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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

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The standard molar enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H^\circ_{\mathrm{m}}$ of 1-methylcyclohexene, 4-methylcyclohexene, 2,4-dimethyl-2-pentene, *cis*-2-heptene, *trans*-4-octene, 1-nonene, 2,6-dimethylheptene, 1-undecene, *trans*-2,2,4,6,6-pentamethyl-3-heptene, and *cis*-2,2,4,6,6-pentamethyl-3-heptene at the temperature $T = 298.15$ K were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. The values of $\Delta_{\mathrm{l}}^{\mathrm{g}}H^\circ_{\mathrm{m}}$(298.15 K) for these compounds and additionally for 3-methylcyclohexene were also measured using the correlation gas-chromatography method. The results from both methods are indistinguishable within the experimental uncertainties of less than ±0.5 kJ·mol^{-1}. Results from this work together with the data available from the literature were used to derive correlations for the prediction of the standard molar enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H^\circ_{\mathrm{m}}$(298.15 K) of monoolefins with linear and branched hydrocarbon chains.

Introduction

The thermodynamic properties of alkenes are of increasing importance. The development of novel processes and products in the chemical, petrochemical, and polymer industries over the past few years has increased the use of olefins as reactants, intermediates, or end products. The significant impact of automobile exhaust gases on the environment is forcing the petrochemical industry to change the process for the production and composition of gasolines providing less polluted products. The new trends try to reduce the emissions of exhaust gases with the help of new oxygenated additives, produced from isoolefins and alcohols (e.g. methyl *tert*-butyl ether or methyl *tert*-amyl ether). Thus, there is a considerable interest in utilizing available olefin resources in the production of the oxygenated additives. Consequently, the accurate knowledge of the vaporization enthalpies and vapor pressures of olefins 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 those terms we have studied the vaporization of some long-chained alkenes of which apparently only few thermodynamic quantities are available in the literature (Steele and Chirico, 1993). In our previous work (Verevkin and Ebenhoch, 1999a) the vaporization enthalpies of some phenyl substituted alkenes and their vapor pressures were measured by the transpiration method. In continuation of this research line, the vaporization enthalpies of other alkenes (see Figure 1) have been measured using two techniques in order to provide the reliability of the experimental results: transpiration method and correlation gas-chromatography method. While diverse group-additivity methods (Chickos et al., 1981) give excellent correlations between observed and calculated $\Delta_{\mathrm{l}}^{\mathrm{g}}H^\circ_{\mathrm{m}}$ values for linear homologues, deviations may arise for the branched members of the series. Because the distribution of the bulky molecules in the liquid and their intermolecular interactions seem to be unique for the branched molecules, for the reliable predictions of the vaporization enthalpies of such species a more detailed study is required. We report here a systematic determination of the vaporization enthalpies $\Delta_{\mathrm{l}}^{\mathrm{g}}H^\circ_{\mathrm{m}}$ of a series of cyclic, linear, and branched monoolefins with an emphasis on the branched species. We used our new experimental results together with the data already available from the literature to obtain practical correlation equations that could be used to predict values for as yet unmeasured $\Delta_{\mathrm{l}}^{\mathrm{g}}H^\circ_{\mathrm{m}}$ of olefins. These predictions

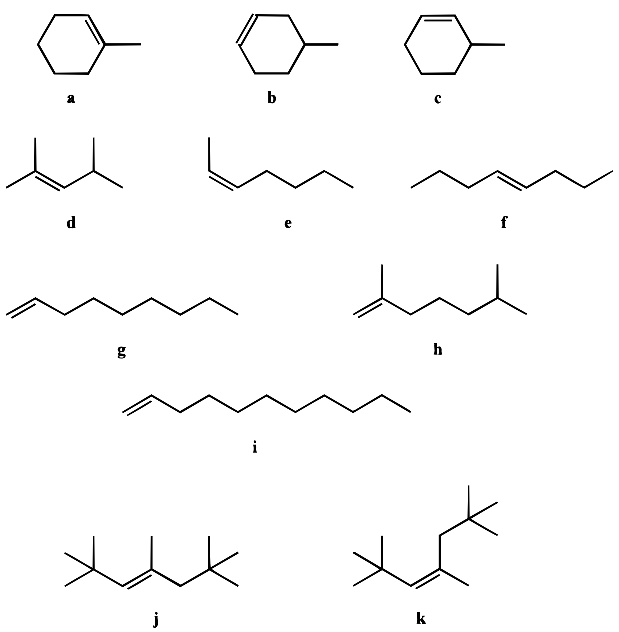

Figure 1. Structures of olefins: 1-methylcyclohexene (a); 4-methylcyclohexene (b); 3-methylcyclohexene (c); 2,4-dimethyl-2-pentene (d); *cis*-2-heptene (e); *trans*-4-octene (f); 1-nonene (g); 2,6-dimethyl-1-heptene (h); 1-undecene (i); *trans*-2,2,4,6,6-pentamethyl-3-heptene (j); and *cis*-2,2,4,6,6-pentamethyl-3-heptene (k).

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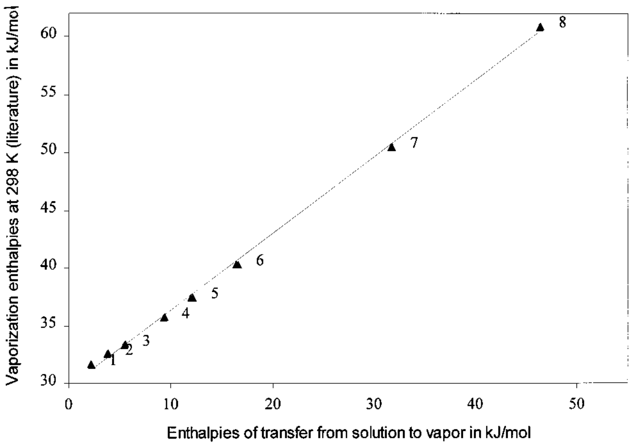


Figure 2. Vaporization enthalpies of olefins, selected as references, plotted against their respective enthalpies of transfer $\Delta_{\mathrm{so}}^{\mathrm{g}}H^{\circ}_{\mathrm{lm}}$ from GC correlation measurements. The numbers on the figure denote the following: 1, 2-methyl-1-pentene; 2, 2,3-dimethyl-2-butene; 3, cyclohexene; 4, 2,4,4-trimethyl-1-pentene; 5, 2,4,4-trimethyl-2-pentene; 6, 1-octene; 7, 1-decene; 8, 1-dodecene.

should help chemists and engineers to design and develop new processes more accurately.

Experimental Procedures and Results

Materials. Samples of olefins (Figures 1 and 2) were available from the collection of chemicals synthesized in the Chemistry Departments of the Universities of Freiburg and Rostock. The structures of the alkenes used were established by NMR spectroscopy. Samples of olefins were purified by distillation in a vacuum. The purities of all specimens determined by GC were better than 0.99 mole fraction.

Transpiration Method. The enthalpies of vaporization of monoolefins (see Figure 1) were determined by using the method of transference in a saturated N_2 stream (Cox and Pilcher, 1970). The method has been described before (Chickos et al., 1995) and has proved to give results being in excellent agreement with other established techniques for determining vapor pressures of pure substances in the range of 0.005 to ca. 10000 Pa and enthalpies of vaporization from the temperature dependence of the vapor pressure. 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 mass of condensed product was determined by GC analysis using an internal standard (*n*-hydrocarbons). The flow rate of the nitrogen stream was measured using a soap bubble flowmeter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. On one hand, flow rate of nitrogen stream in the saturation tube should be not too slow in order to avoid the transport of material from U-tube due to diffusion. On the other hand, the flow rate should be not too fast in order to reach the saturation of the nitrogen stream with a compound. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus the contribution due to diffusion was negligible at a flow rate up to 0.11 $\mathrm{cm^3 \cdot s^{-1}}$. The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration was at a flow rate of 0.82 $\mathrm{cm^3 \cdot s^{-1}}$. Thus, we carried out the experiments in the flow rate interval of (0.26 to 0.52) $\mathrm{cm^3 \cdot s^{-1}}$, which has ensured that transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. With the assumption that Dalton's law of partial pressures applied to the saturated nitrogen stream, values of p were calculated by assuming the validity of the ideal gas law:

$$p = mRT_{\mathrm{a}}/V(\mathrm{N_2})M \qquad (1)$$

Here R = 8.31451 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, m is the mass of transported compound, $V(\mathrm{N_2})$ is the volume of transporting gas, M is the molar mass of the compound, and T_{a} is the ambient temperature. The volume of transporting gas $V(\mathrm{N_2})$ was determined from the flow rate and time measurements. The flow rate was maintained constant with help of the high-precision needle valve (Hoke, C1335G6-BMM-ITA). The accuracy of the volume $V(\mathrm{N_2})$ measurements from flow rate was established to be (±0.001 $\mathrm{dm^3}$) with help of series of experiments, where volume the nitrogen was measured with gas-clock or by water withdrawing from calibrated gasometer. Because the nitrogen stream was measured using a soap bubble flowmeter at the ambient temperature, this temperature was applied for the calculation of the vapor pressure p according eq 1. The vapor pressure p at each saturation temperature was calculated from the mass of product collected within a definite time period, and the small value of the residual vapor pressure of a compound at the temperature of condensation was added. The latter was calculated from a linear correlation between ln(p) and T^{-1} obtained by iteration. Results of the vapor pressure measurements as function of temperature are shown in Table 1. To derive the standard molar enthalpy of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}(T)$ at the mean temperature $\langle T \rangle$ of the experimental temperature range, the form of the integrated linear Clausius−Clapeyron equation

$$\ln(p/\mathrm{Pa}) = a - b(T/\mathrm{K})^{-1} \qquad (2)$$

was used, where $b = \Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}(T)R^{-1}$. The observed enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}(T)$ at the mean temperature $\langle T \rangle$ obtained by this procedure are listed in Table 1 together with the coefficients a and b according to eq 2. The experimental data were approximated with the linear equation $\ln(p) = f(T^{-1})$ (see Table 1) using the method of least squares. The error in the enthalpy of vaporization at $\langle T \rangle$ was defined as average deviation of experimental ln(p) from this linear correlation.

Because of the deviations of $\langle T \rangle$ from T = 298.15 K the observed values of the enthalpies of vaporization of olefins measured by transpiration had to be adjusted to this reference temperature. The corrections were estimated with the help of the correlation

$$\{\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}(\langle T \rangle) - \Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K})\}/(\mathrm{kJ \cdot mol^{-1}}) = -5.44 \times 10^{-2} \cdot \{(\langle T \rangle/\mathrm{K}) - 298.15\} \qquad (3)$$

following the recommendation of Chickos et al., 1993. With these corrections the standard molar enthalpies of vaporization at T = 298.15 K were calculated. They are also listed in Table 1.

GC Correlation Method. 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. Detailed descriptions of the method used can be found elsewhere (Chickos et al., 1995a,b). A plot of ln 1/(t_{r}/s) vs 1/(T/K),

Table 1. Results from Measurements of the Vapor Pressure p by the Transpiration Method

T/K[a]	m/mg[b]	$V(N_2)$/dm^3 [c]	p/Pa[d]	T/K[a]	m/mg[b]	$V(N_2)$/dm^3 [c]	p/Pa[d]
1-Methylcyclohexene [ln(p/Pa) = (23.65 ± 0.10) − (4531 ± 29)(T/K)$^{-1}$]							
275.4	13.0	0.287	1315	293.4	22.0	0.162	3650
278.4	18.1	0.324	1588	298.4	26.5	0.145	4858
281.4	15.1	0.216	1943	303.3	28.8	0.125	6074
284.4	19.0	0.233	2248	303.9	29.3	0.125	6174
287.4	18.2	0.185	2678	308.5	32.4	0.108	7867
290.4	20.4	0.179	3079	313.4	34.0	0.091	9774
$\Delta_l^g H^\circ_m$(294.4 K) = (37.67 ± 0.24)kJ·mol^{-1}; $\Delta_l^g H^\circ_m$ (298.15 K) = (37.46 ± 0.24) kJ·mol^{-1}							
4-Methylcyclohexene [ln(p/Pa) = (23.76 ± 0.25) − (4446 ± 71)(T/K)$^{-1}$]							
275.5	20.0	0.287	2037	287.5	26.5	0.179	4053
278.5	21.0	0.253	2382	290.5	25.2	0.145	4715
281.5	26.2	0.253	2908	293.4	28.6	0.145	5327
284.5	25.8	0.216	3315	296.4	21.7	0.091	6378
$\Delta_l^g H^\circ_m$(285.9 K) = (36.97 ± 0.59) kJ·mol^{-1}; $\Delta_l^g H^\circ_m$(298.15 K) = (36.30 ± 0.59) kJ·mol^{-1}							
2,4-Dimethyl-2-pentene [ln(p/Pa) = (23.62 ± 0.65) − (4234 ± 180)(T/K)$^{-1}$]							
275.5	32.4	0.253	3707	287.5	47.1	0.179	7121
278.5	38.3	0.233	4626	290.5	53.6	0.162	8823
281.5	42.0	0.216	5382	293.5	49.7	0.145	9119
284.5	43.2	0.199	5950	296.5	55.4	0.125	11660
$\Delta_l^g H^\circ_m$(285.6 K) = (35.2 ± 1.5) kJ·mol^{-1}; $\Delta_l^g H^\circ_m$(298.15 K) = (34.5 ± 1.5) kJ·mol^{-1}							
cis-2-heptene [ln(p/Pa) = (24.62 ± 0.13) − (4694 ± 37)(T/K)$^{-1}$]							
275.5	37.1	0.533	1952	289.5	30.6	0.177	4556
277.5	19.9	0.249	2207	292.4	32.3	0.160	5284
280.5	24.2	0.249	2649	296.4	39.6	0.160	6440
283.5	22.4	0.196	3084	300.4	49.4	0.160	7983
286.5	29.8	0.213	3722	304.4	47.3	0.124	9814
$\Delta_l^g H^\circ_m$(289.9 K) = (39.03 ± 0.31) kJ·mol^{-1}; $\Delta_l^g H^\circ_m$(298.15 K) = (38.58 ± 0.31) kJ·mol^{-1}							
trans-4-octene [ln(p/Pa) = (25.11 ± 0.12) − (5199 ± 33)(T/K)$^{-1}$]							
275.5	5.93	0.283	503.6	290.5	11.7	0.196	1360
278.5	6.61	0.249	627.2	293.5	14.4	0.196	1659
281.5	8.70	0.266	763.1	298.4	13.6	0.143	2141
284.5	9.90	0.249	919.3	303.4	14.0	0.107	2930
287.5	11.2	0.230	1119	308.4	18.1	0.107	3767
$\Delta_l^g H^\circ_m$(291.9 K) = (43.23 ± 0.27) kJ·mol^{-1}; $\Delta_l^g H^\circ_m$(298.15 K) = (42.89 ± 0.27) kJ·mol^{-1}							
1-Nonene [ln(p/Pa) = (24.60 ± 0.09) − (5379 ± 27)(T/K)$^{-1}$]							
278.5	11.6	1.200	201.1	296.4	17.0	0.521	650.4
281.5	12.1	1.040	239.7	299.4	12.3	0.319	767.1
284.5	13.2	0.919	294.8	302.4	13.8	0.300	916.9
287.4	13.5	0.761	361.1	305.4	11.1	0.200	1105
290.4	15.6	0.720	438.4	308.4	12.9	0.200	1278
293.4	17.4	0.660	528.5	318.3	17.9	0.160	2205
$\Delta_l^g H^\circ_m$(298.4 K) = (44.72 ± 0.22) kJ·mol^{-1}; $\Delta_l^g H^\circ_m$ (298.15 K) = (44.73 ± 0.22)kJ·mol^{-1}							
2,6-Dimethyl-1-heptene [ln(p/Pa) = (25.73 ± 0.20) − (5573 ± 60)(T/K)$^{-1}$]							
273.4	15.4	1.47	223.5	291.4	34.0	0.818	834.3
276.4	21.0	1.50	293.6	294.4	26.3	0.524	1004
279.4	19.7	1.11	366.4	297.4	23.6	0.392	1203
282.4	22.6	1.08	429.1	300.3	23.9	0.328	1449
285.4	25.8	1.01	521.0	303.3	19.8	0.230	1712
288.3	34.8	1.08	650.9	306.3	16.3	0.163	1985
289.4	34.9	0.981	716.8				
$\Delta_l^g H^\circ_m$(289.8 K) = (46.34 ± 0.50) kJ·mol^{-1}; $\Delta_l^g H^\circ_m$(298.15 K) = (45.89 ± 0.50) kJ·mol^{-1}							
1-Undecene [ln(p/Pa) = (26.16 ± 0.11) − (6530 ± 31)(T/K)$^{-1}$]							
283.4	2.34	1.68	22.85	301.4	7.94	1.44	89.02
286.5	3.09	1.76	28.65	304.4	8.22	1.20	110.4
289.4	3.99	1.76	36.83	307.4	7.12	0.840	136.6
292.4	4.80	1.72	45.28	310.4	7.03	0.680	166.5
295.4	5.53	1.56	57.38	313.1	10.8	0.840	206.2
298.4	7.12	1.60	71.94	312.2	7.44	0.640	187.1
$\Delta_l^g H^\circ_m$(297.8 K) = (54.29 ± 0.26) kJ·mol^{-1}; $\Delta_l^g H^\circ_m$(298.15 K) = (54.27 ± 0.26) kJ·mol^{-1}							
trans-2,2,4,6,6-Pentamethyl-3-heptene [ln(p/Pa) = (27.99 ± 0.19) − (7887 ± 58)(T/K)$^{-1}$]							
291.4	0.450	2.65	2.515	306.3	1.13	1.77	9.434
294.4	0.557	2.49	3.312	309.3	1.46	1.81	11.93
297.4	0.721	2.41	4.422	312.3	1.63	1.54	15.61
300.4	0.848	2.14	5.855	315.2	2.10	1.58	19.60
303.4	0.954	1.97	7.152	318.2	2.66	1.58	24.82
$\Delta_l^g H^\circ_m$(304.8 K) = (65.58 ± 0.48) kJ·mol^{-1}; $\Delta_l^g H^\circ_m$(298.15 K) = (65.93 ± 0.48) kJ·mol^{-1}							
cis-2,2,4,6,6-pentamethyl-3-heptene [ln(p/Pa) = (25.97 ± 0.18) − (7572 ± 54)(T/K)$^{-1}$]							
288.3	0.0733	1.49	0.7308	306.3	0.414	1.77	3.451
291.4	0.173	2.65	0.9655	309.3	0.529	1.81	4.311
294.4	0.214	2.49	1.273	312.3	0.583	1.54	5.585
297.4	0.270	2.41	1.657	315.2	0.744	1.58	6.948
300.4	0.316	2.14	2.184	318.2	0.929	1.58	8.676
303.4	0.380	1.97	2.850				
$\Delta_l^g H^\circ_m$(303.2 K) = (62.96 ± 0.45) kJ·mol^{-1}; $\Delta_l^g H^\circ_m$(298.15 K) = (63.23 ± 0.45) kJ·mol^{-1}							

[a] Temperature of saturation, N_2 gas flow (0.26 to 0.52) 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.

where t_r is the retention time (in seconds) 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 affords $\Delta_{sol}^{g}H^\circ_m$. The value of $\Delta_{sol}^{g}H^\circ_m$ is enthalpy of transfer from the solution of a compound in the stationary phase of the GC column to the vapor phase. It was found (Chickos et al., 1995a) that, in cases where compounds are properly selected with regard to the analogy of their molecular structures, plotting $\Delta_{sol}^{g}H^\circ_m$ versus the known standard molar enthalpy of vaporization, $\Delta_l^gH^\circ_m$, also provides a linear relationship. 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 the substances chosen as standards.

Measurements were made using a Hewlett-Packard Series 5890 gas chromatograph, equipped with a FID, autosampler, and Hewlett-Packard Integrator 3390A. GLC runs were done isothermally on a DB-1 capillary column of length 50 m and diameter 0.32 mm with a film thickness of stationary phase 0.25 μm. Nitrogen was used as carrier gas with a flow rate of 0.333 $\text{cm}^3\cdot\text{s}^{-1}$. At each temperature the corrections of retention times with the value for the nonretained component (methane) were made. The temperature was maintained constant within ±0.1 K. All substances were dissolved in acetonitrile. By using an autosampler, retention times were generally reproducible within (1 to 2) s. The enthalpies of transfer from the solution to the gas phase $\Delta_{sol}^{g}H^\circ_m$ were obtained for each compound by plotting ln 1/(t_r/s) vs 1/(T/K). The slope of this linear correlation $\ln 1/(t_r/\text{s}) = a + b(T^{-1}/\text{K})$ when multiplied by the gas constant, R, gives $\Delta_{sol}^{g}H^\circ_m$. The accuracy of the results depends on the accuracy of the $\Delta_l^gH^\circ_m$ of the reference standards. As standards, we used the experimental results for $\Delta_l^gH^\circ_m$ of olefins available from the literature (see Figure 2).

Results from measurements of the enthalpy of transfer $\Delta_{sol}^{g}H^\circ_m$ obtained by the GC correlation method for the series of 8 reference olefins are presented in Figure 2. Data set of $\Delta_l^gH^\circ_m$ of olefins used as reference substances: 2-methylpentene, 31.6 kJ mol^{-1}, and 2,3-dimethyl-2-butene, 32.6 kJ mol^{-1}, from Camin and Rossini (1956); cyclohexene, 33.4 kJ mol^{-1}, from Steele et al. (1996); 2,4,4,-trimethyl-1-pentene, 35.7 kJ mol^{-1}, and 2,4,4,-trimethyl-2-pentene, 37.4 kJ mol^{-1}, from Camin and Rossini (1960); 1-octene, 40.3 kJ mol^{-1}, 1-decene, 60.8 kJ mol^{-1}, and 1-dodecene, 50.4 kJ mol^{-1}, from Mansson, Sellers et al. (1977). From the correlation of the selected data set the following equation for the estimation of vaporization enthalpies was obtained:

$$\Delta_l^gH^\circ_m/\text{kJ mol}^{-1} = (29.70 \pm 0.11) + (0.663 \pm 0.008)\Delta_{sol}^{g}H^\circ_m \qquad r = 0.9992 \quad (4)$$

Here r is the correlation coefficients of the linear regression. The uncertainty of $\Delta_l^gH^\circ_m$ obtained from this equation is assessed to be ±0.5 kJ mol^{-1}. With this correlation and measured values of $\Delta_{sol}^{g}H^\circ_m$ for olefins (Table 2), the values of the enthalpies of vaporization for the 11 monoolefins of interest (Figure 1) were derived (Table 2). Comparison of vaporization enthalpies $\Delta_l^gH^\circ_m$ calculated from these measurements with those obtained by the transpiration method is also shown in Table 2. The results are practically indistinguishable within their experimental uncertainties of less than 0.5 kJ·mol^{-1}.

Table 2. Results from Measurements of the Enthalpy of Transfer from Solution to the Vapor $\Delta_{sol}^{g}H^\circ_m$ by GC Correlation Measurements for Olefins and Comparison of Vaporization Enthalpies $\Delta_l^g H^\circ_m$ Derived from These Measurements with Those Measured by the Transpiration Method

compd	$\Delta_{sol}^{g}H^\circ_m$/kJ•mol^{-1}	$\Delta_{sol}^{g}H^\circ_m$/kJ•mol^{-1} GC	transpiration
1-methylcyclohexene	11.79	37.52	37.46 ± 0.24
4-methylcyclohexene	9.82	36.21	36.30 ± 0.59
3-methylcyclohexene	13.70	38.78	
2,4-dimethyl-2-pentene	7.01	34.35	34.5 ± 1.5
cis-2-heptene	13.60	38.72	38.58 ± 0.31
trans-4-octene	19.62	42.71	42.89 ± 0.27
1-nonene	22.38	44.54	44.73 ± 0.22
2,6-dimethyl-1-heptene	24.75	46.11	45.89 ± 0.50
1-undecene	36.80	54.10	54.27 ± 0.26
trans-2,2,4,6,6-pentamethyl-3-heptene	54.64	65.86	65.93 ± 0.48
cis-2,2,4,6,6-pentamethyl-3-heptene	50.87	63.43	63.23 ± 0.45

Discussion and Data Reduction

Camin and Rossini (1960) determined the enthalpy of vaporization of 1-methylcyclohexene, $\Delta_l^gH^\circ_m$ = 37.8 kJ mol^{-1}, and of 2,4-dimethyl-2-pentene, $\Delta_l^gH^\circ_m$ = 34.3 kJ mol^{-1}, with great care, using calorimetry. Therefore, redeterminations of enthalpies of vaporization of both compounds were carried out using the methods presented here in order to test the reliability of the experimental techniques and devices. An excellent agreement of our results (see Table 2) with those from Camin and Rossini (1960) has encouraged us to continue our investigation of other substances with similar structures.

Previous determination of the standard molar enthalpy of vaporization of 1-nonene were made by using ebulliometry (Forziati et al., 1950) in the temperature range (339.76 to 421.01) K. Their value of $\Delta_l^gH^\circ_m$ = 46.0 kJ·mol^{-1}, derived from Antoine coefficients recalculated by Afeefy et al. (1998), is also in a good agreement with ours (see Table 2). In the same work (Forziati et al., 1950) vapor pressure measurements of 1-undecene in the temperature range (379.02 to 466.89) K are reported. The value of $\Delta_l^gH^\circ_m$ = 57.6 kJ·mol^{-1}, derived from Antoine coefficients recalculated by Afeefy et al. (1998) is still in acceptable agreement with ours (Table 2), taking into account a uncertainty caused by the extrapolation of this value to the reference temperature.

Vaporization enthalpies in general can often be estimated using group additivity methods (Chickos et al., 1981; Lebedev and Miroshnichenko, 1993). The use of group additivity is straightforward and easy, but this procedure is not precise enough to predict the small differences in the vaporization enthalpies which are for example obvious for cis- and trans-isomers of olefins. Among the empirical schemes, correlating the number of C atoms of the homologues with the vaporization enthalpy has been suggested to be successful. Vaporization enthalpies $\Delta_l^gH^\circ_m$ appear to be a linear function of the number of carbon atoms of the alkanes (Chickos et al., 1997) or aliphatic esters (Koutek et al., 1998). A similar trend was observed recently for branched esters in our laboratory (Verevkin and Heintz, 1999). The accuracy of the prediction depends on the structural similarity of the molecules taken into correlation concerning the number of their carbon atoms. According to the structural peculiarities of the molecules studied in this work, we have divided the linear olefins into three groups: *n*-alkenes (Table 3, Figure 3), *cis*-alkenes (Table 3, Figure 3); *trans*-alkenes (Table 3, Figure 3). Three groups of branched olefins have been defined: methylenealkanes

Table 3. Data Set for the Prediction of the Vaporization Enthalpies of the Linear Olefins at 298.15 K

n-alkene	n_C	$\Delta_l^g H°_m$/kJ·mol^{-1}	*cis*-alkene	n_C	$\Delta_l^g H°_m$/kJ·mol^{-1}	*trans*-alkene	n_C	$\Delta_l^g H°_m$/kJ·mol^{-1}
1-butene	4	20.88[a]	*cis*--2-butene	4	22.70[a]	*trans*--2-butene	4	21.97[a]
1-pentene	5	25.48[b]	*cis*--2-pentene	5	26.78[g]	*trans*--2-pentene	5	27.61[b]
1-hexene	6	30.60[c]	*cis*-2-hexene	6	31.50[c]	*trans*-2-hexene	6	31.50[c]
1-heptene	7	36.07[d]	*cis*-3-hexene	6	31.30[c]	*trans*-3-hexene	6	31.59[c]
1-octene	8	40.27[e]	*cis*-2-heptene	7	38.58[f]	*trans*-4-octene	8	42.89[f]
1-nonene	9	44.73[f]						
1-decene	10	50.43[e]						
1-undecene	11	54.27[f]						
1-dodecene	12	60.78[e]						

[a] Data from Majer and Svoboda, 1985. [b] Lebedev and Miroshnichenko, 1993. [c] Camin and Rossini, 1956. [d] Lister, 1941. [e] Manssonet al., 1977. [f] This work, Table 1. [g] Cox and Pilcher, 1970. [h] Camin and Rossini, 1960.

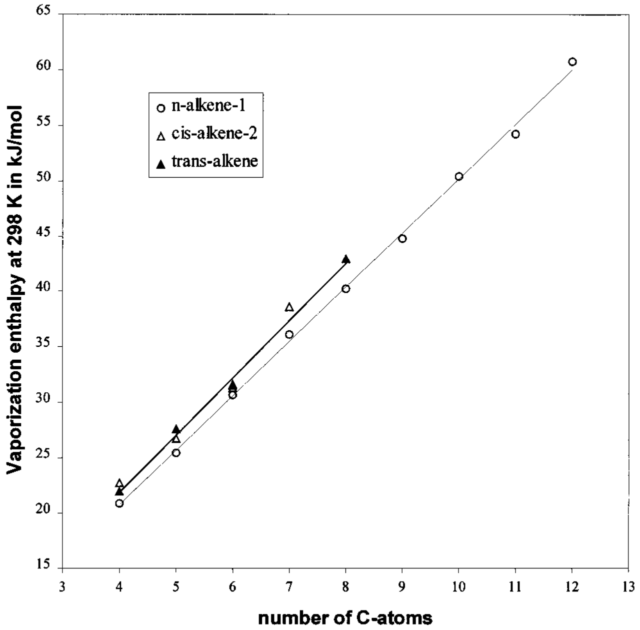
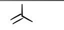
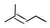
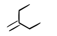
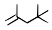
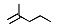
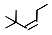
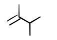
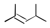
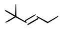
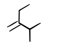
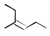
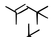
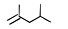
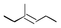
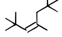
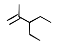
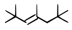
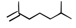


Figure 3. Experimental vaporization enthalpies of selected olefins plotted against their respective number of carbon atoms n_C, as evaluated from the data in Table 3.

Table 4. Data Set for the Prediction of the Vaporization Enthalpies of the Branched Olefins at 298.15 K

methylene-alkanes	n_C	$\Delta_l^g H°_m$/kJ·mol^{-1}	iso-alkenes	n_C	$\Delta_l^g H°_m$/kJ·mol^{-1}	highly branched alkenes	n_C	$\Delta_l^g H°_m$/kJ·mol^{-1}
	4	19.3[g]		5	27.3[a]		6	26.6[c]
	5	26.2[a]		6	31.6[c]		7	32.1[h]
	6	31.0[c]		6	31.3[c]		8	35.7[h]
	6	30.5[c]		6	32.1[c]		8	37.1[h]
	6	29.2[c]		7	34.5[f]		8	37.2[h]
	7	34.4[h]		7	36.4[h]		8	37.4[h]
	7	33.1[h]		7	35.8[h]		12	63.2[f]
	8	37.5[h]					12	65.9[f]
	9	45.9[f]						

[a] Data from Majer and Svoboda, 1985. [b] Lebedev and Miroshnichenko, 1993. [c] Camin and Rossini, 1956. [d] Lister, 1941. [e] Mansson et al., 1977. [f] This work, Table 1. [g] Cox and Pilcher, 1970. [h] Camin and Rossini, 1960.

(Table 4, Figure 4); isoalkenes (Table 4, Figure 5); highly branched alkenes (Table 4, Figure 6). Available vaporization enthalpies for each group of compounds were selected from literature and correlated with the number of C atoms in a molecule using a linear least-squares quadratic treatment.

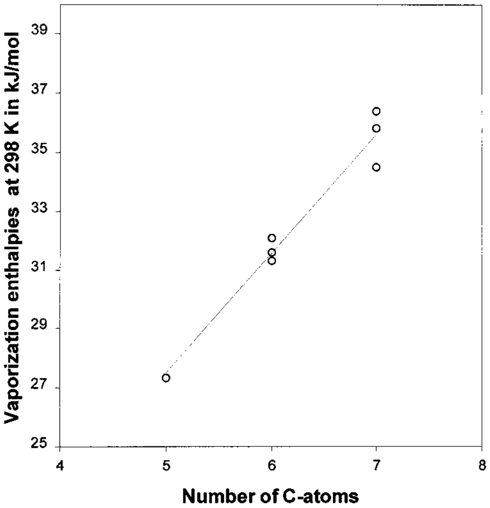


Figure 4. Experimental vaporization enthalpies of selected 2-methylenealkenes plotted against their respective number of carbon atoms n_C, as evaluated from the data in Table 4.

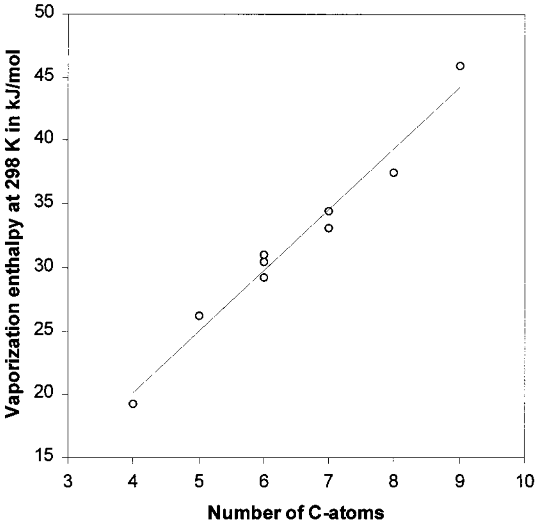


Figure 5. Experimental vaporization enthalpies of selected highly branched olefins plotted against their respective number of carbon atoms n_C, as evaluated from the data in Table 4.

From the correlation of the selected data set for *n*-1-alkene (Table 3) the following equation for the estimation of their vaporization enthalpies was obtained (Figure 3):

$$\Delta_l^g H°_m/\mathrm{kJ\ mol^{-1}} = (1.12 \pm 0.18) + (4.91 \pm 0.07)n_C \qquad r = 0.9987 \quad (5)$$

This classic correlation of the $\Delta_l^g H°_m$ with the number of C atoms of a molecule is a valuable test to check the

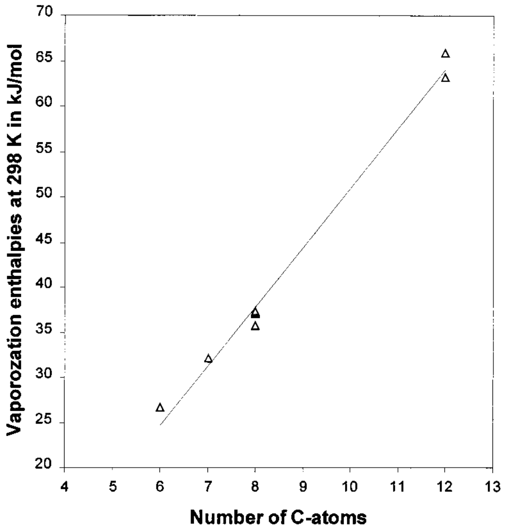


Figure 6. Experimental vaporization enthalpies of selected highly branched olefins plotted against their respective number of carbon atoms n_C, as evaluated from the data in Table 4.

consistency of the data derived from the different experimental techniques. In this respect, it is worth to noting that our values for the vaporization enthalpies of 1-nonene and 1-undecene measured by transpiration method are in excellent correlation with data for other *n*-1-alkene measured by ebulliometry and calorimetry (Figure 3).

The data set for the correlation of the vaporization enthalpies of *cis*-alkenes (Table 3) with the number of C atoms is substantially smaller than for *n*-1-alkene and our new result for *cis*-2-heptene seems to be a valuable contribution. The following equation for the prediction of vaporization enthalpies of *cis*-alkenes was obtained (Figure 3):

$$\Delta_l^g H^\circ_m/\text{kJ mol}^{-1} = (1.37 \pm 0.48) + (5.14 \pm 0.47)n_C \qquad r = 0.9750 \quad (6)$$

The data set for the *trans*-alkenes (Table 3) is similar to that for the cis-isomers; our new value for *trans*-4-octene extends the range of experimental data used to establish the correlation of the vaporization enthalpies of trans-isomers with the number of C atoms. The following equation for the estimation of vaporization enthalpies of *trans*-olefins was obtained (Figure 3):

$$\Delta_l^g H^\circ_m/\text{kJ mol}^{-1} = (1.23 \pm 0.30) + (5.15 \pm 0.22)n_C \qquad r = 0.9944 \quad (7)$$

It is obvious from Figure 3 as well as from eqs 5 and 6 that the correlation for the *cis*-alkenes is practically indistinguishable from that for the *trans*-alkenes within the error bars.

The data set available for the branched alkenes (Table 4) is sufficient for a reasonable prediction of their vaporization enthalpies. From the correlations of the selected data sets the following equations for the estimation of vaporization enthalpies of the branched olefins were obtained (Figures 3−6):

$$\text{methylenealkanes: } \Delta_l^g H^\circ_m/\text{kJ mol}^{-1} = (0.85 \pm 0.46) + (4.82 \pm 0.32)n_C \qquad r = 0.9696 \quad (8)$$

$$\text{isoalkenes: } \Delta_l^g H^\circ_m/\text{kJ mol}^{-1} = (7.20 \pm 0.26) + (4.06 \pm 0.37)n_C \qquad r = 0.9612 \quad (9)$$

$$\text{highly branched: } \Delta_l^g H^\circ_m/\text{kJ mol}^{-1} = -(14.50 \pm 0.54) + (6.54 \pm 0.26)n_C \qquad r = 0.9904 \quad (10)$$

Evaluation of eqs 5−10 reveals sufficient mutual consistency of each data set; in all cases the correlation coefficient r lies in the acceptable range from 0.96 to 0.99.

The vaporization enthalpies of methylcyclohexenes measured in this work have been used in the estimation of their standard molar enthalpies of formation in the liquid state, which is of interest due to the following reason. Some years ago we began an investigation of the chemical equilibrium of reactions of the type

$$\text{carboxylic acid} + \text{methylcyclohexene} \leftrightarrow \text{ester}$$

in the liquid phase (Verevkin et al., 1992; Verevkin and Heintz, 1999b). To obtain standard reaction enthalpies, enthalpies of formation of each pure participant in the reaction are required. Unfortunately, $\Delta_f H^\circ_m$(liq) was available only for 1-methylcyclohexene. Reaction enthalpies $\Delta_r H^\circ_m$ of isomerization of methylcyclohexenes in the gas phase are available in the literature (Table 5). These data could be used to derive the desired values of $\Delta_f H^\circ_m$(liq) for other methylcyclohexenes such as 1-methylcyclohexene (Table 6). However, the difficulty we faced using these data is that the temperature range of the equilibrium studies differ from the reference temperature by (110 to 160) K. The heat capacities $c_p(T)$ of the methylcyclohexenes necessary to adjust $\Delta_f H^\circ_m$ to 298.15 K are not available. In fact a very limited amount of gaseous heat capacity data of hydrocarbons are available in the literature (Lide and Kehiaian, 1994). This thwarted extrapolation of the experimental enthalpies of reaction to $T = 298.15$ K by using Kirchhoff's equation. Since the reactions studied by Yursha et al. (1974) and Coppens et al. (1965) are isomerizations, $c_p(T)$ the of the isomeric compounds should be very similar. In our calculations it was assumed that the enthalpy of reaction remains constant in going from the average

Table 5. Reactions Enthalpies $\Delta_r H^\circ_m$ of the Equilibrium Reactions of Mutual Interconversions of Methylcyclohexenes in the Gaseous Phase

reaction	$\langle T \rangle^a$ / K	$\Delta_r H^\circ_m$ / kJ·mol^{-1}	lit.
4-methylcyclohexene ⟺ 1-methylcyclohexene	463	−5.8 ± 0.3	Yursha et al., 1974
methylenecyclohexane ⟺ 1-methyl-cyclohexene	463	−7.1 ± 0.3	Yursha et al., 1974
	298	−8.1 ± 0.7^b	Rogers et al., 1987
3-methylcyclohexene ⟺ 1-methylcyclohexene	463	−8.1 ± 0.2	Yursha et al., 1974
3-methylcyclohexene ⟺ 4-methylcyclohexene	411	−2.38	Coppens et al., 1965
	298	−2.3 ± 1.1^c	this work

[a] The average temperature of the equilibrium study. [b] Derived in this work from the enthalpies of hydrogenation reported by Rogers et al., 1987. [c] Calculated in this work (see text).

Table 6. Standard Molar Enthalpies of Formation in the Gaseous and Liquid Phase at $T = 298.15$ K, Derived from Combined Results of Equilibrium, Vapor Pressure, and Calorimetric Studies

compd	$\Delta_f H^\circ_m(g)^a$ kJ·mol^{-1}	$\Delta_l^g H^\circ_m$ ^{a} kJ·mol^{-1}	$\Delta_f H^\circ_m(l)^a$ kJ·mol^{-1}
1-methylcyclohexene	−43.7 ± 0.8	37.46 ± 0.24	−81.2 ± 0.8^b
4-methylcyclohexene	−37.9 ± 0.8	36.30 ± 0.59	−74.2 ± 1.0 −75.0 ± 4.0^c
3-methylcyclohexene	−35.6 ± 0.8	38.78 ± 0.50	−74.1 ± 0.9
methylenecyclohexene	−36.5 ± 0.8	36.10 ± 0.30^d	−72.6 ± 0.8 −61.3 ± 3.8^e

[a] Derived in this work. [b] Data from Labbauf and Rossini, 1961. [c] For comparison, data from Lebedev and Smirnova, 1994. [d] Data from Fuchs and Peacock, 1979. [e] For comparison, data from Konovalon, 1926.

experimental temperature to $T = 298.15$ K. Support for this assumption was found by comparison of the data from equilibrium and hydrogenation studies of methylcyclohexenes. The gaseous enthalpy of isomerization of methylenecyclohexane ⇔ 1-methylcyclohexene, $\Delta_r H^\circ_m = -(7.1 \pm 0.3)$ kJ·mol^{-1}, was measured at an average temperature 463 K (Yursha et al., 1974). The enthalpy of the same reaction, $\Delta_r H^\circ_m = -(8.1 \pm 0.7)$ kJ·mol^{-1}, can be estimated from the hydrogenation enthalpies of 1-methylcyclohexene, $\Delta_r H^\circ_m = -(111.4 \pm 0.4)$ kJ·mol^{-1}, and of methylenecyclohexane, $\Delta_r H^\circ_m = -(119.5 \pm 0.6)$ kJ·mol^{-1}, reported at 298.15 K by Rogers et al. (1987). Enthalpies of hydrogenation of the various olefins measured in dilute hydrocarbon solution are claimed to be compatible to those in the gas phase (Fang and Rogers, 1992). Thus, for the methylenecyclohexane ⇔ 1-methylcyclohexene isomerization, the enthalpy based on the equilibrium study at 463 K is in excellent agreement with the enthalpy of the same reaction at 298.15 K obtained from the hydrogenation work.

Starting with gaseous 1-methylcyclohexene itself and the enthalpies of isomerization, we deduced gas-phase enthalpies of formation of the other methylcyclohexene isomers (Table 6). Using the values of the vaporization enthalpies measured in this work and those for methylenecyclohexane available from Fuchs and Peacock (1979), we obtained the enthalpies of formation of the methylcyclohexene isomers in the liquid phase given in column 3 of Table 6. The value of $\Delta_f H^\circ_m$(liq) value for 4-methylcyclohexene derived in this study is in precise agreement with the result from the combustion calorimetry (Lebedev and Smirnova, 1994), which, however, was measured with low accuracy (Table 6). But the enthalpy of formation of methylenecyclohexane derived in this study is in disagreement with result from combustion calorimetry from Konovalon (1926), despite the large error bars of his value. The reason for such discrepancy may be caused by the low degree of purity of the samples used for combustion experiments.

The valuable check of the experimental data from calorimetry, equilibrium, and hydrogenation studies for mutual consistency render the calculation of enthalpy of reaction 3-methylcyclohexene ⇔ 4-methylcyclohexene using the values of $\Delta_f H^\circ_m$(g) of participants from Table 6. The value of $\Delta_r H^\circ_m = -(2.3 \pm 1.2)$ kJ·mol^{-1} at 298.15 K calculated in this way is in precise agreement with the experimental result obtained from the equilibrium study at 411 K (Coppens et al., 1965) (see Table 6), despite the substantial difference of the average temperatures.

The investigation of the vaporization enthalpies of compounds shown in Figure 1 covers a broad range of alkene structures. The new vaporization enthalpies of monoolefins helps to fill the gap in existing thermochemical data for alkenes and provide data to be used for the calculation of the thermochemical properties of other compounds with similar structures. We hope to have provided some practical correlation equations that could be used to predict values for as yet unmeasured enthalpies of vaporization of similar structure.

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