	293.2	3.880	0.153	437.17	−14.98	48.78
288.2^e	9.00	0.479	323.2	4.2	49.25	296.2	3.594	0.112	552.20	−1.20	48.49
293.2^e	9.78	0.351	478.4	26.2	48.78	298.2	3.628	0.102	613.16	−18.20	48.30
298.2^e	10.20	0.263	665.8	34.5	48.30	301.2	3.523	0.081	744.27	−21.84	48.01
303.2^e	10.04	0.191	901.0	31.8	47.82	304.2	4.266	0.081	901.24	−23.79	47.73
308.2^e	12.22	0.175	1199.1	18.6	47.34						
tert-Octyl Methyl Ether; $\Delta_l^g H_m^\circ(298.15\ \mathrm{K}) = (45.28 \pm 0.33)\ \mathrm{kJ{\cdot}mol^{-1}}$ $\ln(p/\mathrm{Pa}) = 290.300/R - 70157.400/[R(T/\mathrm{K})] - 83.43/R\ \ln[(T/\mathrm{K})/298.15]$											
278.3^e	12.00	1.053	195.8	−1.9	46.94	280.3	5.99	0.432	238.3	9.9	46.77
283.2^e	10.21	0.622	281.8	1.4	46.53	283.3	5.45	0.339	275.9	−6.4	46.52
288.1^e	12.73	0.558	391.9	0.2	46.12	286.3	6.39	0.308	356.0	8.9	46.27
293.3^e	13.88	0.423	563.6	13.3	45.69	289.3	5.92	0.247	412.6	−11.7	46.02
298.0^e	13.21	0.303	747.8	9.3	45.30	292.3	5.49	0.185	510.2	−5.9	45.77
303.2^e	12.35	0.208	1021.8	12.8	44.86	295.2	5.45	0.154	606.9	−13.8	45.53
308.0^e	16.79	0.215	1339.3	9.5	44.46	298.2	5.94	0.139	735.2	−12.4	45.28
276.2	4.76	0.493	165.6	−3.8	47.11	301.2	7.98	0.154	888.7	−7.6	45.03
277.3	5.01	0.463	185.9	2.2	47.02	304.2	9.61	0.154	1070.2	0.5	44.78
tert-Octyl Ethyl Ether; $\Delta_l^g H_m^\circ(298.15\ \mathrm{K}) = (46.98 \pm 0.41)\ \mathrm{kJ{\cdot}mol^{-1}}$ $\ln(p/\mathrm{Pa}) = 306.015/R - 75824.207/[R(T/\mathrm{K})] - 96.74/R\ \ln[(T/\mathrm{K})/298.15]$											
274.3	5.01	0.860	91.3	−1.3	49.29	289.2	5.80	0.327	277.2	−0.3	47.85
277.2	4.71	0.614	120.1	4.1	49.01	292.2	4.43	0.205	339.0	−1.2	47.56
280.1	4.81	0.532	141.4	−3.1	48.73	295.2	8.13	0.307	414.6	−0.2	47.27
283.2	5.26	0.450	182.9	1.3	48.43	298.2	8.03	0.246	511.7	8.4	46.98
286.1	5.80	0.409	221.8	−1.7	48.15	301.2	53.50	1.392	601.8	−5.7	46.69

Table 1 (Continued)

T^a	m^b	$V(N_2)^c$	p^d	$p_{exp} - p_{calc}$	$\Delta_l^g H_m^\circ$	T^a	m^b	$V(N_2)^c$	p^d	$p_{exp} - p_{calc}$	$\Delta_l^g H_m^\circ$
K	mg	dm^3	Pa	Pa	kJ·mol^{-1}	K	mg	dm^3	Pa	Pa	kJ·mol^{-1}
tert-Octyl Propyl Ether; $\Delta_l^g H_m^\circ$(298.15 K) = (50.10 ± 0.33) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 316.810/R - 81183.970/[R(T/\mathrm{K})] - 104.27/R \ln[(T/\mathrm{K})/298.15]$											
274.3	1.31	0.559	33.6	−1.2	52.58	298.3	13.47	0.882	219.6	5.9	50.08
277.3	1.26	0.409	44.3	−0.5	52.27	299.3	8.69	0.545	229.3	0.8	49.98
278.2	3.12	0.913	49.1	1.0	52.18	300.3	9.14	0.545	241.1	−3.2	49.87
280.2	1.43	0.354	58.0	1.5	51.97	301.2	9.45	0.531	255.7	−3.6	49.78
283.4	2.65	0.545	70.0	−2.8	51.63	302.2	10.97	0.559	282.5	5.5	49.67
286.2	3.46	0.545	91.3	1.3	51.34	303.2	10.36	0.504	295.6	0.0	49.57
289.3	3.24	0.395	117.9	4.6	51.02	304.3	12.24	0.545	323.1	5.7	49.45
292.3	3.19	0.327	140.4	−0.4	50.71	305.2	12.49	0.545	329.4	−6.7	49.36
294.4	3.83	0.341	161.6	−1.7	50.49	306.2	13.97	0.559	359.5	1.3	49.26
296.3	2.34	0.181	185.8	−0.6	50.29	307.2	23.17	0.872	382.0	0.6	49.15
297.4	6.80	0.487	200.8	−0.2	50.17	308.2	9.97	0.368	389.8	−16.2	49.05
297.8	3.39	0.232	210.3	3.8	50.13						
tert-Octyl Butyl Ether; $\Delta_l^g H_m^\circ$(298.15 K) = (52.87 ± 0.35) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 323.145/R - 86198.631/[R(T/\mathrm{K})] - 111.80/R \ln[(T/\mathrm{K})/298.15]$											
278.3	1.08	1.118	12.8	0.1	55.08	299.2	1.52	0.310	65.4	0.8	52.75
281.3	1.17	0.943	16.5	0.2	54.75	302.2	1.61	0.270	79.7	0.00	52.41
284.3	1.26	0.809	20.6	−0.2	54.41	305.2	1.63	0.216	100.3	2.5	52.08
287.3	1.39	0.687	26.9	0.3	54.08	308.2	1.17	0.135	115.5	−3.7	51.74
290.3	1.31	0.539	32.4	−1.1	53.74	311.2	1.49	0.135	147.4	2.6	51.41
293.3	1.26	0.404	41.3	−0.7	53.41	314.2	1.76	0.135	174.1	−0.9	51.07
296.3	1.50	0.377	53.0	0.5	53.07						
tert-Octyl Amyl Ether; $\Delta_l^g H_m^\circ$(298.15 K) = (55.86 ± 0.28) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 331.733/R - 91438.385/[R(T/\mathrm{K})] - 119.33/R \ln[(T/\mathrm{K})/298.15]$											
277.5	2.04	24.60	3.7	0.1	58.32	291.6	1.85	5.21	12.4	0.2	56.64
279.5	0.56	3.97	4.4	0.1	58.09	294.7	2.54	5.06	15.5	−0.2	56.27
281.5	2.06	12.14	5.2	−0.1	57.85	297.7	2.20	4.09	19.4	−0.3	55.91
283.5	2.44	10.90	6.2	0.0	57.61	300.7	1.80	2.49	24.7	0.1	55.56
285.6	2.22	8.04	7.3	−0.1	57.36	303.2	2.48	32.11	30.0	0.5	55.26
288.6	2.18	6.11	9.5	−0.1	57.00						
tert-Octyl Hexyl Ether; $\Delta_l^g H_m^\circ$(298.15 K) = (59.84 ± 0.64) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 339.808/R - 96692.681/[R(T/\mathrm{K})] - 123.60/R \ln[(T/\mathrm{K})/298.15]$											
295.8	0.72	1.54	5.3	0.1	60.14	314.1	0.85	0.45	21.5	0.1	57.88
298.8	0.84	1.38	6.9	0.1	59.77	317.1	0.68	0.31	25.5	−0.9	57.51
308.0	1.27	1.03	14.1	0.3	58.63	320.1	1.17	0.42	32.1	−0.3	57.13
301.9	0.88	1.18	8.6	−0.1	59.38	320.1	1.17	0.42	32.1	−0.3	57.13
311.0	1.04	0.73	16.2	−1.0	58.26	323.1	0.70	0.20	40.6	1.0	56.76
304.9	1.22	1.26	11.1	0.1	59.01	326.2	0.65	0.15	50.2	1.9	56.38

[a] Temperature of saturation. N_2 gas flow rate = 0.22 to 0.69 cm^3·s^{-1}. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at T = 243 K. [e] Results were measured previously[6] and corrected in this work (see text).

ethers[16] and from values of the isobaric molar heat capacities C_p^g of gaseous species calculated according to a procedure developed by Domalski and Hearing.[16]

2.3. GC-Correlation Method. The second method used was the method of correlation gas-chromatography.[17,18] This method correlates the gas-chromatographical behavior (retention time) of a compound of interest with a series of the retention times of some standard compounds with known enthalpies of vaporization. Correlation gas-chromatography has several advantages over other methods. It is a fast and easy method where low concentrations are used and relatively impure substances are tolerated. A detailed description of the method used can be found elsewhere.[17] A plot of ln 1/(t_r/min) versus 1/(T/K), where t_r is the retention time (in min) of the gas-chromatographic peak of the substance under study corrected for the dead volume, results in a straight line, whose slope when multiplied by the gas constant R gives $\Delta_{sol}^g H_m^\circ$. The value of $\Delta_{sol}^g H_m^\circ$ is the enthalpy of transfer from the solution of a compound in the stationary phase of the GC column to the vapor phase. It was found that, in cases where compounds are properly selected with regard to the analogy of their molecular structures, plotting $\Delta_{sol}^g H_m^\circ$ versus the known standard molar enthalpy of vaporization $\Delta_l^g H_m^\circ$ also provides a linear relationship.[18] This relationship can subsequently be used to evaluate the unknown enthalpy of vaporization of any structurally related species provided that the unknown species is analyzed under the same conditions as those for the substances chosen as standards. We used our own experimental results for $\Delta_l^g H_m^\circ$ of branched ethers obtained from the transpiration method (Table 1), as well the data for *t*-BuOMe, *t*-BuOEt, and *t*-AmOMe available from the literature (Table 2). To our knowledge, methods that are capable of reflecting the effect of minor structural differences in the position and configuration of substituents on $\Delta_l^g H_m^\circ$ better than correlation gas-chromatography have not existed up to now.

Measurements were made using a Hewlett-Packard Series 5890 gas chromatograph, equipped with a FID and Hewlett-Packard Integrator 3390A. GLC runs were done isothermally on a capillary column of length 60 m and diameter 0.32 mm with a film thickness of the stationary phase (nonpolar methyl silicone DB-5) of 0.25 μm. Nitrogen was used as carrier gas with a flow rate of 0.333 cm^3·s^{-1}. At each temperature, the corrections of retention times with the dead retention time were made. The latter was adjusted with help of the retention times of linear aliphatic hydrocarbons according to established procedure.[35] The temperature was maintained constant within ±0.1 K. All substances were dissolved in methanol. Retention times

Table 2. Compilation of Data of Enthalpies of Vaporization $\Delta_l^g H_m^\circ$(298.15 K) for Branched Ethers

compd	technique[a]	C_p^l(298 K)[b] J·mol^{-1}·K^{-1}	C_p^g(298 K)[b] J·mol^{-1}·K^{-1}	$-\Delta_l^g C_p$(298 K)[c] J·mol^{-1}·K^{-1}	$\Delta_l^g H_m^\circ$(298 K) kJ·mol^{-1}	ref
t-BuOMe [1634-04-4]		190.65	130.96	59.69	30.04[e]	19
t-BuOEt [637-92-3]	E	224.29	151.29	73.00	32.97[e]	19
	E				33.78[d]	21
	S				33.69[d]	22
t-BuOPr [29072-93-3]]	GC	254.71	174.18	80.53	38.34	this work
t-BuOiPr [17348-59-3]	E	252.69	174.47	78.22	34.67	19
	E				35.10	23
	E				35.92[d]	22
	GC				36.18	this work
t-BuOiBu [33021-02-2]	E	282.15	197.10	85.05	39.12	19
	C				40.12 ± 0.13	24
	T				41.19 ± 0.31[d]	this work
t-BuOsBu [32970-45-9]	C	283.11	197.36	87.57	40.34 ± 0.18	24
	GC				41.31	this work
t-BuOBu [1000-63-1]	C	285.13	197.07	88.06	42.33 ± 0.25	24
	GC				43.18	this work
t-BuOAm [10100-95-5]	GC	315.55	219.96	95.59	47.39[d]	37
					48.25	this work
t-BuOHex [69775-79-7]	GC	345.97	242.85	103.12	53.22	this work
t-BuOHep [78972-97-1]	GC	366.17	271.77	94.40	56.60	this work
t-BuOOct [51323-70-7]	GC	396.59	294.66	101.9	61.41	this work
t-AmOMe [994-05-8]	E	221.07	153.85	67.22	35.74[d]	25
	E				35.47[d]	20, 26
	E				35.30[d]	21
	E				35.01[d]	27
	E				35.21[d]	28
	E				34.29[d]	29
	E				34.80[d]	30
	T				35.27 ± 0.39[d]	this work
t-AmOEt [919-94-8]	E	254.71	174.18	80.53	38.78[d]	21
	E				37.79[d]	30
	T				39.22 ± 0.39[d]	this work
t-AmOPr [74058-13-2]	T	285.13	197.07	88.06	43.76 ± 0.65[d]	this work
t-AmOiPr [3249-46-5]	GC	283.11	197.36	85.75	41.57	this work
t-AmOiBu	GC	291.19	199.91	91.28	46.25	this work
t-AmOsBu	GC	313.53	220.25	93.28	46.75	this work
t-AmOBu [3249-47-6]	T	315.55	219.96	95.59	48.30 ± 0.56[d]	this work
t-AmOAm	GC	345.97	242.85	103.12	53.53	this work
t-AmOcycloHex	T	362.25	260.35	101.90	54.24 ± 0.19[d]	6, this work
t-AmOHex	GC	376.39	265.74	110.65	58.57	this work
t-OctOMe [62108-41-2]	E	304.27	220.84	83.43	45.32[d]	31
	T				45.28 ± 0.33[d]	this work
t-OctOEt [1698120]	T	337.91	241.17	96.74	46.98 ± 0.41[d]	this work
t-OctOPr	T	368.33	264.06	104.27	50.10 ± 0.33[d]	this work
t-OctOiBu	GC	395.77	286.98	108.78	51.55	this work
t-OctOBu	T	398.75	286.95	111.80	52.87 ± 0.35[d]	this work
t-OctOAm	T	429.17	309.84	119.33	55.86 ± 0.28[d]	this work
t-OctO(4-methylpentyl)[f]	GC	456.61	332.76	123.85	57.50	this work
t-OctO(3-methylpentyl)[g]	GC	456.61	332.76	123.85	57.96	this work
t-OctO(3,3-dimethylbutyl)[h]	GC	451.53	331.05	120.48	56.43	this work
t-OctOHex	T	459.59	332.73	126.86	59.84 ± 0.64[d]	this work

[a] Technique: C, calorimetric method; E, ebulliometry; T, transpiration; S, static method. [b] Molar heat capacity of liquid and gas, respectively, calculated according ref 16. [c] The molar heat capacity difference between gaseous and liquid phases. [d] Derived using eqs 7 and 8 with the molar heat capacity difference ΔC_p. [e] Value recommended in ref 19. [f] This product is prepared according to the reaction of 2,4,4-trimethyl-2-pentene with 2-methyl-1-pentanol. [g] This product is prepared according to the reaction of 2,4,4-trimethyl-2-pentene with 3-methyl-1-pentanol. [h] This product is prepared according to the reaction of 2,4,4-trimethyl-2-pentene with 3,3-dimethyl-1-butanol.

were generally reproducible within (1 to 2) s. The enthalpies of transfer from the solution to the gas phase $\Delta_{sol}^g H_m^\circ$ were obtained for each compound by plotting ln 1/(t_r/min) versus 1/(T/K). The slope of this linear correlation ln 1/(t_r/min) = $A + B(T^{-1}$/K) when multiplied by the gas constant gives $\Delta_{sol}^g H_m^\circ$.

3. Results and Discussion

3.1. Enthalpies of Vaporization from the Transpiration Method. Data for the vapor pressures and enthalpies of vaporization of branched ethers are scarce.[19] A critical survey of the available $\Delta_l^g H_m^\circ$(298.15 K) values and some new experimental results on the branched ethers have been reported recently by Verevkin et al.[6] A transpiration method has been used to derive enthalpies of vaporization for *t*-BuOiBu, *t*-AmOBu, and *t*-OctOMe in the laboratory at University of Freiburg. After the data were already published, we detected a minor mistake by GC calibration experiments for these three ethers. This report gave us an opportunity to correct our previous $p-T$ mesurements.[6] To ascertain our results, in this work we decided to extend the temperature range as well as the saturation conditions of the transpiration experiments with these branched ethers. The N_2 gas flow range in each experiment was changed in several steps from (0.22 to 0.69) cm^3·s^{-1} in order to check saturation of the stream with the transported compound. No impact of the flow was detected within the investigated range. Results obtained in this

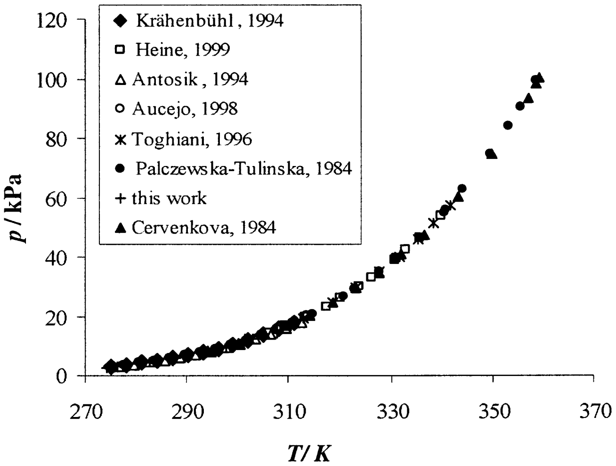

Figure 1. Comparison of the vapor pressure mesurements for methyl *tert*-amyl ether.

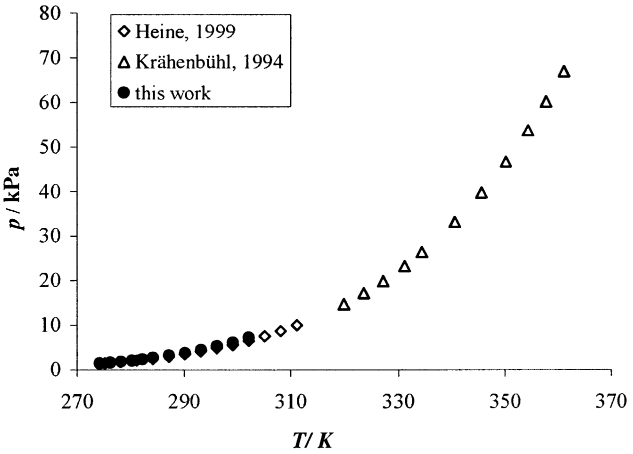

Figure 2. Comparison of the vapor pressure mesurements for ethyl *tert*-amyl ether.

work were consistent with the corrected results for the vapor pressure measurements published earlier.[6] Thus, Table 1 presents results of the joint treatment of both data sets of vapor pressures for *t*-BuOiBu, *t*-AmOBu, and *t*-OctOMe. The values of $\Delta_l^g H_m^\circ$ in the last column of Table 1 have been obtained using eq 8 with data of $\Delta_l^g C_p$ from Table 2. Gmehling and co-workers[21,22] made vapor pressure measurements of a number of branched ethers over a wide range of temperature. The vapor pressures of *t*-OctOMe were measured by Uusi-Kyyny et al.[31] The comparison of the vapor pressures reported by these authors with our results is presented in Figures 1−3. However, none of the aforementioned investigations gave calculated values of vaporization enthalpies for the compounds studied. To derive enthalpies of vaporization at 298.15 K and to get comparison with our results, the $p-T$ data available from the literature have been treated by using eqs 7 and 8. Comparison of values of $\Delta_l^g H_m^\circ(298.15\ \text{K})$ obtained from literature data by this procedure is shown in Table 2. Our values for vapor pressures of *t*-AmOMe, *t*-AmOEt, and *t*-OctOMe obtained by the transpiration method as well as their values of $\Delta_l^g H_m^\circ(298.15\ \text{K})$ are in very close agreement with those measured by ebulliometry[21,25−29] and the static method[22] (see Figures 1−3 and Table 2).

3.2. Enthalpies of Vaporization from the GC-Correlation Method. We used our experimental results for $\Delta_l^g H_m^\circ(298.15\ \text{K})$ of ethers obtained from the transpiration method (see Table 1), as well the data for *tert*-butyl methyl and *tert*-butyl ethyl ether available from the literature (see Table 2), as standards for the GC-correlation method.

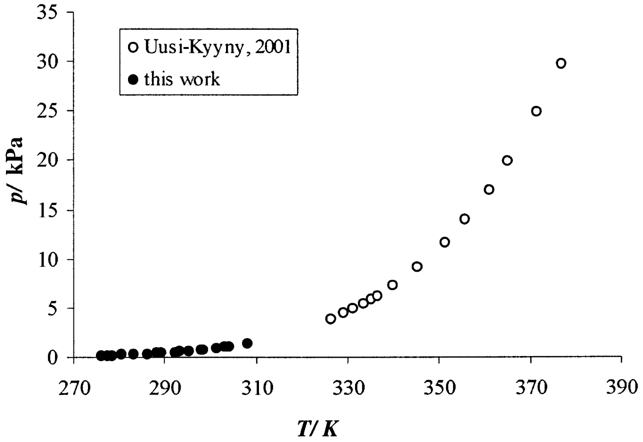

Figure 3. Comparison of the vapor pressure mesurements for methyl *tert*-octyl ether.

The experimental results for the temperature dependence of the corrected retention time in the form of equation $\ln(1/t_r) = A + B/T$ for a series of seven reference *t*-BuOR and *t*-AmOR ethers and their derived values of $\Delta_{sol}^g H_m^\circ$ are listed in Table 3. From the correlation of the selected data set, the equation for the estimation of vaporization enthalpies was obtained,

$$\Delta_l^g H_m^\circ/\text{kJ}\cdot\text{mol}^{-1} = -(4.54 \pm 1.04) + (1.41 \pm 0.04)\Delta_{sol}^g H_m^\circ \ (r = 0.9972) \quad (9)$$

The uncertainty of $\Delta_l^g H_m^\circ$ obtained from this equation is estimated to be ±0.5 kJ·mol^{-1}. With this correlation and measured values of $\Delta_{sol}^g H_m^\circ$ for the branched ethers, which are products of the aforementioned reaction, the values of the enthalpies of vaporization for the 14 compounds of interest were derived (see Tables 2 and 3).

The experimental results for the temperature dependence of the corrected retention time in form of the equation $\ln(1/t_r) = A + B/T$ for a series of five reference *t*-OctOR ethers and their derived values of $\Delta_{sol}^g H_m^\circ$ are listed in Table 4. From the correlation of the selected data set, the equation for the estimation of vaporization enthalpies was obtained,

$$\Delta_l^g H_m^\circ/\text{kJ}\cdot\text{mol}^{-1} = (18.57 \pm 0.55) + (0.85 \pm 0.02)\Delta_{sol}^g H_m^\circ \ (r = 0.9991) \quad (10)$$

The uncertainty of $\Delta_l^g H_m^\circ$ obtained from this equation is estimated to be ±0.3 kJ·mol^{-1}. With this correlation and measured values of $\Delta_{sol}^g H_m^\circ$ for the branched ethers, which are products of the reaction, the values of the enthalpies of vaporization for the five compounds of interest were derived (see Tables 2 and 4).

3.3. Modification of the GC-Correlation Method. The vaporization enthalpies determined by the GC-correlation method are entirely dependent on the compounds chosen as standards. A lack of reliable vaporization enthalpies for a set of suitable standards is a major limitation of this technique.[32] Good correlations of $\Delta_l^g H_m^\circ$ and $\Delta_{sol}^g H_m^\circ$ have been observed for esters,[18] alkenes,[2] and acids,[33] regardless of the structure. In this respect, a combination of the transpiration technique with the GC-correlation method, as was done in this work, provides the possibility to obtain the necessary set of the $\Delta_l^g H_m^\circ$ values and use them

Table 3. Results for the Branched Ethers: *t*-BuOR and *t*-AmOR. Parameters *A* and *B* and $\Delta_{sol}^{g}H_{m}^{\circ}$ According to Eqs 9 and 10, as Well as Kovat's Indices J_x and Vaporization Enthalpies $\Delta_{l}^{g}H_{m}^{\circ}$ Derived from These Measurements[a]

	$\ln(1/t_r) = A + B/(T/K)$		$\Delta_{sol}^{g}H_{m}^{\circ}$	$\Delta_{l}^{g}H_{m}^{\circ}(298\ K)^{b}$	$\Delta_{l}^{g}H_{m}^{\circ}(calc)(298\ K)^{c}$		$\Delta_{l}^{g}H_{m}^{\circ}(calc)(298\ K)^{d}$
compd	A	$-B\ (\times 10^3)$	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	J_x(333 K)	kJ·mol^{-1}
t-BuOMe	9.81	2.975	24.74	30.04	30.45		
t-BuOEt	10.04	3.215	26.73	33.69	33.28	620.3	33.70
t-BuOiPr	10.05	3.363	27.96		35.01	668.1	36.18
t-BuOPr	10.90	3.770	31.34		39.80	709.6	38.34
t-BuOBu	11.14	4.121	34.27		43.94	803.0	43.18
t-BuOsBu	10.73	3.885	32.30		41.16	767.0	41.31
t-BuOiBu	10.82	3.886	32.31	41.19	41.17	762.8	41.10
t-BuOAm	11.91	4.650	38.66		50.16	901.8	48.25
t-BuOHex	12.53	5.120	42.57		55.68	997.8	53.22
t-BuOHep						1063.0	56.60
t-BuOOct						1156.0	61.41
t-AmOMe	10.06	3.408	28.33	35.27	35.54	655.1	35.51
t-AmOEt	10.48	3.682	30.61	39.22	38.77	726.0	39.19
t-AmOiPr	10.64	3.870	32.17		40.98	771.9	41.57
t-AmOPr	11.01	4.104	34.12	43.76	43.73	812.2	43.66
t-AmOsBu	11.30	4.366	36.30		46.82	871.6	46.75
t-AmOBu	11.69	4.512	37.51	48.3	48.53	905.9	48.52
t-AmOi-Bu	11.26	4.325	35.96		46.33	862.1	46.25
t-AmOAm	12.38	5.083	42.26		55.25	1003.8	53.53
t-AmOcHex	11.05	4.323	35.94		46.31	886.4	47.51
t-AmOHex	13.06	5.573	46.33	59.84	61.01	1101.0	58.57

[a] The temperature range of the GC experiments was 303−373 K. [b] Taken from Table 2. [c] Calculated using the values of $\Delta_{sol}^{g}H_{m}^{\circ}$ according to Chickos.[17] [d] Calculated by the J_x method.

Table 4. Results for the Branched Ethers: *t*-OctOR. Parameters *A* and *B* and $\Delta_{sol}^{g}H_{m}^{\circ}$ According to Eqs 9 and 10, as Well as Kovat's Indices J_x and Vaporization Enthalpies $\Delta_{l}^{g}H_{m}^{\circ}$ Derived from These Measurements[a]

	$\ln(1/t_r) = A + B/(T/K)$		$\Delta_{sol}^{g}H_{m}^{\circ}$	$\Delta_{l}^{g}H_{m}^{\circ}(298\ K)^{b}$	$\Delta_{l}^{g}H_{m}^{\circ}(calc)(298\ K)^{c}$		$\Delta_{l}^{g}H_{m}^{\circ}(calc)(298\ K)^{d}$
compd	A	$-B\ (\times 10^3)$	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	J_x(393 K)	kJ·mol^{-1}
t-OctOMe	9.547	3.757	31.24	45.28	45.14	897.3	45.47
t-OctOEt	10.02	4.042	33.60	46.98	47.15	939.4	46.90
t-OctOPr	10.60	4.469	37.16	50.10	50.17	1027.0	49.87
t-OctOi-Bu	10.85	4.682	38.93		51.68	1076.6	51.55
t-OctOBu	11.01	4.834	40.19	52.87	52.76	1116.0	52.89
t-OctOAm	11.60	5.276	43.86	55.86	55.88	1206.4	55.95
t-OctO(3,3-diMe-butyl)	11.63	5.317	44.20		56.17	1220.6	56.43
t-OctO(4-Me-pentyl)	11.86	5.481	45.57		57.33	1251.9	57.50
t-OctO(3-Me-pentyl)	11.87	5.516	45.86		57.57	1265.6	57.96
t-OctOHex	12.21	5.729	47.63	59.84	59.08	1301.6	59.18

[a] The temperature range of the GC experiments was 383−423 K. [b] Taken from Table 2. [c] Calculated using the values of $\Delta_{sol}^{g}H_{m}^{\circ}$ according to Chickos.[17] [d] Calculated by the J_x method.

Table 5. Results for the Linear and Branched Alcohols. Parameters *A* and *B* and $\Delta_{sol}^{g}H_{m}^{\circ}$ According to Eqs 9 and 10, as Well as Kovat's Indices J_x and Vaporization Enthalpies $\Delta_{l}^{g}H_{m}^{\circ}$ Derived from These Measurements[a]

	$\ln(1/t_r) = A + B/(T/K)$		$\Delta_{sol}^{g}H_{m}^{\circ}$	$\Delta_{l}^{g}H_{m}^{\circ}(298\ K)^{b}$	$\Delta_{l}^{g}H_{m}^{\circ}(calc)(298\ K)^{c}$		$\Delta_{l}^{g}H_{m}^{\circ}(calc)(298\ K)^{d}$
compd	A	$-B\ (\times 10^3)$	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	J_x(393 K)	kJ·mol^{-1}
butanol-1	10.19	3.406	28.32	51.0	51.12	663.9	51.31
pentanol-1	11.31	4.082	33.94	57.0	56.65	773.5	56.53
hexanol-2	11.50	4.24	35.22	57.9	57.91	800.6	57.82
3,3-dimethylbutanol-1	11.49	4.218	35.07	58.0	57.76	796.2	57.61
2-methylpentanol-1	11.88	4.464	37.11	59.4	59.78	837.6	59.58
hexanol-1	12.07	4.609	38.32	61.1	60.97	867.8	61.02
3-methylpentanol-1	11.91	4.506	37.46	61.7	60.13	848.1	60.08
octanol-1	10.73	4.621	38.42	70.1	70.44	1071.3	70.70
decanol-1	11.99	5.573	46.34	80.9	79.97	1272.8	80.29
undecanol-1	12.76	6.102	50.74	84.7	85.27	1374.4	85.13
dodecanol-1	13.39	6.577	54.68	90.0	90.02	1475.3	89.93

[a] The temperature range of the GC experiments was 383−423 K. [b] Taken from refs 3 and 4. [c] Calculated using the values of $\Delta_{sol}^{g}H_{m}^{\circ}$ according to Chickos.[17] [d] Calculated by the J_x method.

together with the net of the retention indices to calculate the vaporization enthalpies for the chosen compounds of interest.

Another limitation of the GC-correlation method is the requirement of a large collection of samples within each homologous series of interest for creating a net of retention indices. Even if the amount of the sample required for the GC injection is very small, synthesis, identification, and cost expenses could be immense. To circumvent this limitation, we decided to test whether the retention time derivative $\Delta_{sol}^{g}H_{m}^{\circ}$ could be replaced with the Kovat's index J_x.[34] In the Kovat's index or Kovat's retention index used in gas chromatography, *n*-alkanes serve as the standards and logarithmic interpolation is utilized as defined by

$$J_x = \frac{lg(t_x) - lg(t_N)}{lg(t_{N+1}) - lg(t_N)} \times 100 + 100N \qquad (11)$$

where x refers to the adjusted retention time t, N is the number of carbon atoms of the *n*-alkane eluting before the peak of interest, and $(N + 1)$ is the number of carbon atoms of the *n*-alkane eluting after the peak of interest. According to the established GC procedure, all retention times are corrected for the "dead" retention time adjusted from the retention times of the homologues linear aliphatic hydrocarbons.[35] Thus, the retention time t_x of the compound of interest x is caged by the retention times of the two *n*-alkanes. Kovat's index is the retention characteristics acknowledged among analytical chemists for the identification of the individual compounds in diverse mixtures. There are some comprehensive libraries containing J_x values available from the literature,[35] which are generally standardized for the common stationary phases. The advantages of the Kovat's indices (J_x indices) in comparison with $\Delta^{g}_{sol}H^{\circ}_{m}$ are as follows. The experimental procedure for evaluating J_x values is easier and consists only of three steps. The first GC run is usually performed with the mixture of the homologues *n*-alkanes, followed by a run with the mixture of the compounds of interest. Then the value of J_x for each compound is calculated using eq 11. The Kovat's indices are generally specified by the choice of the stationary phase of the GC column. As a rule, the isothermal Kovat's indices are only slightly dependent on the GC oven temperature.[35,36] Thus, the J_x method seemingly does not have restrictions associated with the choice of the temperature interval for investigation, as the original Chickos method[17] and any set of the homologues available from the literature could be used for a linear correlation with the reliable data on vaporization enthalpies. But the question arises concerning if there is any correlation between Kovat's indices and vaporization enthalpy. To answer this question, Kovat's indices for branched ethers (Tables 3 and 4) as well as for some linear and branched alkanols (Table 5) have been measured on the same GC column as that used for the $\Delta^{g}_{sol}H^{\circ}_{m}$ measurements in this work. Comparison of experimental vaporization enthalpies $\Delta_{l}^{g}H^{\circ}_{m}$ with those calculated from $\Delta^{g}_{sol}H^{\circ}_{m}$ and with those obtained by the J_x method is shown in Tables 3−5. The results from both methods are indistinguishable and are very close to the direct experimental values of $\Delta_{l}^{g}H^{\circ}_{m}$ within their uncertainties of less than ± 0.5 kJ·mol^{-1}. As can be seen from Table 5, the J_x method was applied to the linear as well as to branched alkanols. As a consequence, it turns out that linear and branched species belong to the same line (the linear correlation between J_x and $\Delta_{l}^{g}H^{\circ}_{m}$ was obtained with $r = 0.9978$), and it follows that the homologous series can be used in the approximation and probably regardless of their structure. However, this aspect needs further investigation. Thus, the procedure of obtaining the retention GC indices could be substantially simplified by using the J_x method without any loss of accuracy instead of determining values of $\Delta^{g}_{sol}H^{\circ}_{m}$. The J_x method can be recommended for correlation of vaporization enthalpies. The combination of the transpiration method and the J_x method is especially successful for the determination of vaporization enthalpies of vaporization within a homologues series.

Literature Cited

(1) Marsh, K. N.; Niamskul, P.; Gmehling, J.; Bolts, R. Review of thermophysical property measurements on mixtures containing MTBE, TAME, and other ethers with non-polar solvents. *Fluid Phase Equilib.* **1999**, *156*, 207−227.

(2) Verevkin, S. P.; Wandschneider, D.; Heintz, A. Determination of Vaporization Enthalpies of Selected Linear and Branched C$_7$, C$_8$, C$_9$, C$_{11}$, and C$_{12}$ Monoolefin Hydrocarbons from Transpiration and Correlation Gas-Chromatography Methods. *J. Chem. Eng. Data* **2000**, *45*, 618−625.

(3) Kulikov, D.; Verevkin, S. P.; Heintz, A. Determination of vaporization enthalpies of the aliphatic branched C$_5$ and C$_6$ alcohols from transpiration method. *J. Chem. Eng. Data* **2001**, *46*, 1593−1600.

(4) Kulikov, D.; Verevkin, S. P.; Heintz, A. Enthalpies of vaporization of a series of linear aliphatic alcohols. Experimental results and predicted values using the ERAS-model. *Fluid Phase Equilib.* **2001**, *192*, 187−207.

(5) Chickos, J. S.; Hyman, A. S.; Ladon, L. H.; Liebman, J. F. Measurement and Estimation of the Heats of vaporization of Hydrocarbons. *J. Org. Chem.* **1981**, *46*, 4294−4296.

(6) Verevkin, S. P.; Beckhaus, H.-D.; Belen'kaja, R. S.; Rakus, K.; Rüchardt, C. Geminal Substituent Effects. 9. Enthalpies of Formation and Strain Free Increments of Branched Esters and Ethers. *Thermochim. Acta* **1996**, *279*, 47−64.

(7) Verevkin, S. P.; Heintz, A. Simultaneous study of chemical and vapor-liquid equilibria in the reacting system of the methyl cumyl ether synthesis from methanol and α-methyl-styrene. *Fluid Phase Equilib.* **2001**, *179*, 85−100.

(8) Verevkin, S. P.; Heintz, A. Chemical equilibria study in the reacting system of the alkyl cumyl ether synthesis from *n*-alkanols and α-methyl-styrene. *J. Chem. Eng. Data* **2001**, *46*, 41−46.

(9) Verevkin, S. P.; Heintz, A. Chemical equilibria study in the reacting system of the (1-alkoxy-ethyl)benzene synthesis from alkanols and styrene. *J. Chem. Eng. Data* **2001**, *46*, 984−990.

(10) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC—A Group Contribution Method*; Elsevier: Amsterdam, 1977.

(11) Heintz, A. A new theoretical approach for predicting excess properties of alkanol/alkane mixtures. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 172−181.

(12) Pedley, J. P. *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series; Texas, 1994.

(13) Allinger, N. L.; Zhu, Z. S.; Chen, K. Molecular Mechanics (MM3) Studies of Carboxylic Acids and Esters. *J. Am. Chem. Soc.* **1992**, *114*, 6120−6133.

(14) Planck, M. *Ann. Phys.* **1887**, *30*, 574.

(15) Haase, R. *Thermodynamik der Mischphasen*; Springer: 1956.

(16) Domalski, E. S.; Hearing, E. D. Estimation of Thermodynamic Properties of C−H−N−O- Halogen Compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805−1159.

(17) Chickos, J. S.; Hosseini, S.; Hesse, D. G. Determination of vaporization enthalpies of simple organic molecules by correlations of changes in gas chromatographic net retentions times. *Thermochim. Acta* **1995**, *249*, 41−62.

(18) Verevkin, S. P.; Heintz, A. Determination of Vaporization Enthalpies of the Branched Esters from Correlation Gas-Chromatography and Transpiration Methods. *J. Chem. Eng. Data* **1999**, *44*, 1240−1245.

(19) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation*; Blackwell Scientific Publications: Oxford, 1985; p 300.

(20) Rozhnov, A. M.; Safronov, V. V.; Verevkin, S. P.; Sharonov, K. G.; Alenin, V. I. Enthalpy of combustion and enthalpy of vaporization of 2-ethyl-2-methoxypropane and thermodynamics of its gas-phase synthesis from (methanol + α-2-methylbutene). *J. Chem. Thermodyn.* **1991**, *23*, 629−635.

(21) Krähenbühl, M. A.; Gmehling, J. Vapor pressures of methyl *tert*-butyl ether, ethyl *tert*-butyl ether, isopropyl *tert*-butyl ether, *tert*-amyl methyl ether, and *tert*-amyl ethyl ether. *J. Chem. Eng. Data* **1994**, *39*, 29−32.

(22) Rarey J.; Horstmann, S.; Gmehling, J. Vapor-Liquid Equilibria and Vapor Pressure Data for the Systems Ethyl *tert*-Butyl Ether + Ethanol and Ethyl *tert*-Butyl Ether + Water. *J. Chem. Eng. Data* **1999**, *44*, 532−538.

(23) Smutny, E. J.; Bondi, A. Di-*tert*-butyl ether: Strain energy and physical properties. *J. Phys. Chem.* **1961**, *65*, 546−550.

(24) Sharonov, K. G.; Mishentseva, Y. B.; Rozhnov, A. M.; Miroshnichenko, E. A.; Korchatova, L. I. Molar enthalpies of formation and vaporization of *tert*-butoxybutanes and thermodynamics of their synthesis from a butanol and 2-methylpropene 2. Enthalpies of combustion and vaporization of *tert*-butoxybutanes. *J. Chem. Thermodyn.* **1991**, *23*, 637−642.

(25) Palczewska-Tulinska, M.; Cholinski, J.; Szafranski, A. M.; Wyrzykowska-Stankiewicz, D. Experimental vapor pressure and maximum-likelihood Antoine-equation constants for 1,1,1-methoxydimethylpropane, thiacyclopentane and 1,4-butanediol. *Fluid Phase Equilib*. **1984**, *15*, 295−307.

(26) Cervenkova, I.; Boublik, T. Vapor Pressures, Refractive Indexes, and Densities at 20.0 °C, and Vapor−Liquid Equilibrium at 101.325 kPa, in the *tert*-Amyl Methyl Ether−Methanol System. *J. Chem. Eng. Data* **1984**, *29*, 425.

(27) Antosik M.; Sandler, S. I. Vapor-Liquid Equilibria of Hydrocarbons and *tert*-Amyl Methyl Ether. *J. Chem. Eng. Data* **1994**, *39*, 584−587.

(28) Toghiani, R. K.; Toghiani, H.; Verkateswarlu, G. Vapor-liquid equilibria for methyl *tert*-butyl ether + methanol and *tert*-amyl methyl ether + methanol. *Fluid Phase Equilib*. **1996**, *122*, 157−168.

(29) Aucejo, A.; Loras, S.; Munoz, R.; Reich, R.; Segura, H. Isobaric Vapor-Liquid Equilibrium in the Systems 2-Methylpentane + Methyl 1,1-Dimethylethyl Ether, + Ethyl 1,1-Dimethylethyl Ether, and + Methyl 1,1-Dimethylpropyl Ether. *J. Chem. Eng. Data* **1998**, *43*, 973−977.

(30) Heine A.; Fischer, K.; Gmehling, J. Various Thermodynamic Properties for Binary Systems with Tertiary Ethers. *J. Chem. Eng. Data* **1999**, *44*, 373−378.

(31) Uusi-Kyyny, P.; Pokki, J.-P.; Aittamaa, J.; Liukkonen, S. Vapor-Liquid Equilibrium for the Binary Systems of Methanol + 2,4,4-Trimethyl-1-pentene at 331 K and 101 kPa and Methanol + 2-Methoxy-2,4,4-trimethylpentane at 333 K. *J. Chem. Eng. Data* **2001**, *46*, 1244−1248.

(32) Nichols, G.; Orf, J.; Reiter, S.; Chickos, J. S.; Gokel, G. W. The vaporization enthalpies of some crown ethers by correlation gas-chromatography. *Thermochim. Acta* **2000**, *346*, 15−28.

(33) Verevkin, S. P. Measurement and Prediction of Monocarboxylic Acids Thermochemical Properties. *J. Chem. Eng. Data* **2000**, *45*, 953−960.

(34) McNair, H. M.; Bonelli, E. J. *Basic Gas Chromatography*; Consolidated Printers: Oakling, CA, 1967.

(35) Pacakova, V.; Feltl, K. *Chromatographic Retention Indices; An Aid to the Identfication of Organic Compounds*; Ellis Horwood: London, 1992.

(36) Spieksma, W. Determination of vapor liquid equilibrium from Kovat's retention index on dimethylsilicone using the Wilson mixing model. *J. High Resolut. Chromatogr*. **1999**, *22*, 565−588.

(37) Rozhnov, A. M.; Barkov, V. I.; Sharonov, K. G.; Tsvetkov, V. S. Investigation of the equilibria of the reaction: CH3(CH2)4OH + (CH3)2C:CH2 = CH3(CH2)4OC(CH3)3. *J. Chem. Thermodyn*. **1990**, *22*, 327−333.

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